Materials Letters ∎ (∎∎∎∎) ∎∎∎–∎∎∎

Contents lists available at ScienceDirect

Materials Letters

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

Synthesis of BiOI hierarchical nanospheres and their application in photocatalysis

Yongyu Li [a,b,*], Huian Qin [a], Haijie Sun [a], Miao Zhang [a], Jichao Wang [b], Hongchang Yao [b], Zhongjun Li [b,**]

[a] Institute of Environmental & Catalytic Engineering, School of Chemistry and Chemical Engineering, Zhengzhou Normal University, Zhengzhou 450044, PR China
[b] College of Chemistry and Molecular Engineering, Zhengzhou University, Zhengzhou 450001, PR China

ARTICLE INFO

Article history:
Received 28 January 2015
Accepted 26 March 2015

Keywords:
BiOI
Nanosphere
Particles
Microstructure

ABSTRACT

We report the synthesis of BiOI hierarchical nanospheres in the presence of octadecene and oleic acid. The BiOI nanospheres show an average diameter of 150 nm and are composed with nanocrystals of about 5 nm in size, which is the smallest BiOI hierarchical nanospheres reported at present. The samples exhibit high photocatalytic activity on methyl orange, which was testified by the photoelectrochemical performance to be benefited from the effective separation of the photogenerated carriers.

1. Introduction

Bismuth oxyiodide (BiOI), as an important V–VI–VII ternary compound, has initiated considerable interest in the fields of photocatalysis due to its unique layer structure and excellent visible light absorption [1–3]. There have been studies of shape-controlled synthesis about BiOI in order to obtain high catalytic activity, including microspheres [4–8], microflowers [9,10], nanoparticles [11], nanosheets [12,13] and nanoplates [14]. Although BiOI with the above multiple morphologies have been successfully synthesized, most of the present architectures are on larger scales, which would restrict their potential applications.

Recently, hierarchical nanospheres have been regarded as fascinating nanomaterials in the field of photocatalysis, partly due to their high quantum yield and low light scattering from the nanoparticle surface [15]. However, so far the hierarchical nanospheres of BiOI have rarely been realized and reported although the shape-controlled synthesis has been a continuous research topic about BiOI materials. Herein, we report the synthesis of BiOI nanospheres in the presence of octadecene and oleic acid. To the best of our knowledge, this is the first report of a BiOI hierarchical nanosphere structure. The BiOI nanospheres exhibit excellent photocatalytic activity on the degradation of MO. The effective separation of photo-induced carriers was testified to be the origin of photocatalytic activity of BiOI nanospheres.

2. Experimental

Typically, a mixture of bismuth subsalicylate (0.10 mmol), oleic acid (10 mL), and octadecene (ODE, 15 mL) was heated to 160 °C to form a clear solution. A solution of potassium iodide (0.10 mmol) in methanol was injected into this cooled solution, and the reaction mixture was allowed to swiftly heat to 200 °C for the growth of BiOI nanospheres. The synthesis was carried out under argon to avoid the oxidation of iodide and oleic acid. The product was obtained after washed with ethanol and cyclohexane and dried at room temperature. For comparison, BiOI microspheres were synthesized according to Ref. [16].

The XRD pattern of the sample was measured on an X'Pert PRO X-ray powder diffractometer. TEM and HRTEM analysis was performed on a FEI Tecnai G20 electron microscope. UV–vis diffuse reflectance spectra (DRS) were obtained using a Cary 5000 UV–vis spectrometer (Agilent Technologies, USA) by using $BaSO_4$ as a reference. Photocurrents were obtained on an electrochemical workstation (CHI 660E Chenhua Instrument Company, Shanghai, China). Nitrogen adsorption–desorption isotherms were collected on a NOVA 1000e surface area and porosity analyzer (Quantachrome, USA) at 77 K.

A 300 W Xe arc lamp (PLS-SXE300, Beijing Trusttech Co., Ltd.) equipped with an ultraviolet cutoff filter to provide visible light

* Corresponding author at: Institute of Environmental & Catalytic Engineering, School of Chemistry and Chemical Engineering, Zhengzhou Normal University, Zhengzhou 450044, PR China. Tel.: +86 371 65502309.
** Corresponding author. Tel.: +86 371 65502309.
E-mail addresses: zzsylyy@163.com (Y. Li), lizhongjun@zzu.edu.cn (Z. Li).

http://dx.doi.org/10.1016/j.matlet.2015.03.126
0167-577X/© 2015 Published by Elsevier B.V.

($\lambda > 400$ nm) was used as the light source. The photodegradation experiments were performed with the sample powder (100 mg) suspended in MO aqueous solution (100 mL, 10 mg L^{-1}) with constant stirring. Prior to the irradiation, the suspensions were magnetically stirred in the dark for 30 min to establish the adsorption/desorption equilibrium. At the given time intervals, about 5 mL of the suspension was taken for further analysis after centrifugation. The concentration of MO was estimated by measuring the absorption at a wavelength of 464 nm.

