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Hydrothermal synthesis of dumbbell-shaped ZnO microstructures

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Abstract

Dumbbell-shaped ZnO microstructures have been successfully synthesized by a facile hydrothermal method using only $Zn(NO_3)_2 \cdot 6H_2O$ and $NH_3 \cdot H_2O$ as raw materials at 150 °C for 10 h. The results from X-ray diffraction (XRD), Fourier transform infrared (FTIR) spectroscopy, scanning electron microscopy (SEM), and transmission electron microscopy (TEM) show that the prepared ZnO samples exhibit dumbbell-shaped morphology and hexagonal wurtzite structure. The length of ZnO dumbbells is about 5–20 μm, the diameters of the two ends and the middle part are about 1–5 μm and 0.5–3 μm, respectively. The dumbbell-shaped ZnO microstructures may be formed by self-assembly of ZnO nanorods with 1–5 μm in length and 100–200 nm in diameter. The photoluminescence (PL) spectrum of dumbbell-shaped ZnO microstructures at room temperature shows three emission peaks at about 362, 384 and 485 nm.

Keywords: D. ZnO; Microstructures; Hydrothermal synthesis; Photoluminescence

1. Introduction

Zinc oxide (ZnO) has been extensively investigated owing to their outstanding optical and electrical properties, such as wide direct band gap of 3.37 eV and high exciton binding energy of 60 meV at room temperature [1–3]. As a very important semiconductor material, ZnO has been widely used in many fields as light-emitting diodes [4], dye-sensitized solar cells [5], photocatalyst [6], chemical and gas sensors [7], biosensors [8], and so on. As a result, many methods, such as sol–gel method [9], hydrothermal synthesis [10], chemical vapor deposition (CVD) [11], solvothermal synthesis [12], oxidation of zinc [13] and thermal evaporation [14], have been developed to synthesize ZnO materials with different morphologies and structures. Among the above-mentioned methods, the hydrothermal synthesis is an effective and promising route with low cost, low temperature, high yield, easy operation, and simple equipment, etc. In recent years, ZnO nano/micromaterials with novel morphologies and structures have been prepared by using the hydrothermal synthesis. For example, Lian et al. [15] synthesized hexagonal ZnO micro-cups and micro-rings assembled by nanoparticles via a template-free hydrothermal synthetic method. Sun et al. [16] prepared flower-like ZnO microstructures with high photocatalytic performance by a hydrothermal method using TEA and NaOH as alkaline sources. Moulahi et al. [17] fabricated ZnO nanoshuttles by hydrothermal approach using Zn $(NO_3)_2 \cdot 6H_2O$ as zinc sources and CTAB as structure-directing agent. Baghbanzadeh et al. [18] obtained ultrafine ZnO hexagonal microrods of about 3–4 mm in length and 200–300 nm in width by a rapid, microwave-assisted hydrothermal method using a 1:5 zinc nitrate/urea precursor system. Mohammad et al. [19] synthesized ZnO nanorod arrays on glass substrates by hydrothermal process. Besides, Qin et al. [20] reported the bush-like ZnO nanosheets film on conductive transparent oxide substrates using a facile hydrothermal method without any surfactant or further heat treatment. Li et al. [21] presented the growth of two-dimensional ZnO nanoflakes on the stainless steel mesh coated by Al through low-temperature hydrothermal route. However, those works have some disadvantages in raw materials, solvents, costs, environmental protection, reaction temperature and time, and so on.

In this communication, we report a facile, low-cost and green hydrothermal route to synthesize dumbbell-shaped ZnO

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microstructures using only $Zn(NO_3)_2 \cdot 6H_2O$ and $NH_3 \cdot H_2O$ as raw materials. The PL spectrum of the dumbbell-shaped ZnO microstructures at room temperature shows three emission peaks at about 362, 384 and 485 nm.

2. Experimental procedure

All chemical reagents were of analytical grade and used without further purification. In a typical experiment, 1.8 g Zn $(NO_3)_2 \cdot 6H_2O$ was dissolved into distilled water (20 ml) under stirring at room temperature. Then, $NH_3 \cdot H_2O$ was added into the above solution to adjust PH value (about 8). After being stirred for 20 min, the solution was transferred into a 25 ml Teflon-lined stainless steel autoclave. The autoclave was heated to 150 °C and maintained for 10 h in an oven and then cooled down to the room temperature naturally. The products were washed with distilled water and absolute ethanol several times and dried at 80 °C for 12 h. Finally, the white products were obtained.

The crystalline phase of the white products was characterized by X-ray powder diffraction (XRD) with a Rigaku D/max2500VPC diffractometer using Cu*K*α radiation. IR spectrum of ZnO was recorded on a Fourier transform infrared (FTIR, MAGNA550, KBr) spectrometer from 400 to 4000 cm^{-1} range. The morphology and structure of the products were examined by scanning electron microscopy (SEM, JSM-5610LV) and transmission electron microscopy (TEM, JSM-1234). Photoluminescence (PL) spectrum of the dumbbell-shaped ZnO microstructures was measured in a LS55 fluorescence spectrometer with a Xe lamp at room temperature.

