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Template-free sonochemical synthesis of flower-like ZnO nanostructures

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ABSTRACT

Flower-like ZnO nanostructures have been successfully synthesized via a facile and template-free sonochemical method, using zinc acetate and potassium hydroxide as reactants only. The as-synthesized flower-like ZnO nanostructures were composed of nanorods with the width of ~300–400 nm and the length of ~2–3 μm. The structures, morphologies and optical properties of the as-prepared products were characterized by X-ray diffraction, scanning electron microscope, transmission electron microscopy, UV-Vis spectrophotometry and Raman-scattering spectroscopy. A plausible formation mechanism of flower-like ZnO nanostructures was studied by SEM which monitors an intermediate morphology transformation of the product at the different ultrasonic time ($t = 80, 90, 95, 105$, and 120 min).

1. Introduction

In recent years, ZnO nanostructures have attracted considerable attention due to their unique piezoelectric, semiconducting and catalytic properties and wide range of applications in sensors, optoelectronics, transducers and medical sciences [1–4]. Many interesting nanostructures of ZnO including nanobelts, nanobridges, nanonails, and nanoribbons have been fabricated by different methods [5–7]. As a representative semiconductor, ZnO has a direct band gap of 3.37 eV and a large exciton binding energy of 60 MeV at room temperature, thus becoming one of the most potential nano materials. Over the past decade, various methods, such as conventional sputter deposition technique [8], thermal evaporation process [9], sol–gel reaction [10], solution growth process [11] and hydrothermal process [12] have been used to synthesize nano- or micro-scaled ZnO structures in various sizes and morphologies. However, these methods are expensive and usually require high vacuum or other stringent conditions. Therefore, the development of a simple and fast synthetic route that can control the shape of ZnO nanostructures under ambient conditions remains an important topic of investigation. Furthermore, sonochemical method has been proven to be a versatile approach for preparation of ZnO nanostructures due to the convenience and simplicity.

Recently, several researchers have synthesized different morphologies of ZnO nano-/micro-structures using sonochemical methods. For example, Jung et al. reported a simple sonochemical route for the synthesis of vertically aligned ZnO nanorods on various substrates [13]. Shortly afterwards, this team reported sonochemical preparation of shape-selective ZnO nanostructures, such as nanorods, nanocups, nanodisks, nanoflowers, and nanospheres [14]. Deng et al. synthesized ZnO hollow spherical structures by a facile template-free sonochemical process [15]. Pholnak et al. fabricated octahedral zinc oxide by ultrasonic reaction of zinc nitrate hexahydrate and hexamethylenetetramine [16]. Zak et al. prepared hierarchical ZnO–NS from Zn salt, sodium hydroxide and ammonia solution precursor by sonochemical method [17]. However, to the best of our knowledge, the preparation of flower-like nanostructures via a facile template-free sonochemical method using zinc acetate and potassium hydroxide as reactants only has not been reported yet. Herein, we report a simple sonochemical method for the preparation of flower-like ZnO nanostructure. Our method does not require either complicated apparatus nor other additives. This is a facile and economical route to prepare flower-like ZnO nanostructure. Additionally, a possible formation mechanism was proposed.

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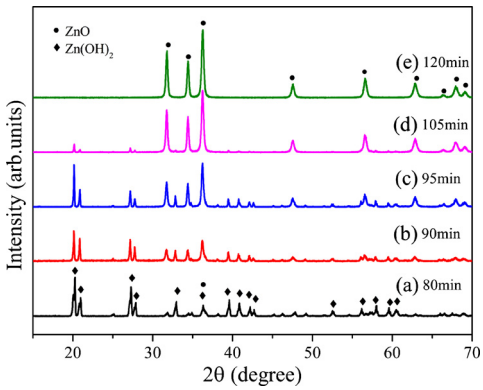

Fig. 1. XRD patterns of the samples obtained at different ultrasonic time.

2. Experimental

Flower-like ZnO nanostructures were synthesized by a simple sonochemical method using sonochemical bath. All chemicals used in this work were analytical-grade reagents without any further purification. In a typical experiment, 10 ml 0.1 M zinc acetate aqueous solution and 10 ml 1 M potassium hydroxide aqueous solution were added to 80 ml double distilled water. After vigorous magnetic stirring for 30 min, the resulting mixture containing beaker was then immediately kept in sonication bath (25 kHz, 300 W) at ambient temperature for different ultrasonic time ($t = 80, 90, 95, 105$, and 120 min). Initial temperature of reaction mixture was 20 °C. After 2 h, the temperature had risen to 50 °C. The precipitates were centrifuged, washed with water and alcohol several times, and finally dried in an oven at 60 °C for 24 h. ZnO samples obtained at different ultrasonic time ($t = 80$, 90, 95, 105, and 120 min) were prepared for investigating the formation mechanism of flower-like ZnO nanostructure.

The X-ray powder diffraction (XRD) data were collected on a diffractometer (X'Pert MPD, Philips, Eindhoven, The Netherlands). Scanning electron microscopy (SEM) images were performed by using a microscope (JEOL-6700F, JEOL, Tokyo, Japan) operating at 20 kV. Transmission electron-microscopy (TEM, JEM-3010, Questar, New Hope, USA) was performed with an acceleration voltage of 300 kV. The UV-Vis spectra were recorded in the range of 200–600 nm by an evolution spectropohometer system (300 UV-Vis, Thermo Scientific, Waltham, MA, USA). The Raman spectra (Invia, Renishaw, Gloucestershire, UK) were excited by a 532 nm Nd: YAG laser at room temperature.