3. Results and discussion

Microstructure, morphology and crystal structures of BiOI nanospheres: Fig. 1a is the low-magnification TEM image of the BiOI nanospheres, suggesting that the nanoparticles are nearly monodisperse nanospheres with an average diameter of 150 nm. The high-magnification TEM image (the inset in Fig. 1a) shows that the nanospheres have a rough surface, indicating that each nanosphere is made of many small nanoparticles building blocks, leading to the formation of hierarchical BiOI nanospheres. The TEM image shown in Fig. 1b reveals the hierarchical structure of a typical nanosphere consisting of nanocrystals of about 5 nm in size. The HRTEM image (Fig. 1c) exhibits clear lattice fringes with *d* spacings of 0.301 nm, which can be indexed to the (1 0 2) plane of tetragonal BiOI. The X-ray diffraction (XRD) pattern shown in Fig. 1d reveals that the as-prepared BiOI is well crystallized in a single phase and all the diffraction peaks can be indexed to the tetragonal phase BiOI (space group *P4/nmm*, JCPDS 10-0445). No other impurities can be detected. Significantly, the broadening peaks of the BiOI nanospheres could be attributed to the small size of the building units from the hierarchical structures, and imply the lattice distortion in the as-prepared samples which would supply more oxygen vacancies [10,17]. Meanwhile, the strengthening (1 1 0) diffraction peak of the BiOI nanospheres also indicates the different crystallographic direction under the preparation conditions [10].

Photoabsorption and photocatalytic activity: The optical property of BiOI nanospheres was measured by UV–vis diffuse reflectance spectroscopy, as shown in Fig. 2. According to the spectrum, the BiOI nanospheres exhibit photo-absorption from UV light to visible light region shorter than ca. 680 nm. Its optical band gap was determined to be 1.60 eV according to the energy dependence relation of $(\alpha h\nu)^{1/2}$ coefficient versus $h\nu$ (as shown in the inset of Fig. 2). The small band gap implies the possibility of high photocatalytic activity of this material under visible light irradiation.

Methyle orange (MO) was used to estimate the adsorption abilities and photocatalytic activities of the as-prepared samples. The changes in the absorption spectra of the extracted MO solution in the presence of the BiOI nanospheres are shown in Fig. 3a. The continuous reduction of the absorption intensity at 464 nm indicates the gradually decreasing concentration of MO with the extended irradiation time. This result is consistent with the color change of the suspension from orange to colorless (the inset in Fig. 3a). The dependency of the degradation rate on the irradiation time is revealed in Fig. 3b. There was almost no photocatalytic decolorization of MO after irradiation for 60 min as shown by the black line in Fig. 3b. Therefore, BiOI catalysts play

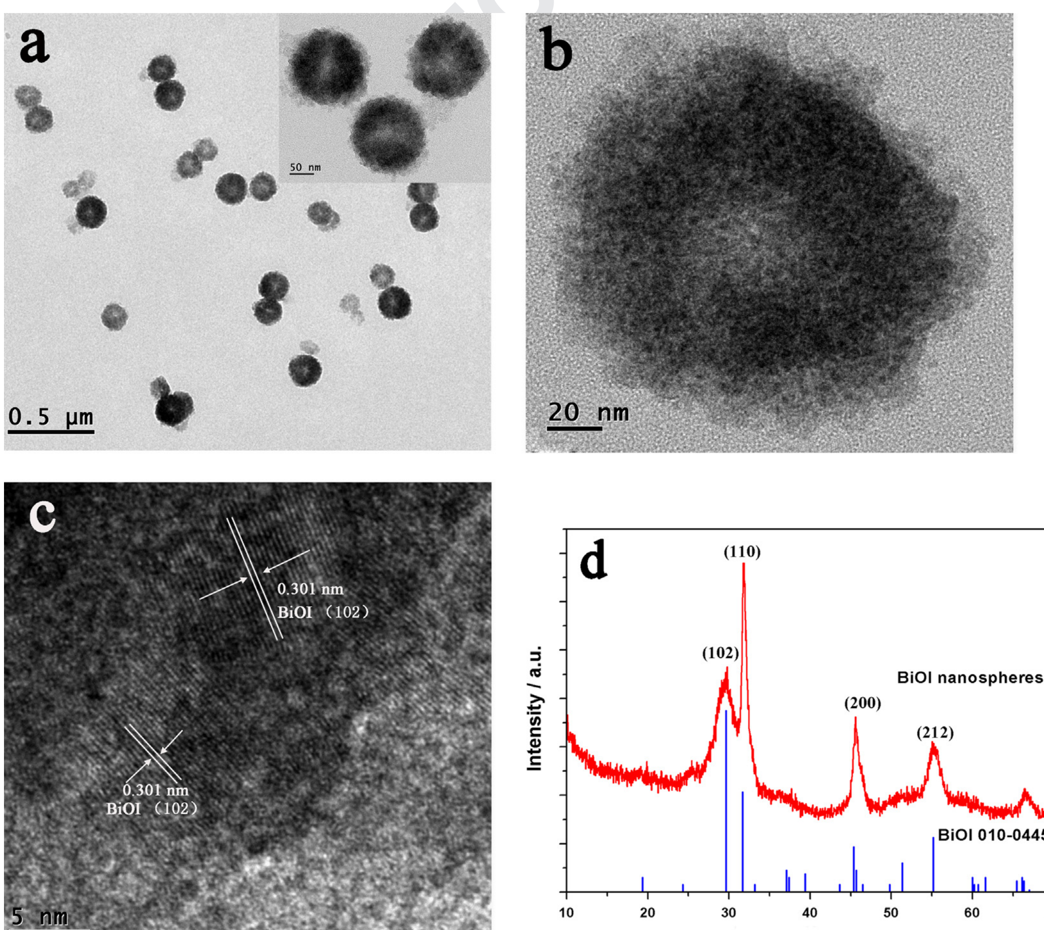

Fig. 1. TEM images of BiOI nanospheres with different magnification (a and b), HRTEM image (c) and XRD pattern (d) of BiOI nanospheres.

Please cite this article as: Li Y, et al. Synthesis of BiOI hierarchical nanospheres and their application in photocatalysis. Mater Lett (2015), http://dx.doi.org/10.1016/j.matlet.2015.03.126