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Facile synthesis of β-Bi_2O_3/$Bi_2O_2CO_3$ nanocomposite with high visible-light photocatalytic activity

Guiyu Cai [a], Lingling Xu [a,*], Bo Wei [b], Jixin Che [c], Hong Gao [a], Wenjun Sun [a]

[a] Key Laboratory of Photonic and Electric Bandgap Materials, Ministry of Education, School of Physics and Electronic Engineering, Harbin Normal University, Harbin 150025, PR China
[b] Department of Physics, Harbin Institute of Technology, Harbin 150080, PR China
[c] The Aviation University of Air Force, Changchun 130022, PR China

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ABSTRACT

β-Bi_2O_3/$Bi_2O_2CO_3$ composite nanosheets are synthesized via a rational heat-treatment of $Bi_2O_2CO_3$ precursor. The precursor transforms to β-Bi_2O_3/$Bi_2O_2CO_3$ composites and α-Bi_2O_3 phase under different calcination conditions. The photocatalytic activities are evaluated and compared through the photodegradation of methylene blue (MB) under visible-light irradiation. β-Bi_2O_3/$Bi_2O_2CO_3$ composites exhibit much higher photodegradation activity than $Bi_2O_2CO_3$ and α-Bi_2O_3 products. The significant enhancement is attributed to the formation of β-Bi_2O_3/$Bi_2O_2CO_3$ heterojunctions, which is favorable for the low recombination rate of the electron–hole pairs.

1. Introduction

Semiconductor photocatalysis has been extensively studied to solve growing environment problems, like air purification and wastewater treatment [1–5]. Recently, bismuth-based compounds like $Bi_2O_2CO_3$ and Bi_2O_3 have received considerable attention as potential candidates of photocatalysts [6–12]. Aurivillius-type $Bi_2O_2CO_3$, with alternative $(Bi_2O_2)^{2+}$ and $CO_3{}^{2-}$ layers, has been studied as an efficient photocatalyst [6–9]. The application of $Bi_2O_2CO_3$ in photocatalysis was first reported by Cheng et al. [6]. However, it is only active under ultraviolet light due to its wide band gap (~3.5 eV). Therefore, it is very important and interesting to broaden the adsorption spectra to the visible light range. Combining $Bi_2O_2CO_3$ with suitable semiconductors is an efficient way to enlarge light absorption. For example, Chen et al. synthesized $Bi_2O_2CO_3$/BiOI heterojunction, which presents effective photocatalytic activities on the photodegradation of organic dyes [7]. Using a cation exchange method, Wang et al. fabricated $Bi_2O_2CO_3$/Bi_2S_3 hierarchical microspheres with enhanced visible light-driven photocatalytic activity [8]. In the composites, the heterojunction forms an inner electric field that can inhibit the combination of photoinduced electrons and vacancies.

Through the thermal decomposition of $Bi_2O_2CO_3$ precursor, Bi_2O_3 oxides (α- or β-phases) can be obtained with excellent photocatalytic activity and stability [9,10]. With a lower band gap energy and a special electronic structure, β-Bi_2O_3 (2.47 eV) has been verified with higher photocatalytic activity than α-Bi_2O_3 (2.58 eV) [11,13]. Several reports on β-Bi_2O_3 are documented [14,15]. In this study, instead of complete decomposition, we report the first synthesis of β-Bi_2O_3/$Bi_2O_2CO_3$ nanosheet composites through a rational heat treatment of $Bi_2O_2CO_3$ precursor. The composites presented much higher activity than pure $Bi_2O_2CO_3$ and α-Bi_2O_3 phases under visible light irradiation, and possible enhancement mechanism was discussed.

2. Materials and methods

$Bi_2O_2CO_3$ powder was synthesized through a hydrothermal process. 4 mL HNO_3 (65%) was dissolved in 40 mL deionized water, and then 2.0 mmol of $Bi(NO_3)_3 \cdot 5H_2O$ was added to form a transparent solution. Subsequently, 4.0 mmol of ethylenediaminetetraacetic acid (EDTA) and 18.5 mL of NaOH (4 M) solution were added to the above solution with vigorous stirring for 2 h. Afterward, the suspension was transferred into a 40 mL Teflon-lined autoclave and hydrothermally treated at 160 °C for 12 h. After cooling naturally, the precipitate was filtered, washed with deionized water and dried at 60 °C for 12 h. Finally, $Bi_2O_2CO_3$ precursor was calcined at 200–500 °C for 2 h in air to get different products.