3. Results and discussions

The XRD patterns of the samples obtained with the different ultrasonic time ($t = 80, 90, 95, 105$, and 120 min) are shown in Fig. 1. In Fig. 1(a), the sample obtained at 80 min ultrasonication time is identified as $Zn(OH)_2$ phase with orthorhombic structures (JCPDS 38-0385). After 90 min ultrasonication, the phase transformation is performed from $Zn(OH)_2$ phase to ZnO phase, which is clearly shown from Fig. 1(b) to (d). When the reaction time is prolonged to 120 min, the samples are characteristic as ZnO (JCPDS 36-1451) with hexagonal wurtzite type crystalline structure, as shown in Fig. 1(e). No diffraction peaks from other phases are detected, indicating that all the $Zn(OH)_2$ have completely transformed into ZnO phase. The average size of the ZnO nanostructures obtained at the ultrasonication time of 120 min could be estimated by the Debye–Scherrer formula [18] from the peak (101) to be about 37 nm.

To understand the formation process of flower-like ZnO nanostructure and possible growth mechanism, the evolutional morphology of the intermediates obtained at different ultrasonic time ($t = 80, 90, 95, 105$, and 120 min) is investigated in detail and the results are shown in Fig. 2. In Fig. 2(a), the SEM image of the sample synthesized after 80 min of ultrasonication is shown. It can be observed that the sample consists of some irregularly polyhedral. XRD pattern of the sample indicates that the majority of the products are $Zn(OH)_2$ phase. When the ultrasonic time is increased to 90 min, the surface of the $Zn(OH)_2$ crystals is slowly dissolved while ZnO is nucleated in the beginning in Fig. 2(b). After 95 min of ultrasonication, some hazy flower-like ZnO nanostructures form initially in Fig. 2(c). The high-magnification SEM image in Fig. 2(d) shows that the core of the flower and most of the branched structure are immersed into dissolving $Zn(OH)_2$ crystals while the tips of branch are exposed to the outside of the crystals. It seems that the flower-like ZnO nanostructures follow the ingrowth of ZnO into $Zn(OH)_2$ crystals. In the ingrowth of ZnO into $Zn(OH)_2$, ZnO nucleated and grew from inside the $Zn(OH)_2$ octahedron and flower-like ZnO nanostructures assembled by several ZnO nanorods were immersed into the $Zn(OH)_2$ octahedron. The random ingrowth of ZnO into the $Zn(OH)_2$ octahedron indicates that no epitaxial growth exists between ZnO and $Zn(OH)_2$ [19]. When branched structures pass through the surface of dissolving $Zn(OH)_2$ crystal, growth units of $Zn(OH)_4^{2-}$ provided by dissolving $Zn(OH)_2$ can facilitate the further growth of branched structures. As the sonochemical process is prolonged to 105 min, the flower-like ZnO nanostructures with sizes of ~2–3 μm begin to appear in Fig. 2(e), with a little fraction aggregations. After 120 min, the flower-like ZnO nanostructures became larger and clearer in Fig. 2(f). Compared with the product at 105 min, the diameter of flower-like ZnO nanostructures is increased from ~3 μm to ~5 μm on average. The high-magnification SEM image in Fig. 2(g) shows that a single flower is composed of rod-like crystals in diameter irradiated from the center. Strikingly, some branches of flower-like ZnO nanostructures are single rods while the others consist of several rods.

Fig. 3 shows the TEM images of the as-prepared flower-like ZnO nanostructure at ultrasonic time of 120 min. As shown in Fig. 3(a), the typical flower-like ZnO nanostructures are composed of nanorods with the width of ~300–400 nm and the length of ~2–3 μm which matches well with the SEM image and the core of the flower is formed of aggregated ZnO nanoparticles. A typical high resolution TEM image of an individual ZnO nanorods obtained from the flower-like ZnO nanostructures is presented in Fig. 3(b). It shows that the fringes of (002) planes with a lattice spacing are 0.26 nm. The selected area electron diffraction (SAED) pattern inserted in Fig. 3(b) indicates that the ZnO nanorods are single-crystalline and grow along the [0001] direction, demonstrating a typical phenomenon of wurtzite structural materials.

The simple growth mechanism for flower-like ZnO nanostructure under sonochemical condition is proposed. In the initial stage of sonochemical reaction, the $Zn(OH)_2$ is obtained readily when Zn^{2+} cation reacts with OH^- anions. Then, the interior of $Zn(OH)_2$ begins to dehydrate and generates the ZnO nuclei. Once the ZnO nucleus is initiated in $Zn(OH)_2$ octahedron, the remaining $Zn(OH)_2$ simply serves as a template for holding the crystal growth of the ZnO nanorod and even flower-like ZnO nanostructure until its complete dissolution. In this stage, the growth should involve a direct solid–solid phase transformation from $Zn(OH)_2$ to ZnO, since phase transformation happens in interior of $Zn(OH)_2$ where no alkaline solution can reach the phase boundary to facilitate the growth by dissolution and reprecipitation. So growth involves in situ crystallization transformation from $Zn(OH)_2$ to ZnO accompanied by dehydration and internal atomic rearrangements [19]. Because $Zn(OH)_2$ has a more open crystal structure and lower packing density than ZnO, dehydration of $Zn(OH)_2$ takes place between every two nearest hydroxyl groups in a $Zn(OH)_2$ structure. After dehydration, subsequent lattice contraction and rearrangement give rise to