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One-step solution synthesis and formation mechanism of flower-like ZnO and its structural and optical characterization

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ABSTRACT

The regular hierarchical flower-like ZnO nanostructures assembled by nanosheets were successfully synthesized by one-step solution route with citrate assistance at room temperature. It was demonstrated that the concentration of citrate and the molar ratio of Zn^{2+}/OH^{-} had strong effect on the formation of nanosheets and self-assembly flower-like nanostructures. A reasonable formation mechanism of the flower-like nanostructures was proposed. According to UV–vis spectrum, the flower-like ZnO nanostructures exhibited strong light absorption, and the value of band gap of the obtained ZnO was estimated to be 3.26 eV. Moreover, the room-temperature photoluminescence (PL) spectrum of the sample presented only a near-band edge emission at 382 nm.

1. Introduction

Over the past decades, researchers have been focused increasingly on the study of metal-oxides nanomaterials [1–3] due to their unique properties, including excellent electrical, good optical, and so on. And meanwhile, due to these outstanding properties, metal-oxides nanomaterials are considered to be some of the most promising functional materials and have been widely exploited in various applications, such as solar cells [4], light-emitting diodes [5], gas sensors [6], and photocatalysis [7].

Among metal oxides, zinc oxide (ZnO) is perhaps the most intensively investigated oxide material due to its wide band gap of 3.37 eV and large exciton binding or Rydberg energy of ~60 mV, which makes it the most functional materials used for many applications, such as biosensors [8], solar cells [9], photocatalysis [10], light-emitting diodes [11], piezoelectric transducers [12], filed-emission [13] and other applications. Currently, a variety of methods such as hydrothermal, solthermal, sol–gel, electrodeposition technology have been developed to synthesized ZnO nanomaterials. Enormous efforts have so far been made to synthesize and characterize ZnO nanostructures in the form of zero-dimensional (0D) quantum dots [14]; one-dimensional (1D) nanowires [15], nanorods [16], nanotubes [17], nanobelts [18], etc; two-dimensional (2D) nanosheets [19] and even three-dimensional (3D) nanoflower [20], nanodisk [21], etc.

In the case of ZnO, 3D hierarchical structure assembled by 1D and 2D nanostructure has attracted considerable attention for many researchers because it exhibits outstanding optical, electronic, and catalytic properties. Flower-like morphology, as a special 3D structure of ZnO has been paid much attention in recent years due to its excellent function in photoluminescence [22] and photocatalysis [23]. Miao et al. [24] and Zhou et al. [25] synthesized 3D flower-like ZnO architectures assembled with numerous nanosheets with hydrothermal route assisted by sodium dodecyl sulfate. Allagui et al. [26] reported that flower-like ZnO microstructures were prepared using bipolar electrochemical process in deionized water. Comparing with these methods, solution route is a facile, cost-efficient and environmentally-friendly way to synthesize flower-like ZnO materials without the need of special experimental conditions and other critical environment. Moreover, the solution method is free from the (nature/type) of substrates or templates and is considered to be the most promising way to synthesize flower-like ZnO materials on a large scale for commercial application. We synthesized hierarchical flower-like ZnO nanostructures assembled by nanosheets at room temperature and no requirement of any special experimental setup.

Herein, the regular hierarchical flower-like ZnO nanostructures assembled by nanosheets were successfully synthesized by one-step solution route on a large scale with citrate assistance at room temperature. Some key factors including the concentration of citrate, the molar ratio of Zn^{2+}/OH^{-} and zinc source were studied to explore the formation mechanism of flower-like nanostructures assembled by nanosheets. All the samples were characterized by X-ray (XRD), filed emission scanning electron microscopy (FESEM). Based on the results of all characterization, a reasonable mechanism was proposed to explain the growth process of flower-

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like ZnO nanostructures from the terms of crystal growth. Besides, the optical properties of flower-like nanostructures were also investigated by UV–vis absorption spectroscopy and photoluminescence (PL) spectroscopy in our experiment.

2. Experimental section

2.1. Synthesis of flower-like ZnO nanostructures

All the reagents used in the present investigation were of analytical grade and used without further purification. Deionized water was used for preparation of all solutions. In the work, zinc acetate dehydrate (0.1 M) and citrate (0.24 M) were dissolved into 60 mL deionized water under stirring to form a transparent solution. And then 0.5 M of sodium hydroxide (NaOH) was slowly dropped into the transparent solution under constantly stirring. Subsequently, the reaction solution was stirred for 2 h at room temperature. Finally, the white samples were obtained by centrifugation, repeatedly washed with deionized water and anhydrous ethanol to remove impurities, and dried overnight in an oven at 60 °C in air.

2.2. Characterization

The synthesized samples were characterized with multiple technologies. The general morphology of the synthesized samples was investigated with field emission scanning electron microscopy (FESEM, SU8010, HITACHI). The samples were pretreated with a thin amorphous gold on their surface before FESEM analysis. The element composition of the samples was measured with energy dispersive X-ray spectrometer (EDS) attached to the FESEM. The structure and crystal phase of the samples were characterized by powder X-ray diffraction (XRD, D8 Advanced XRD, BrukerAXS). UV–vis diffuse reflectance spectra were recorded with an UV–vis spectrophotometer (UV-3600, Shimadzu, Tokyo, Japan).The room temperature photoluminescence (PL) spectrum of the sample was measured by using fluorescence spectrophotometer (F-4500, HITACHI) equipped with a Xe lamp (Excitation wavelength is 249 nm).

