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Short communication

Morphology development of ZnO produced by sonothermal process

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Abstract

Wurtzite ZnO (hcp) was produced by the 80 °C sonothermal reactions of 1:5, 1:10, and 1:20 molar ratios of $Zn(NO_3)_2{\cdot}6H_2O$:NaOH in water, containing 2 g, 5 g, 10 g, and 20 g of polyethylene glycol (PEG) with the molecular weights (MWs) of 6000, 10000, and 20000 for 1 h, 3 h, and 5 h. ZnO phase with different morphologies was detected. When the amount of NaOH, both MW and the amount of PEG, and the experimental time were increased, the products still retain their single phase, but their morphologies were changed from nanoplates in clusters to nanospears with sharp tips gathering together in the shape of flowers, and long nanorods with oval tips in clusters. In the present work, formation mechanism of these products was also discussed.

Keywords: Sonothermal reactions; Zinc oxide; Nanoplates in clusters; Nanospears in flower-shaped clusters; Nanorods in clusters

1. Introduction

Zinc oxide (ZnO) is a semiconducting material, which has a 3.37 eV wide band gap and large exciton binding energy of 60 meV. It can be used in a wide range of applications: solar cells, gas sensors, optoelectronic devices, and surface acoustic waveguides. Recently, one-dimensional nanostructured ZnO has shown very attractive for use in a number of applications: short-wavelength light-emitting devices, transparent conducting films, piezoelectric materials, and room temperature ultraviolet (UV) lasing or the creation of laser beams by exciting electrons into high energy levels [1–5]. ZnO products with different morphologies were produced using a variety of methods: nanorod arrays and branched microrods by aqueous solution route and rapid thermal processing [3], nanodisks with bulk quantity by vapor-phase transport method [6], nanoparticles and nanosheets by sonochemistry [7–9], hexagonal zinc oxide microtubes by simple soft aqueous solution method [10], uniform rod-like and multi-pod-like whiskers by simple hydrothermal process [11], nanorods by solvothermal method [12], nanostructured tetrapods by catalyst-free rapid thermal evaporation [13], nanobelts by vapor phase growth [14], and nanostructured zinc oxide by microwave irradiation [15].

Ultrasonic radiations (20 kHz – 10 MHz) have been used to produce nanoparticles. The reactions are caused by the acoustic cavitation - formation, growth, and implosive collapse of gaseous bubbles in liquids. There are two regions that are reactive – the inside collapsing bubbles and the bubble-liquid interfaces. The cavitation may generate local temperature over 5,000 K and pressure over 20 MPa, which are extremely high for the chemical reactions to proceed. The implosive collapse of bubbles is able to generate localized hot spots by the adiabatic compression or shock wave formation within the gas phase, and has been used to produce nanostructured materials with different morphologies [16–18].

The purpose of the present research was to study the roles of moles of NaOH, amount and molecular weight (MW) of polyethylene glycol (PEG), and of length of time in the morphology development and degree of crystallinity of ZnO produced by the sonothermal method (a combination of ultrasonic vibration and direct heating) without any further calcination.

2. Experiment

To produce nanostructured ZnO, 0.005 mole $Zn(NO_3)_2{\cdot}6H_2O$ and different contents (0.025, 0.050, and

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0.100 mole) of NaOH were dissolved in 100 ml water containing 2 g, 5 g, 10 g, and 20 g polyethylene glycol (PEG) with molecular weights (MWs) of 6000, 10000, and 20000, and stirred for 15 min. The mixtures were sonicated at 80 °C (sonothermally processed) for 1 h, 3 h, and 5 h to produce precipitates. Then they were washed with water and ethanol, dried at 70 °C for 24 h, and characterized using an X-ray diffractometer (XRD) operated at 20 kV, 15 mA and using Cu K_α radiation with 0.1542 nm wavelength in the 2θ angular range of 10 - 60 deg, a scanning electron microscope (SEM) operated at 15 kV, and a transmission electron microscope (TEM) – including the selected area electron diffraction (SAED) technique operated at 200 kV, and compared with the electron diffraction patterns obtained by simulation [19].

3. Results and discussion

XRD spectra (Fig. 1) were indexed and interpreted as wurtzite ZnO (hcp) with $P6_3mc$ space group – JCPDS no 36-1451 [20], consisting of a hexagonally close-packed O^{2-} array in which one type of the tetrahedral holes was filled by Zn^{2+} [21]. The strongest intensity, corresponding to the (101) plane, was at 2θ = 36.3 deg. No impurities were detected in the products, although they were produced using different contents of NaOH, molecular weights (MWs) of polyethylene glycol (PEG), and variable lengths of time. The XRD intensities became stronger as more NaOH was added to the solutions until at 1:10 and 1:20 molar ratios of $Zn(NO_3)_2{\cdot}6H_2O$:NaOH, PEG20000 was used, and the sonothermal time increasing to 5 h long. These strongest intensity peaks indicated that the degree of crystallinity of the products was the highest, and the atoms resided in the perfect crystal lattice. For 1:10 molar ratio $Zn(NO_3)_2{\cdot}6H_2O$:NaOH, 20 g PEG20000, and 5 h long (result not shown), the degree of crystallinity decreased, due to the excessive PEG. At the present stage, PEG molecules dominantly played the role in inhibiting the arrangement of ZnO atoms in the lattice. It should be noted that these products still retain their ZnO (hcp) phase, although they were produced under different conditions. The degree of crystallinity of the products was also summarized in Table 1.

