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Coprecipitation synthesis of hollow Zn_2SnO_4 spheres

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Abstract

Pure and Dy^{3+}-doped Zn_2SnO_4 (ZTO) hollow spheres, integrated with nanoparticles, have been synthesized using the coprecipitation method. The ZTO spheres have been characterized with X-ray diffraction and scanning electron microscope. The photoluminescence and photocatalytic properties are investigated. The influences of Dy^{3+} ions on the morphology and the photoluminescence of ZTO have been explained in detail.

Keywords: Zn_2SnO_4; Photoluminescence; Photocatalytic properties

1. Introduction

Transparent conducting oxides (TCOs) have widespread applications such as in smart windows, flat-panel displays, thin-film photovoltaic, polymer-based electronics and architectural windows [1–3]. As an important example of TCO materials, the ternary semiconductor Zn_2SnO_4 (ZTO) is known for having high electron mobility, high electrical conductivity, and attractive optical properties, all of which make it suitable for a wide range of applications, such as photovoltaic devices and sensors for humidity, combustible gases [4–6]. Quite a number of researches on ZTO have primarily been limited to ZTO thin films [7–10].

In recent years, many efforts have been made to control the sizes and shapes of nanostructures, because these parameters determine their electrical and optical properties [11–15]. Organizing nanoscale building blocks into complex nanostructures is always a target for researchers [16–19]. Although the ZTO nanowires and nanobelts have been prepared in the past two years by using a thermal evaporation method [20,21], the synthesis condition is tied up by many rigid aspects. In this paper, ternary semiconductor Zn_2SnO_4 hollow spheres were prepared using the simple coprecipitation method without any surfactant. This method offers several attractive advantages such as: simplicity of the process, availability of mass production and good repeatability with low cost. To the best of our knowledge, this type of ZTO hollow spheres synthesized without any surfactant has never been reported before. Growth of these hollow spheres will open a new option for assembling nanoscale blocks into low-dimensional structure.

2. Experiment

All reagents were analytical reagent grade and used without further purification. The zinc nitrate [$Zn(NO_3)_2$] solution was obtained by dissolving ZnO in nitric acid. Stannic chloride pentahydrate ($SnCl_4 \cdot 5H2O$) and $Zn(NO_3)_2$ in a 1:2 molar ratio were dissolved in a minimum amount of distilled water. The mixture was added dropwise into ammonia ($NH_3 \cdot H_2O$) aqueous solution ($V_{NH_2 \cdot H2O}$:V_{H_2O}=2:3) under magnetic stirring. The final solution was alkalescence with a pH value around 8 to make the reagents react completely. The as-synthesized precursor was filtered and washed with distilled water to remove undesirable anions such as Cl^- and NO_3^-, dried at 120 °C for 2.5 h, then calcined in an oven at 1000 °C for 1 h.

The crystal phase of the product was determined by X-ray diffraction with CuKα radiation (RigaKu RIN2200). Scanning electron microscopy (SEM) images were performed with a JEOL JSM-6700f scanning electron microscope. The photoluminescent properties were measured with a Hitachi 850

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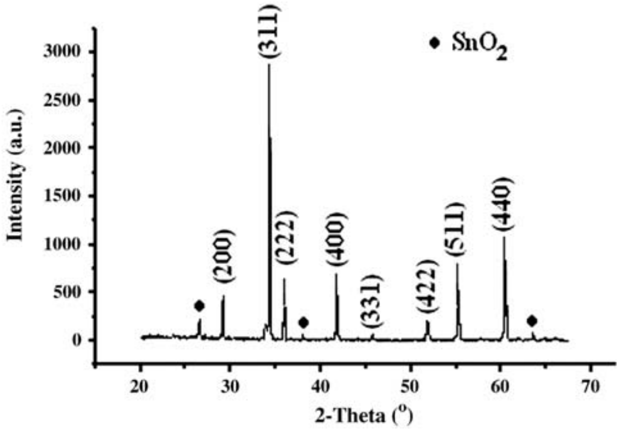

Fig. 1. XRD pattern of the as-synthesized product.

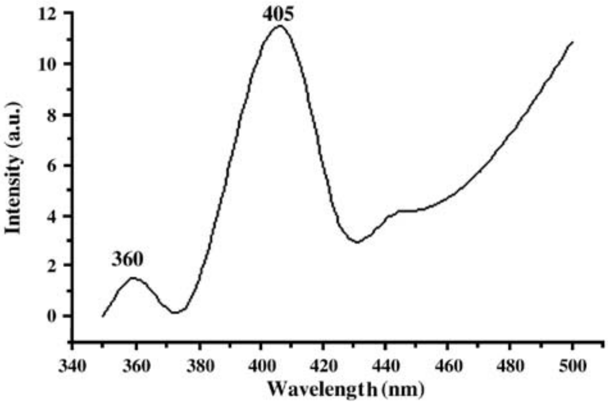

Fig. 3. Photoluminescent spectrum of the as-synthesized ZTO.

fluorescence spectrometer. Photocatalytic activity of the prepared powers was evaluated by the degradation of methyl orange.