3. Results and discussion

3.1. Morphology and structure

As shown Fig. 1(a) and (b), it can be seen clearly that the ZnO samples is composed of numerous hierarchical flower-like nanostructures aggregates. The flowers have similar shape and different size. Single flower exhibits spheroidal hierarchical nanostructure and has an average diameter in the range 1–2 μm, as shown in Fig. 1(c). Moreover, we can easily find that each of flowers is assembled by a large number of nanosheets with an average thickness of ~10 nm. The nanosheet looks like petal, interacting with each other, which results in the morphology of hierarchical flower-like structures. In addition, each of nanosheets has irregular boundary, and each of flowers has porous surfaces. Due to the existence of plenty of boundaries and numerous porous surfaces, it can be speculated that the flower-like ZnO possess more outstanding properties than others structures [27].

The XRD pattern of the as-synthesized ZnO sample is displayed in Fig. 1(d). All of the diffraction peaks can be ascribed to the hexagonal wurtzite ZnO having a lattice constants of a=2.2495 Å and c=5.2069 Å (JCPDS card no. 89–7102). And there are no characteristic peaks of other impurities detected, which indicates that the pure hexagonal wurtzite ZnO crystals without any

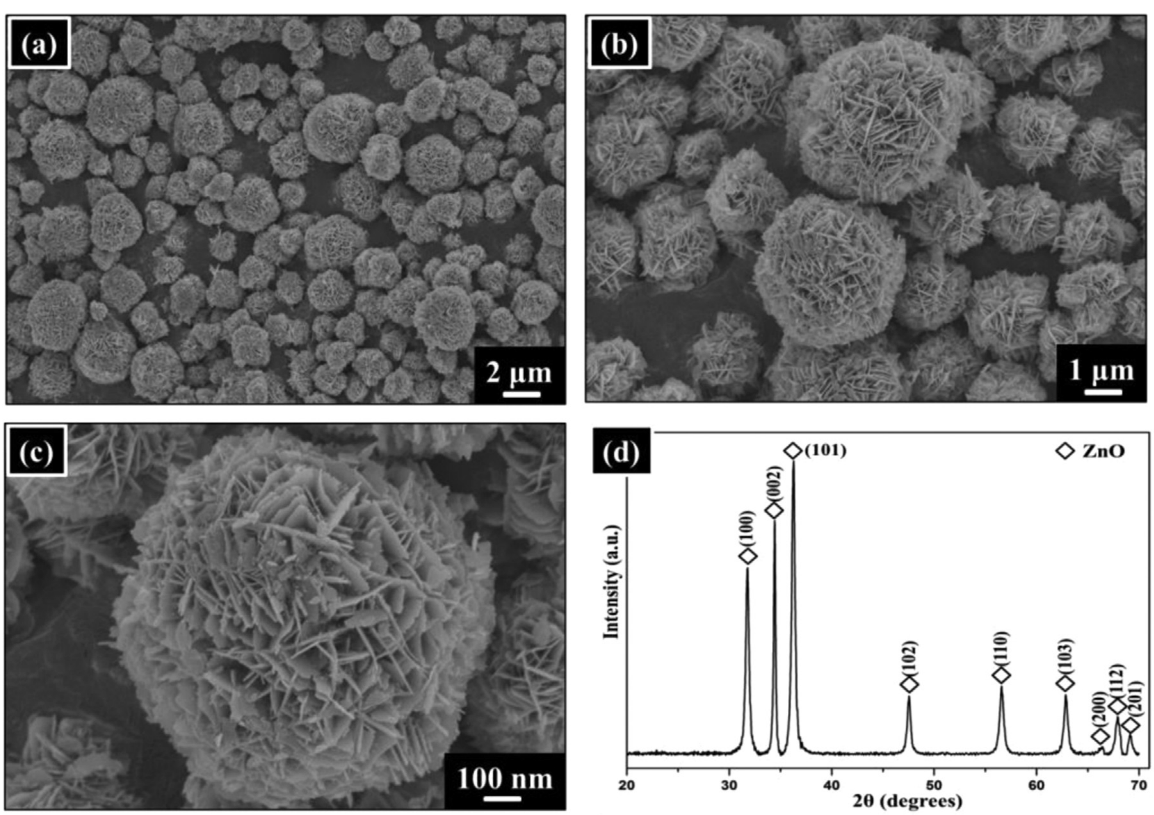

Fig. 1. FESEM images and XRD pattern of ZnO structures synthesized from the reaction of 0.1 M zinc acetate, 0.24 M citrate and 0.5 M sodium hydroxide at room temperature under stirring for 2 h. (a, b, and c) FESEM images of the sample, (d) XRD pattern of the sample.