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Surfactant-free synthesis of Bi_2WO_6 multilayered disks with visible-light-induced photocatalytic activity

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ABSTRACT

The synthesis of bismuth tungstate (Bi_2WO_6) multilayered disk which was constructed by oriented square nanoplates was easily realized via a simple surfactant-free hydrothermal method. X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), and high-resolution transmission electron microscopy (HRTEM) were used to investigate the as-obtained product. The results indicated that the three-dimensional (3D) Bi_2WO_6 multilayered disk was constructed by self-assembly of square nanoplates via a perfect oriented manner. The formation mechanism of the product was carefully investigated on the basis of the results of time-dependent experiments. In addition, studies of the photocatalytic property demonstrated that the as-obtained Bi_2WO_6 could exhibit excellent visible-light-driven photocatalytic activity for the degradation of Rhodamine B (RhB).

1. Introduction

Aiming at novel materials, methods for fabricating nanoscaled building blocks into desired superstructures are of great concern in the realization of designing new nanostructures and assembling nanoscaled devices with better physical or chemical properties [1]. Among the special superstructures to be addressed, the so-called "oriented assembly" is of great importance as a promising method for creating advanced functional devices with distinct micro and nanostructures [2]. The oriented assembly of nanocrystals, as a main growth mode of nanoparticles especially evident in aqueous solutions, often involves spontaneous self-organization of adjacent nanoparticles in a precise, crystallographically controlled manner [3]. During the coalescence process, grains rotate with respect to each other until a low index crystallographic orientation is achieved. Nowadays, the technique of shaping nanoscaled building blocks into oriented assembled superstructures has not only been reported on some simple metals [4] and metal binary compounds [2,5–8] but also been extended to the synthesis of multicomponent complex oxides with unique properties [9].

In the past decades, degradation of organic contaminants by semiconductor-based photocatalyst has attracted extensive interest since Fujishima and Honda discovered the photocatalytic splitting of water on the TiO_2 electrodes in 1972 [10]. But poor solar efficiency (maximum 5%) hinders the practicality of TiO_2 because its large band gap (3.2 eV) in anatase crystalline phase makes it only effective under ultraviolet irradiation ($\lambda < 400$ nm). Taking sunlight into account, many researchers try to exploit new photocatalyst with high visible-light-driven photocatalytic activity to overcome this drawback. Recently, bismuth tungstate (Bi_2WO_6), as one of the simplest members of the Aurivillius oxide family, has a crystal structure composed of accumulated layers of alternating bismuth oxide $(Bi_2O_2)^{2+}$ layers and octahedral $(WO_4)^{2-}$ sheets. It has received great interest since the discovery of its photocatalytic activity for O_2 evolution from an aqueous silver nitrate solution. Furthermore, Zou and co-workers have reported that Bi_2WO_6 can also degrade both $CHCl_3$ and CH_3CHO under visible-light irradiation [11]. Their work reveals the potential application Bi_2WO_6 may have in environmental purification. So far considerable progress has been achieved in the preparation of Bi_2WO_6 nanoplates and nanoparticles by soft chemical method [12–16], which are believed to perform better photocatalytic activity than their bulk counterparts prepared by solid-state reaction due to the smaller crystal and higher surface area. Until recently, many researchers have diverted their attention to exploit Bi_2WO_6 with special 3D morphologies constructed from ordered nano-substructures, and great progress has been made with the successfully synthesis of various novel superstructures, including flower-like structure [17,18], nest-like structure [19], hierarchical microspheres [20], and octahedron-like assemblies [21]. Their

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researches not only offer an opportunity to understand the formation process of these specific superstructures, but also introduce a new way to improve the photocatalytic activity of Bi_2WO_6, since these hierarchical mesoporous configurations constructed by Bi_2WO_6 nanoplates have reported to have enhanced UV–vis absorbance and visible-light-driven photocatalytic activity due to the high physicochemical properties and more abundant transport paths for small molecules. However, most of their work is done in the presence of organic additives or surfactants which not only increase the production cost but also make the synthesis more difficult to scale up production. In all, the increasing interest generated by Bi_2WO_6 has inspired innovated strategies for the surfactant-free synthesis of other novel superstructures that would have smaller sizes but higher order.

In this work, we have synthesized Bi_2WO_6 multilayered disk constructing by square nanoplates via a simple surfactant-free hydrothermal method. The formation mechanism of the multilayered disk is investigated, which reveals the self-assembly of the square nanoplates via a perfect oriented manner. The photocatalytic property of the as-obtained product is investigated under visible-light irradiation.