The structure of the as-prepared powders was determined by X-ray diffraction (XRD, Rigaku-D/max 2600/PC) with Cu Kα radiation. Thermogravimetric analysis/differential thermal analysis

* Corresponding author. Tel.: +86 451 88060554.
E-mail address: xulingling_hit@163.com (L. Xu).

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(TGA–DTA) of $Bi_2O_2CO_3$ precursor was performed on a TA SDT 2960 at a heating rate of 10 °C/min in air. The morphology was examined by a scanning electron microscope (SEM, Hitachi S-4800). UV–vis diffuse reflectance spectra (DRS) were measured by a Shimadzu UV-2550 spectrophotometer. X-ray photoelectron spectroscopy (XPS) test was carried out using a Thermofisher K-Alpha spectrometer with Al Kα excitation. Photocatalytic activity was evaluated by photodegradation of MB solution (100 mL, 1.0×10^{-5} M). A 300 W Xe lamp with a cut off filter ($\lambda \geq 420$ nm) was used for visible light irradiation. 0.02 g catalysts were dispersed in MB solution, and before irradiation, the suspension was stirred for 30 min in dark to reach the adsorption/desorption equilibrium. The concentration change was analyzed by a Perkin-Elmer Lambda-35 UV–vis spectrophotometer.

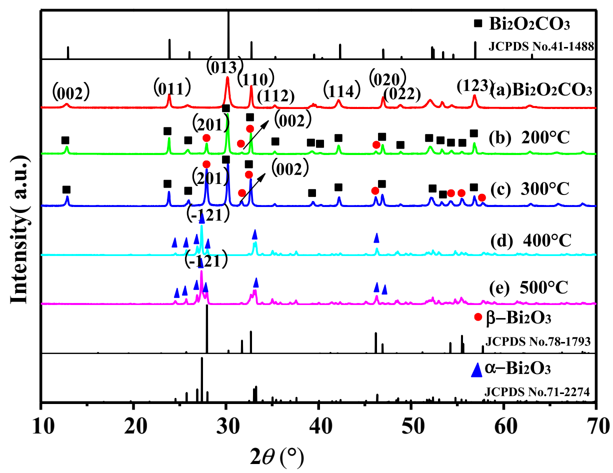

Fig. 1. XRD patterns of as-prepared samples: (a) $Bi_2O_2CO_3$, (b) $Bi_2O_2CO_3$ precursor after heat treatment at 200 °C, (c) 300 °C, (d) 400 °C and (e) 500 °C.

3. Results and discussion

XRD patterns of $Bi_2O_2CO_3$ samples before and after heat-treatment are shown in Fig. 1. All diffraction peaks in Fig. 1(a) can be perfectly indexed as the tetragonal phase $Bi_2O_2CO_3$ (JCPDS 41-1488). The calculated lattice constants are $a=b=$ 3.865 Å and $c=13.673$ Å, which are in good agreement with the reported values [6]. For the 200 °C annealed sample (Fig. 1b), the peaks are similar to that of $Bi_2O_2CO_3$ precursor. But some new peaks at 27.92°, 31.69°, 32.68°, and 46.18° can be observed, which can be ascribed to the formation of monocline β-Bi_2O_3 (JCPDS 78-1793). As shown in TG–DTA curves in Fig. 2(a), about 6% mass loss was obtained up to 200 °C, because of the release of adsorbed H_2O and partial decomposition of precursor. This partial transformation results in the co-existence of $Bi_2O_2CO_3$ and β-Bi_2O_3 phases. When annealing temperature was elevated to 300 °C (Fig. 1c), more intense peaks of β-Bi_2O_3 appeared, suggesting a considerable