3. Results and discussion

X-ray diffraction (XRD) was used to examine the crystal structure and phase purity of the final sample (Fig. 1). From the XRD pattern, most of the sharp diffraction peaks can be assigned well with face-centered spinel-structure Zn_2SnO_4 (JCPDS No: 24-1470). The residual peaks marked with black dot symbols can be assigned to SnO_2 (JCPDS No: 41-1445). These peaks of SnO_2 are much lower than those of ZTO and much fewer than the standard data of SnO_2 phase, indicating that an infrequent amount of SnO_2 exists in the as-synthesized sample.

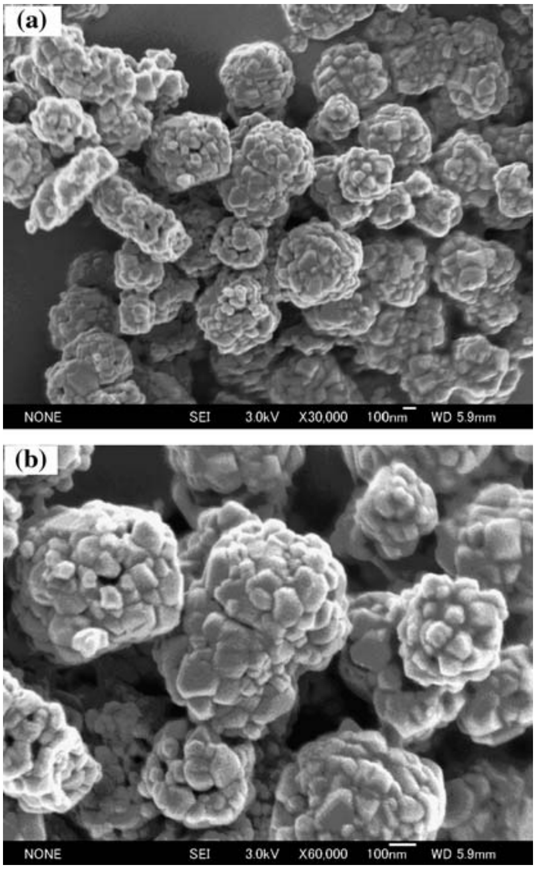

Fig. 2. SEM images with different magnifications of ZTO hollow spheres.

The coexistence of SnO_2 may be caused by two aspects: 1) the evaporation of a part of ZnO, and 2) thermal decomposition of the as-synthesized precursor. Stambolova et al. [9] and Hashemi et al. [22] had indicated that the evaporation of part of ZnO was the present problem for preparing the single phase of Zn_2SnO_4. On the other hand, $ZnSn(OH)_6$ precursor with a cubic structure will be synthesized after the Zn^{2+} and Sn^{4+} solutions were thoroughly mixed under vigorous stirring at room temperature. The final product, Zn_2SnO_4 with an infrequent amount of SnO_2, is obtained by thermal decomposition of $ZnSn(OH)_6$ precursor. The reactions for formation of Zn_2SnO_4 can be summarized as follows:

$$2Zn^{2+} + 2Sn^{4+} + 12OH^{-} \rightarrow 2ZnSn(OH)_6\downarrow \rightarrow Zn_2SnO_4 + SnO_2 + 6H_2O\uparrow$$

It is hard to detect the diffractions according to the phase with a 1:1 cation ratio ($ZnSnO_3$) under the present synthetic procedure. This may be due to the fact that the only stable phases at high temperature (>750 °C) in the ZnO–SnO_2 system are Zn_2SnO_4, ZnO and SnO_2, and the thermal decomposition of $ZnSn(OH)_6$ can only yield amorphous $ZnSnO_3$ stable within the temperature range 350 °C–750 °C [23].

The morphology of the synthesized product was indicated with the typical SEM images (Fig. 2a and b). The SEM images show that the

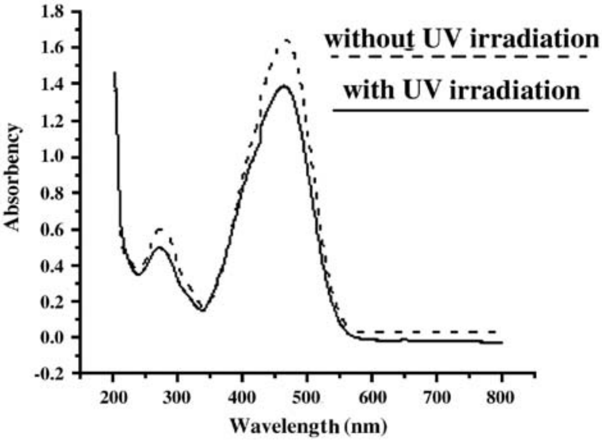

Fig. 4. Results for photocatalytic activity of ZTO to methyl orange.