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Synthesis of flower-like ZnO microstructures via a simple solution route

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Abstract

Well-defined flower-like ZnO microstructures with different sizes and shapes have been successfully synthesized via a simple aqueous solution route, using zinc chloride and sodium hydroxide as the reactants, triethanolamine (TEA) as the modifying agent. The XRD pattern indicated that the obtained ZnO microcrystals were of wurtzite structure. SEM and TEM images illustrated that the flower-like ZnO bundles consisted of some prism-like or petal-like branches, which can be further characterized as single crystals in nature and preferentially growing up along [0 0 0 1] by SAED and HRTEM studies. The solution basicity has determinative effects on the morphology, size, as well as dimensionality of the obtained ZnO microcrystals by mediating the nucleation and crystal growth rate. Furthermore, the uneven adsorption of TEA on (0 0 0 1) plane of the growing ZnO crystal leads to the tapering feature of the branches, which resemble vividly the flower petals in appearance.

Keywords: ZnO microstructures; 3D flower-like; Aqueous solution route; Synthesis; Growth process

1. Introduction

Recently, the control of size, morphology and dimensionality of inorganic materials has rapidly developed into a promising field in materials chemistry. Zinc oxide, a versatile semiconductor material with a wide direct-band gap of 3.37 eV and high-exciton binding energy of 60 meV, has shown extensive applications in light-emitting diodes, field-effect transistors, flat panel displays, ultraviolet nanolasers, and so on [1–3]. Various chemical and physical processes, such as conventional sputter deposition technique [4], chemical vapor deposition (CVD) [5,6], thermal evaporation [7,8], and hydrothermal process [9–12], can be used to synthesize nano- or microscaled ZnO crystals in various sizes and morphologies. Well-defined ZnO nano- or microstructures with various shapes, such as nanorods [6,13–17], nanowires [4,5,18], nanotubes [19,20], nanobridges and nanonails [21], have been obtained over the past few years. Some novel morphologies, including tower- [22,23], star- [24], dendrite- [25], and flower-like [12,26–30] ZnO nano- or microstructures, have also been achieved via different chemical solution routes very recently. These complex structures are expected to have more potential applications in building functional electronics devices with special architectures and distinctive optoelectronic properties. Therefore, development of morphologically controllable synthesis of ZnO nano- or microstructures is urgently important to answer the demand for exploring the potentials of ZnO.

Herein, we report a simple and novel approach toward the growth of flower-like ZnO microcrystals directly from aqueous solution. In comparison with the hydrothermal process which is used so extensively in the very recent years, the presented approach is requiring very mild reaction conditions under normal atmospheric pressure, i.e. the reaction temperature is relatively low (<100 °C) and the reaction time is short (3–4 h). This is owing to the novel experimental procedure which can produce $Zn(OH)_4^{2-}$ precursor with much lower solution basicity (Zn^{2+}:OH^- = 1:4–1:8) than the others (Zn^{2+}:OH^- < 1:10). We control over the morphology, size and dimensionality of ZnO samples just by regulating the molar ratio of Zn^{2+} to OH^-, which has never been reported by other authors up to now. With the greatly increased reactant concentration ($[Zn^{2+}]$ = 0.2 M), the product yield is up to 95%. So it is believed a promising option

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for large-scale production of ZnO microcrystals owing to its simple, fast and less expensive virtues.

2. Experimental section

All chemicals purchased from Beijing Chemicals Co. Ltd. were of analytical reagent grade and used as received without further purification. The solvent medium used for the reaction system was distilled water. The well-defined flower-like ZnO microcrystals were synthesized by a following procedure: 20 mL of 1 M zinc chloride aqueous solution was diluted with 40 mL distilled water and then cooled to 3 °C. Under the above constant temperature, 35 mL of 4 M NaOH and 5 mL of 2 M TEA solutions were dropped with stirring into the $ZnCl_2$ solution, respectively, to get a 100 mL solution ([$ZnCl_2$]:[NaOH] = 1:7). Then the solution was maintained at room temperature under mild continuous stirring for 1.5 h, and subsequently transferred to a 250 mL ground-glass stoppered conical flask, aging at 85 °C in water bath for 2 h. For the comparison, two groups of similar experiments were performed. One was with different amount of NaOH, and the other was without TEA. Finally, the resulting white solid products were centrifuged, washed with distilled water, and dried in air at ambient temperature.

The structures and morphologies of the products were characterized by X-ray diffraction (XRD; Bruker-AXS D8 ADVANCE), field emission scanning electron microscopy (FESEM; JEOL JSM-6700F), scanning electron microscopy (SEM; Hitachi S-570), transmission electron microscopy (TEM; Hitachi H-9000), and high-resolution transmission electron microscopy (HRTEM; Hitachi H-9000) equipped with ED.