3. Results and discussion

Fig. 1 shows the XRD pattern of ZnO products obtained at 150 °C for 10 h. From the XRD pattern, it can be seen that all the diffraction peaks can be indexed as hexagonal wurtzite ZnO structures. The lattice constants calculated from the XRD data are $a=3.21$ Å and $c=5.19$ Å, which are also in good agreement with those of hexagonal wurtzite ZnO ($a=3.25$ Å and $c=5.21$ Å, JCPDS No. 36-1451) [15,22]. No other diffraction peaks are founded, indicating a high purity ZnO phase. The strong intensity and narrow width of the diffraction peaks exhibit an excellent crystalline structure. Further characterization of ZnO products is made by FTIR spectroscopy. Fig. 2 shows FTIR spectrum of the prepared ZnO products in the range 400–4000 cm^{-1}. In FTIR spectrum, the ZnO samples show four absorption peaks at about 3420, 1631, 1385, and 459 cm^{-1}. The absorption peak at 3420 cm^{-1} can be assigned to the stretching vibration and bending vibration of OH groups of adsorbed water molecules during the FTIR measurements [23]. The band at 459 cm^{-1} can be attributed to the Zn–O stretching vibration modes in ZnO [24]. The other two absorption peaks at 1631 and 1385 cm^{-1} in FTIR spectrum of our sample are also assigned to ZnO [25,26]. The FTIR results indicate the formation of ZnO in present experiment, which is consistent with the XRD results.

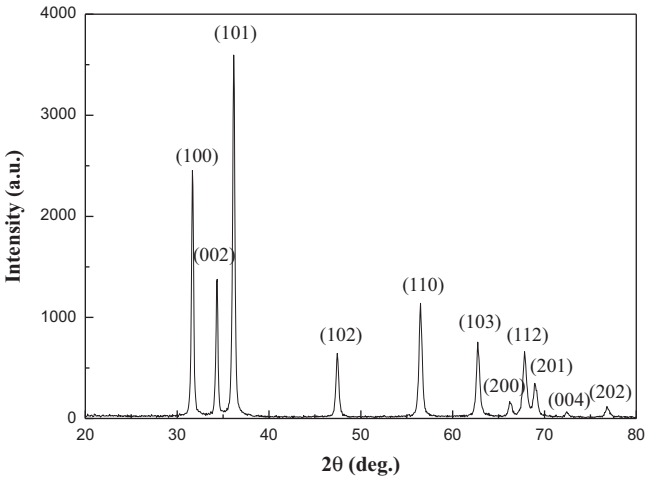

Fig. 1. XRD pattern of the obtained ZnO samples by hydrothermal synthesis at 150 °C for 10 h.

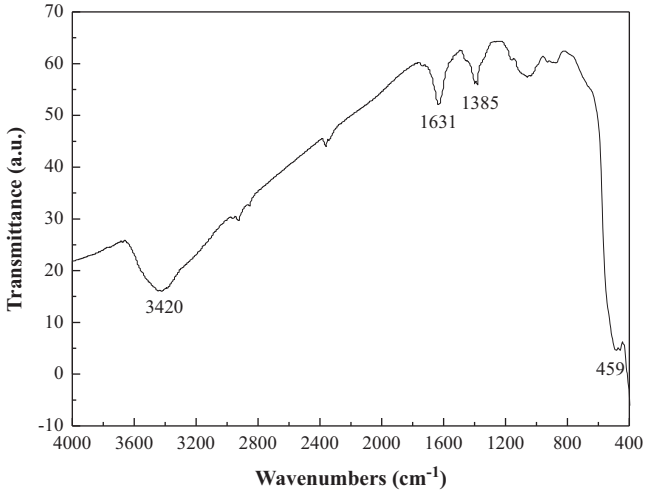

Fig. 2. FTIR spectrum of the obtained ZnO samples by hydrothermal synthesis at 150 °C for 10 h.

