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Hydrothermal synthesis of hierarchical flower-like Bi_2WO_6 microspheres with enhanced visible-light photoactivity

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ABSTRACT

Three-dimensional (3D) hierarchical flower-like Bi_2WO_6 microspheres assembled from 2D nanosheets were successfully prepared by a simple hydrothermal route using the non-ionic surfactant F127 (EO_{100}–PO_{65}–EO_{100}) as the morphology director. On the basis of the evolution of the morphologies as a function of reaction time, a possible formation mechanism for the hierarchical architecture was proposed. The photocatalytic activities of the as-prepared Bi_2WO_6 samples were evaluated for the degradation of Rhodamine B (RhB) under visible-light irradiation. Due to the combined effects of large surface area and efficient separation of charge carriers, the hierarchical flower-like Bi_2WO_6 microspheres exhibited improved photocatalytic performances.

1. Introduction

Over the past few years, visible-light-driven photocatalysts have attracted extensive attention in view of the efficient utilization of solar energy. Bismuth tungstate (Bi_2WO_6), one of the simplest Aurivillius oxides, was found to possess excellent photocatalytic performance for water splitting and photodegradation of organic contaminants under visible light irradiation [1]. Generally, nanoscale Bi_2WO_6 photocatalysts exhibit good photocatalytic activity due to their relatively large specific surface areas and low recombination rates of photoinduced charges. Hence, considerable efforts have been devoted to the synthesis of nanosized Bi_2WO_6 photocatalysts with various nanostructures including nanoplates [2], nanoparticles [3], nanocages [4] etc. Nevertheless, in view of practical applications, how to separate and recycle the nano-photocatalyst effectively after fulfillment of the photocatalysis process has become an issue. Comparatively speaking, 3D hierarchical structures constructed by nanosized building blocks have the advantages of both mico- and nano-sized materials, such as easy separation and recyclability, abundant transport paths for reactant molecules, efficient separation of charge carriers and high photocatalytic performance. Recently, Bi_2WO_6 with 3D hierarchical structures have been fabricated by several research groups. For example, Qian et al. produced hierarchical Bi_2WO_6 architectures by a simple inorganic salt-assisted hydrothermal method [5]. Tayade et al. successfully prepared spherical and flower-like Bi_2WO_6 architectures with and without SiO_2 protected calcination [6].

However, despite of these recent progresses, it still remains a great challenge to develop a simple and reliable method for the synthesis of 3D Bi_2WO_6 hierarchical structures with high visible-light-driven photocatalytic activity. Herein, we report the fabrication of hierarchical flower-like Bi_2WO_6 microspheres assembled from 2D nanosheets by an efficient F127-assisted hydrothermal method. The possible formation mechanism of hierarchical architectures was proposed on the basis of a series of time-dependent experiments. The photodegradation of RhB solution was carried out to evaluate the photocatalytic performances of the as-prepared Bi_2WO_6 photocatalysts under visible light irradiation.

2. Experimental

Materials and synthesis: In a typical procedure, 0.12 g Pluronic F-127 was mixed with 20 mL of 0.001 M $(NH_4)_{10}W_{12}O_{41}\cdot 6H_2O$ solution under magnetic stirring until a homogeneous solution was obtained. Then, 20 mL of 0.024 M $Bi(NO_3)\cdot 5\,H_2O$ was added to the above solution dropwise. The as-formed mixture solution was transferred into a 100 mL Teflon-lined autoclave and kept at 180 °C for 24 h. After the autoclave was cooled down to room temperature naturally, the as-obtained white precipitation was separated by centrifugation, washed with distilled water and absolute ethanol and dried under vacuum at 60 °C for 12 h. To remove F127, the as-prepared samples were calcined in muffle furnace at 400 °C for 1 h to obtain the Bi_2WO_6 microspheres

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(denoted as BWO-F127). For comparison, Bi_2WO_6 sample was also synthesized without using F127 (denoted as BWO), while the other experimental conditions remained the same.

Characterization: Characterization of the samples was carried out by employing X-ray Diffraction (XRD), Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM), UV–vis Diffuse Reflectance Spectroscopy, BET surface area analysis, Fluorescence Spectrophotometer (PL). The transient photocurrent responses of samples were measured under visible light irradiation by electrochemical workstation and the detailed process was described in our previous study [7].

Photocatalytic test: Typically, 0.1 g of Bi_2WO_6 sample was added into 100 mL RhB solution (5 mg L^{-1}). Before irradiation, the suspension was dispersed in an ultrasonic bath for 10 min and then stirred for 30 min in the dark to establish the adsorption–desorption equilibrium. After that, the solution was irradiated by a 300 W xenon lamp equipped with a UV cut off filter ($\lambda > 400$ nm). At given time intervals, 5 mL suspension was taken from the reactor and centrifuged to remove the photocatalyst particles. The concentration of RhB solution was analyzed using an UV–vis spectrophotometer at λ_{max} of 553 nm.

3. Results and discussion

The crystal structure and phase purity of the samples were characterized by XRD. As shown in Fig. 1a, the diffraction peaks of both samples can be assigned to the pure orthorhombic phase of Bi_2WO_6 (JCPDS Card no. 39-0256). No peaks of other impurities or phases can be detected, indicating the high phase purity of the as-obtained samples. Moreover, there are no obvious differences in diffraction peak intensity for both samples, indicating that F127 has no effects on the crystallinity of BWO-F127.