3. Results and discussion

A powder XRD pattern of the obtained ZnO microcrystals is shown in Fig. 1. All the diffraction peaks can be indexed as the hexagonal phase ZnO reported in the standard card (JCPDS 36-1451). Even if prepared at the low temperature, the flower-like ZnO microparticles are well crystallized, according to the intensity and half width of the XRD pattern.

Fig. 2a and b show the SEM images of the flower-like ZnO microcrystals obtained with molar ratio of Zn^{2+}/OH^- = 1:7 (0.1 M TEA). It can be seen that the flower-like ZnO bundles consist of many well-aligned nanorods with 400–500 nm in width and about 1 μm in length, which possess the typical tapering feature with pointed tips. The flower petals route from the individual crystalline nucleus, as further confirmed by the TEM image shown in Fig. 2c. In fact, the microstructures much resemble beautiful flowers in nature. In our experiments, it is impossible that the flower-like structures result from the agglomeration of monodispersed ZnO particles, because long time ultrasonic treatment could not destroy them. Fig. 2d shows the SAED pattern of an individual petal crystal taken from area 1 marked by the black box in Fig. 2c, indicating the single crystalline nature and hexagonal phase of the individual nanorod, which is consistent with the results of XRD characterization. While the SAED pattern (Fig. 2e) taken from the center of the flower (area 2 marked by the white box in Fig. 2c) is characterized by the symmetrical stripes rather than polycrystalline circles or arrayed spots, justifying the presence of some ordered arrangement of crystallites in this terrain. Fig. 2f shows the high-resolution transmission election microscopy (HRTEM) image taken from area 1. The image clearly reveals only the fringes of (0 0 2) planes with a lattice spacing of about 0.26 nm can be observed, indicating that the individual ZnO nanorod is a single crystal. Furthermore, the spacing of 0.26 nm between two adjacent lattice planes corresponds to the distance between (0 0 2) planes', indicating that [0 0 0 1] is the growth direction of the ZnO nanorods.

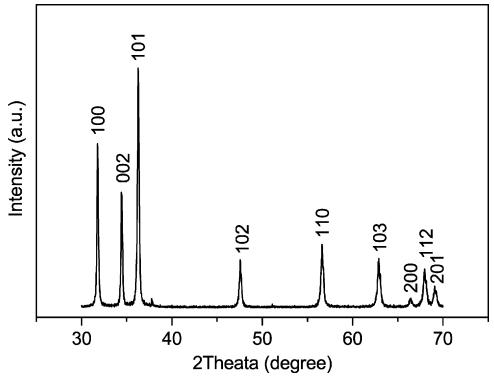

Fig. 1. XRD pattern of flower-like ZnO microstructures.

Synthesis of ZnO nano- or microstructures from aqueous solution containing $Zn(OH)_4^{2-}$ ions has been reported just from the near recent years. It is generally considered a very simple and novel process. However, the investigation of the growth process and mechanism from $Zn(OH)_4^{2-}$ to ZnO has not yet been adequately reported until now. The growth process of ZnO crystallites is generally accepted via the following mechanism:

$$Zn^{2+} + 2OH^- \rightarrow Zn(OH)_2\downarrow \quad (1)$$

$$Zn(OH)_2 + 2OH^- \rightarrow Zn(OH)_4^{2-} \quad (2)$$

$$Zn(OH)_4^{2-} \rightarrow ZnO + 2H_2O + 2OH^- \quad (3)$$

We can easily understand and obviously observe that at the beginning of this process, a $Zn(OH)_2$ precipitate was obtained. As more of the NaOH solution was added, the $Zn(OH)_2$ precipitate dissolved to yield a homogenous aqueous solution containing $Zn(OH)_4^{2-}$ ions. Then with the increase in temperature (85 °C), ZnO nuclei formed from the dehydration of $Zn(OH)_4^{2-}$ ions and followed by crystal growth. During the process, $Zn(OH)_4^{2-}$ is proposed to be the growth unit that is directly incorporated into ZnO crystallites under given conditions. In liquid medium, although the habit of ZnO crystal is mainly determined by its intrinsic structure, it is also affected by the external conditions such as pH value of the solution, certain additive, and so on. These will be discussed in detail in the following content.

3.1. Role of solution basicity

In the growth process, solution basicity was proved to be a critical factor that determined the morphology, size and dimensionality of the obtained ZnO microcrystals. To examine the function of NaOH in the process, a series of experiments were performed with different molar ratios of Zn^{2+}/OH^- when the concentration of Zn^{2+} remained constant (0.2 M). Results show that, when the molar ratios of Zn^{2+}/OH^- are controlled at the range of 1:6–1:7 and without any additive, monodispersed 1D ZnO nanorods are obtained, with diameters ranging from 200 to 300 nm and average length of 3.3 μm (aspect ratio ∼13),