2. Experimental

2.1. Synthesis of the samples

In our work, Bi_2WO_6 superstructures were synthesized through a hydrothermal process. All chemicals were of analytical grade used without further treatments. In a typical procedure, 10 mmol Bi $(NO_3)_3{\cdot}5H_2O$ was first dissolved in a 6 mL 15% nitric acid solution. A white precipitate was formed when the above solution was added into 30 mL 5 mmol Na_2WO_4 solution. Then the pH value of the precipitate was adjusted to 6 by adding KOH solution (2.24 g, 4 mL). After being magnetic stirred at room temperature for 1 h, the resulting precursor suspension was added to a 50 mL Teflon-lined autoclave. Then the autoclave was sealed in a stainless steel tank and heated at 180 °C for 24 h. Subsequently, the reactor was cooled to room temperature naturally. The resulting samples were washed with deionized water several times and dried at 100 °C in air.

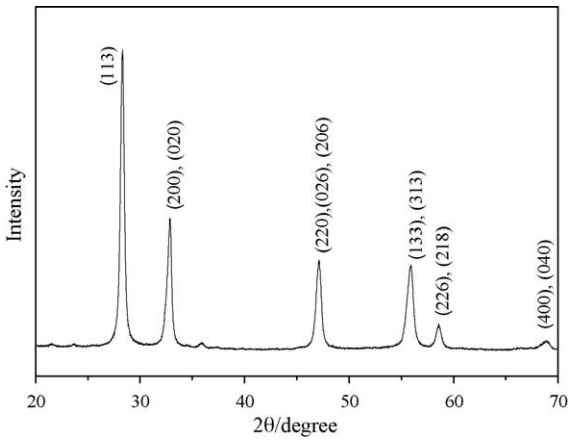

Fig. 1. XRD pattern of the hydrothermally synthesized sample at 180 °C for 24 h.

2.2. Characterization

The purity and crystalline structure of the product were analyzed by a Rigaku X-ray diffractometer (XRD) with a step size of 0.02 for CuKα radiation (λ = 1.5406 Å). The morphology of the product was further characterized by field-emission scanning electron microscopy (FESEM, Eindhoven, the Netherlands) oper-

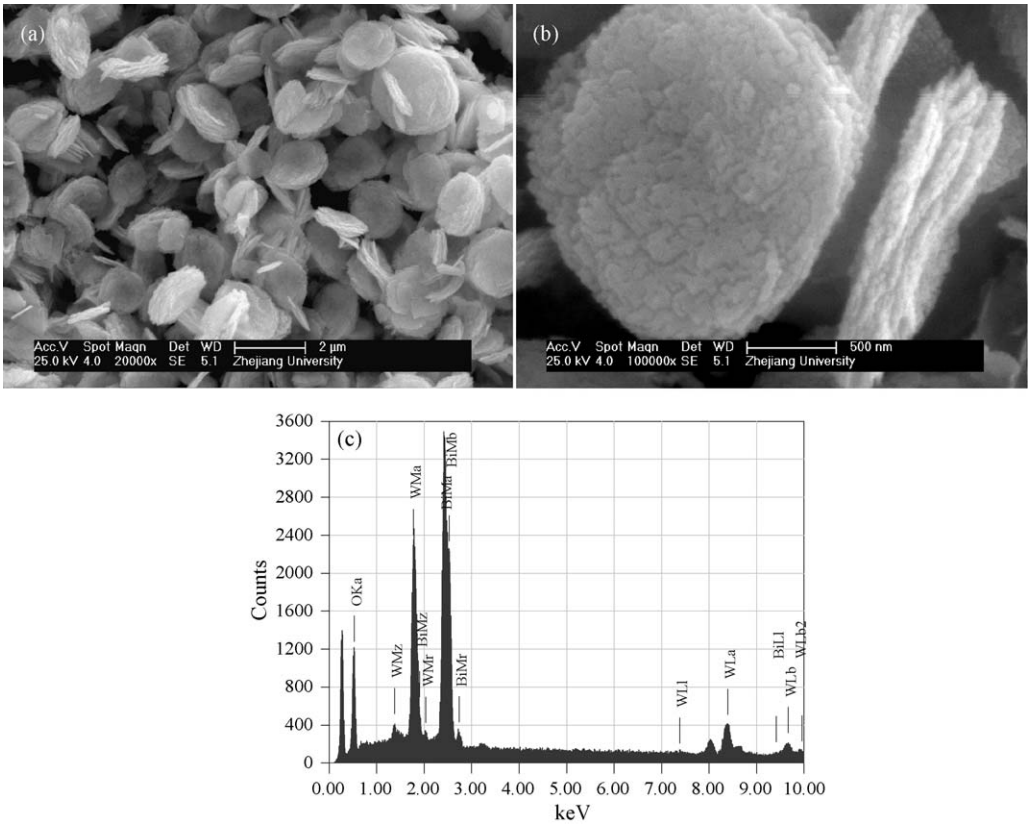

Fig. 2. (a) Low- and (b) high-magnification SEM images of the hydrothermally synthesized sample at 180 °C for 24 h. (c) EDX result of the same sample as in (a) and (b).