The typical SEM images of BWO and BWO-F127 are shown in Fig. 1b and c, respectively. The obtained BWO, which was synthesized without F127, was composed of aggregates of irregular flakes and particles. On the other hand, 3D hierarchical microspheres with the average diameters varying from 4 to 5 μm were observed in BWO-F127. These microspheres exhibit a flower-like microstructure and each flower is built from numerously well-developed nanosheets as the petals. As illustrated in Fig. 1c, these nanosheets are interwoven with each other to form a porous structure, which can serve as transport paths for reactant molecules and thereby enhance the photocatalytic performances of the samples. Fig. 1d is the TEM image of an individual microsphere, which further proves the flower-like microstructure of as-prepared BWO-F127 sample. In the HRTEM image (inset of Fig. 1d) taken from the edge of the individual microsphere, the lattice interplanar spacing is determined as 0.273 nm, corresponding to the (020) plane of orthorhombic Bi_2WO_6.

To reveal the growth process of the flower-like Bi_2WO_6 microspheres, SEM observations were carried out at different time periods as depicted in Fig. 2. Irregular small Bi_2WO_6 nanoparticles and their aggregates were firstly developed within the initial 1 h (Fig. 2a). As the reaction time was prolonged to 6 h (Fig. 2b), the Bi_2WO_6 crystals tended to form sheet-like structures because of the intrinsic anisotropic growth of the Bi_2WO_6 crystal. After 12 h of reaction time (Fig. 2c), sphere-like structures were obtained through self-assembly of nanosheets with certain crystallographic orientation. Finally, highly regular flower-like Bi_2WO_6 microspheres were obtained after aging for a longer period up to 24 h (Fig. 2d). On the basis of above results, the formation mechanism of flower-like Bi_2WO_6 microspheres was proposed to be as follows (Fig. 2e): self-aggregation, anisotropic growth and self-assembly.

Optical absorption properties of BWO and BWO-F127 were determined by UV–vis diffuse reflectance spectroscopy. As illustrated in Fig. 3a, both samples exhibit strong absorption in the ultraviolet and visible light regions and the band gaps of BWO and BWO-F127 (inset of Fig. 3a) are calculated to be 2.91 and 2.96 eV, respectively, being a little larger than that of bulk Bi_2WO_6 (2.60 eV) produced at high temperature [8]. The increase in the band gaps of the as-obtained Bi_2WO_6 can be attributed to the quantum

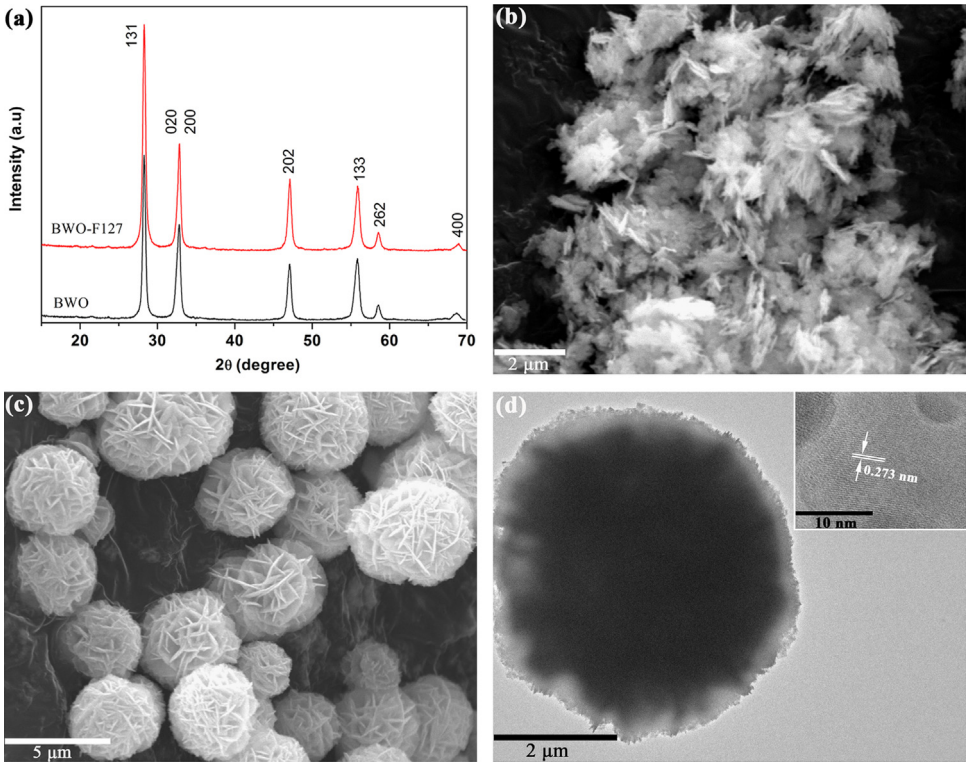

Fig. 1. (a) XRD patterns, (b) SEM image of BWO, (c) SEM image of BWO-F127, (d) TEM image of BWO-F127 (inset is the corresponding HRTEM image).