The morphology and structure of the prepared ZnO products are first characterized by SEM. Fig. 3 indicates SEM images of the prepared ZnO products with different magnification. From the low magnification SEM images (Fig. 3a and b), it can be seen that the prepared ZnO products are mainly composed of dumbbell-shaped microstructures with a few nanorods. The length of the dumbbell-shaped ZnO microstructures is about 5–20 μm, the diameters of the two ends and the middle part (waist) are about 1–5 μm and 0.5–3 μm, respectively. The high magnification SEM images (Fig. 3c and d) show that the ZnO dumbbells have a rough surface and sharp end structure, and which are obvious difference compared with the previously reported dumbbell-shaped ZnO microstructures [27–29]. As Fig. 3d, the obtained ZnO dumbbells mainly consist of nanorods with 1–5 μm in length and 100–200 nm in diameter. The structures of ZnO dumbbells are further characterized by TEM, as shown in Fig. 4. A typical TEM image of the ZnO dumbbells is revealed in Fig. 4a, which shows the ZnO dumbbells are different in size. Half a dumbbell with a regular

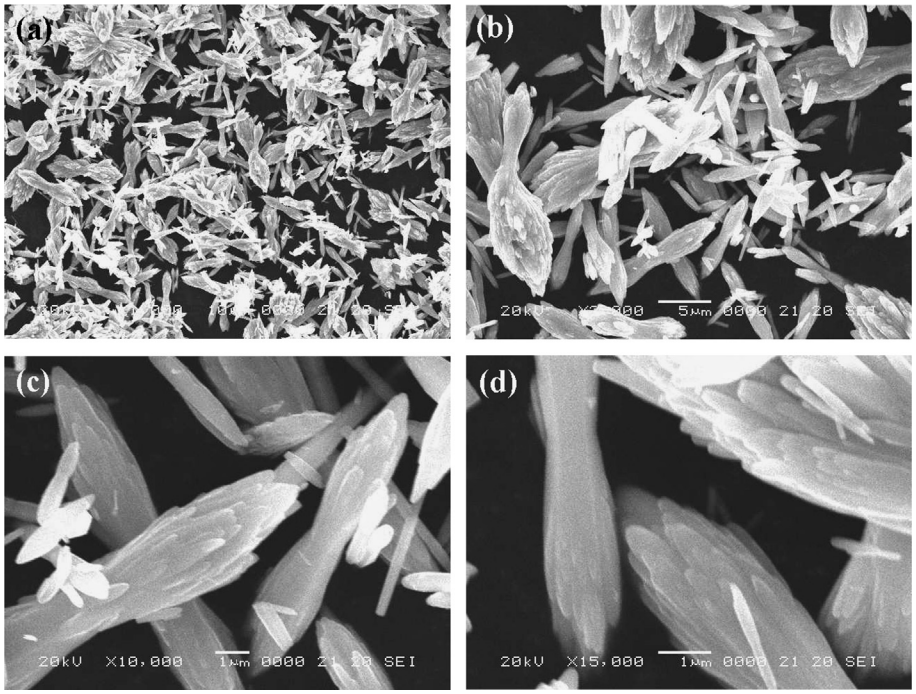

Fig. 3. SEM images of the dumbbell-shaped ZnO microstructures with different magnification: (a and b) low magnification; (c and d) high magnification.

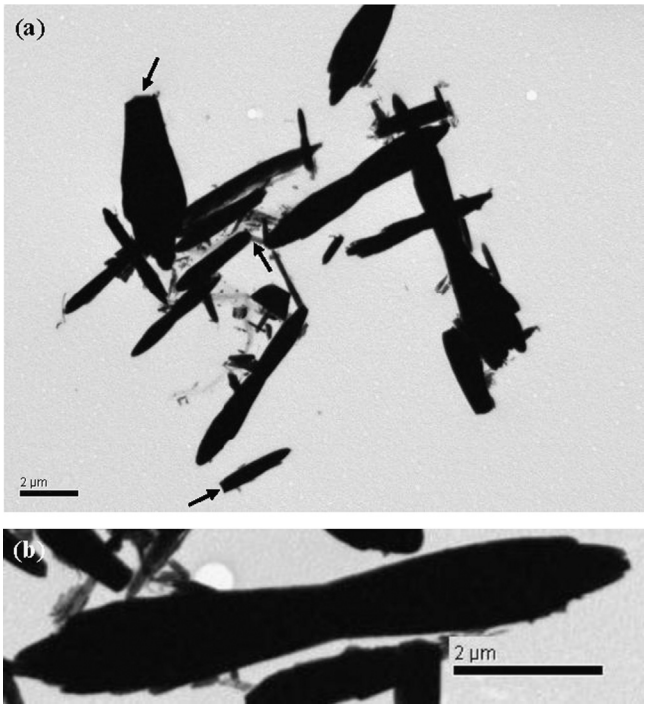

Fig. 4. (a) Typical TEM image of the dumbbell-shaped ZnO microstructures and (b) TEM image of a complete ZnO dumbbell.