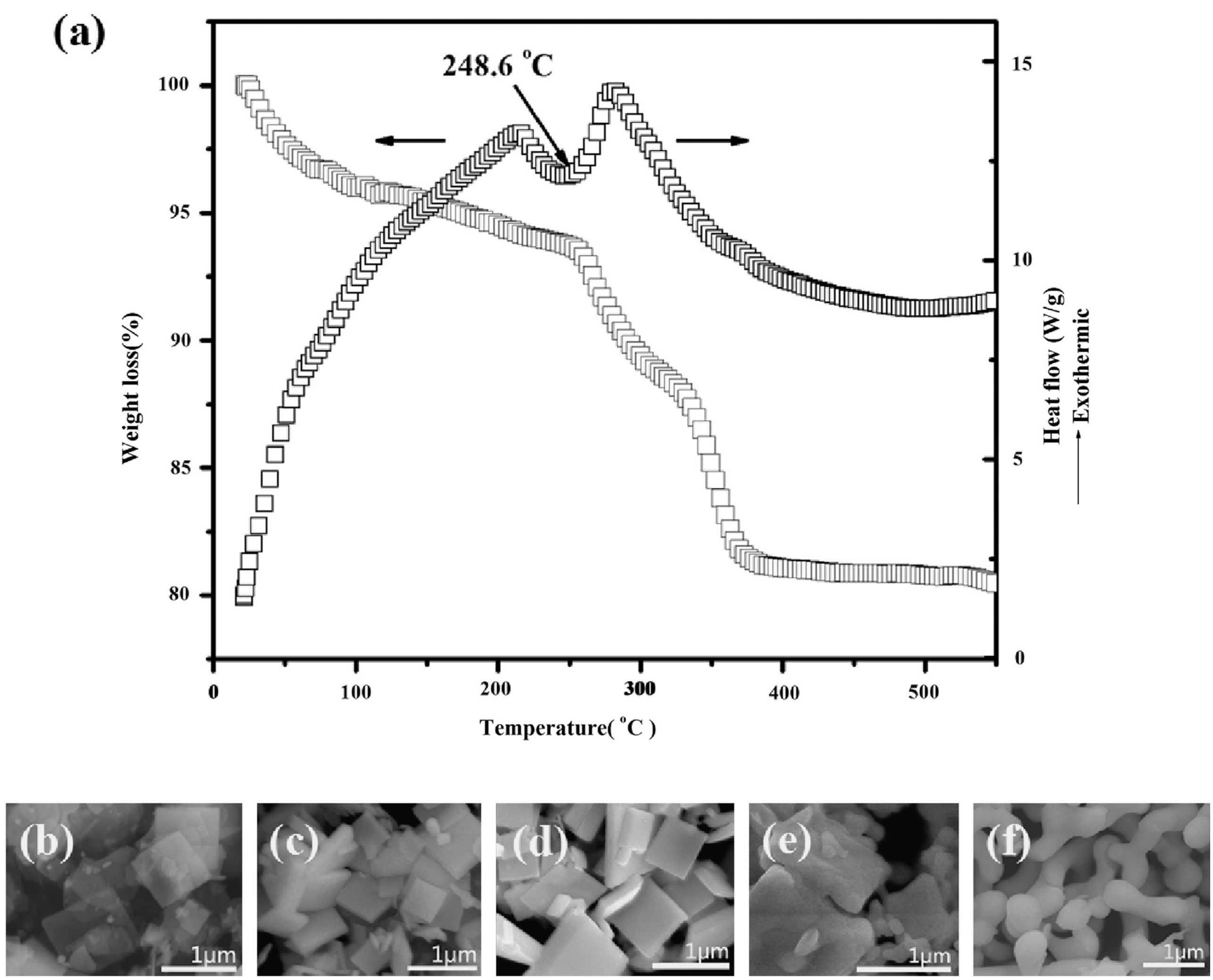

Fig. 2. (a) TG and DTA curves of the precursor; SEM images of (b) $Bi_2O_2CO_3$ precursor and heat treatment at (c) 200 °C, (d) 300 °C, (e) 400 °C, and (f) 500 °C.