fracture surface can also be found in TEM image marked with black arrows. Fig. 4b shows TEM image of a complete ZnO dumbbell. The TEM image clearly reveals that the obtained ZnO samples exhibit the well-defined dumbbell-shaped morphology with a length of about 8 μm and a diameter of about 0.5–1.3 μm. At the same time, a wavy surface structure can be also observed from TEM image of ZnO dumbbell. The SEM and TEM results show that the dumbbell-shaped ZnO microstructures may be formed by self-assembly of ZnO nanorods in present experiment. The possible formation mechanism of the dumbbell-shaped ZnO microstructures can be illustrated in Fig. 5. Firstly, the precursor precipitates of ZnO were obtained when ammonia ($NH_3 \cdot H_2O$) was added into zinc nitrate ($Zn(NO_3)_2$) aqueous solutions. Then a lot of ZnO nuclei (Fig. 5a) were formed rapidly via the decomposition of the precursor precipitates under the hydrothermal conditions (150 °C). Previous works show that the high concentration of $NH_3 \cdot H_2O$ is favorable for the formation of ZnO with rod-like morphology [30]. The concentration of $NH_3 \cdot H_2O$ is 15 mol/L in present experiment, and therefore a large number of ZnO nanorods were synthesized from the growth of ZnO nuclei at the *C*-axis direction with the reaction time, as shown in Fig. 5b. However, these nanorods are not stable in thermodynamics because of their higher surface energy. To decrease the total energy of the system, the nanorods have a tendency of preferential-oriented aggregation to form dumbbell-shaped structures, as shown in Fig. 5c. With increasing the reaction time, the dumbbell-shaped ZnO microstructures are formed by self-assembly of ZnO nanorods.

The photoluminescence (PL) property of dumbbell-shaped ZnO microstructures was carried out at room temperature with an excitation wavelength of 325 nm. The PL spectrum of dumbbell-shaped ZnO microstructures is indicated in Fig. 6. The PL spectrum shows that dumbbell-shaped ZnO microstructures exhibit there emission peaks centered at about 362, 384 and 485 nm. The strong ultraviolet (UV) emission peaks at 362 and 384 nm are attributed to the near-band-edge emission of the ZnO samples, which originates from the direct

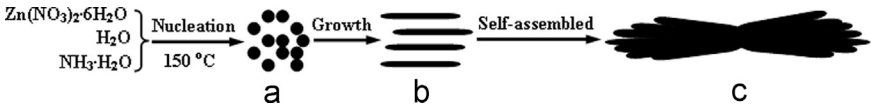

Fig. 5. Schematic illustration of the formation mechanism of the dumbbell-shaped ZnO microstructures.

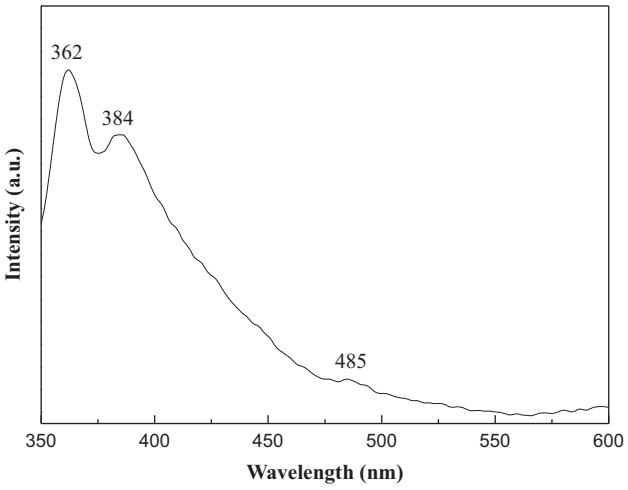

Fig. 6. PL spectrum of the dumbbell-shaped ZnO microstructures at room temperature.

recombination of the conduction band electrons and the valence band hole [29,31]. Compared with previous studies [27,29], the dumbbell-shaped ZnO microstructures with rough surface and sharp ends have a blue-shift in UV emission peaks, which may be owing to the effect of the morphology and structures. On the other hand, PL property can be enhanced for the dumbbell-shaped ZnO with rough surface and sharp ends because of more stacking defects. The weak emission peak at 485 nm may be correlated to a singly charged oxygen vacancy and a charge state of the specific defect [32,33]. Therefore, the dumbbell-shaped ZnO microstructures with rough surface and sharp ends will be a very good optical material for wide application in photocatalytic field.

4. Conclusions

In summary, the dumbbell-shaped ZnO microstructures have been synthesized by using a facile hydrothermal method. The length of ZnO dumbbells is about 5–20 μm, the diameters of the two ends and the middle part are about 1–5 μm and 0.5–3 μm, respectively. The dumbbell-shaped ZnO microstructures may be formed by self-assembly of ZnO nanorods with 1–5 μm in length and 100–200 nm in diameter. The PL spectrum of dumbbell-shaped ZnO microstructures at room temperature shows three emission peaks at about 362, 384 and 485 nm. The PL spectrum is improved for the dumbbell-shaped ZnO with rough surface and sharp ends owing to the effect of the morphology and structures. The dumbbell-shaped ZnO microstructures will has wide application in photocatalytic field as a very good optical material.

Acknowledgments

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