Morphologies of the products produced under different conditions are shown by SEM and TEM images (Figs. 2–4). In general, the products produced in the solutions containing 1:10 molar ratio $Zn(NO_3)_2{\cdot}6H_2O$:NaOH were composed of a number of nanoplates and nanospears with different orientations in clusters. At 2 g and 5 g PEG20000, and 5 h long (Fig. 2a and b), the nanoplates gathered themselves into 3-4 μm clusters. When more polyethylene glycol was added until the solution contained 10 g PEG20000 (Figs. 2c and 3a,b), the nanoplates turned into sharp-tip nanospears with flower-like clusters. In order to save the energy consumption, the sonothermal time was shortened. The products became nanoplates in 1 μm spherical clusters (Fig. 2d) and 3 μm flower-shaped clusters (Fig. 2e) for 1 h and 3 h long, respectively. When 10 g PEG6000 (Fig. 2f) and 10 g PEG10000 (Fig. 2g) instead of 10 g PEG20000 (Fig. 2c) were used, the degree of crystallinity decreased and the products slowly changed from flower-shaped clusters of nanospears to ordinary clusters of very tiny nanoplates. By lowering and raising the amount of NaOH in the solutions, the nanospears in flower-shaped clusters for the 1:10 molar ratio of $Zn(NO_3)_2{\cdot}6H_2O$:NaOH solution (Fig. 2c) changed to the nanoplates in spherical clusters for the 1:5 molar ratio $Zn(NO_3)_2{\cdot}6H_2O$:NaOH solution (Fig. 2h), and the long nanorods in clusters for the 1:20 molar ratio $Zn(NO_3)_2{\cdot}6H_2O$:NaOH solution (Figs. 2i and 4a, b). Detail

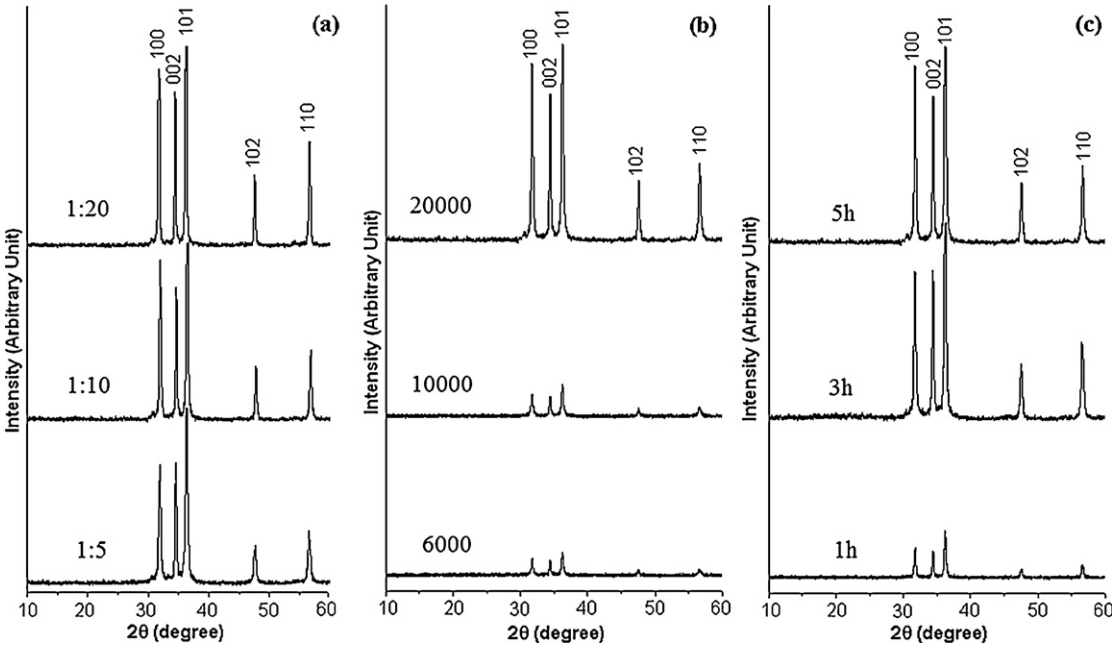

Fig. 1. XRD spectra of ZnO produced by the 80 °C sonothermal process in 100 ml water containing (a) 10 g PEG20000 and different molar ratios of $Zn(NO_3)_2{\cdot}6H_2O$ to NaOH for 5 h, (b) 10 g PEG with different MWs and 1:10 molar ratio of $Zn(NO_3)_2{\cdot}6H_2O$ to NaOH for 5 h, and (c) 10 g PEG20000 and 1:10 molar ratio of $Zn(NO_3)_2{\cdot}6H_2O$ to NaOH for variable lengths of time.

Table 1
The degree of crystallinity and morphologies of wurtzite ZnO (hcp) produced by the 80 °C sonothermal process under different conditions.

$Zn(NO_3)_2{\cdot}6H_2O$:NaOH(molar ratio)	Mass of PEG (g)	MW of PEG	Length of time (h)	Degree of crystallinity	ZnO morphology
1:20(Excessive NaOH)	10	20,000	5	Highest	Long nanorods in clusters
1:10	20(Excess)	20,000	5	Lower	-
1:10	10	20,000	5	Highest	Nanospears in flower-shaped clusters
1:10	10	10,000	5	Lower	Very tiny nanoplates in ordinary clusters
1:10	10	6,000	5	Lowest	Very tiny nanoplates in ordinary clusters
1:10	10	20,000	3	Lower	Nanoplates in 3 μm flower-shaped clusters
1:10	10	20,000	1	Lowest	Nanoplates in 1 μm spherical clusters
1:10	5	20,000	5	-	Nanoplates in 3-4 μm clusters
1:10	2	20,000	5	-	Nanoplates in 3-4 μm clusters
1:5	10	20,000	5	Lower	Nanoplates in spherical clusters

morphologies of the products were also summarized in Table 1. These investigations indicated that the amount and MWs of PEG, the amount of NaOH, and lengths of time have the strong influence to model the morphologies of ZnO produced by the sonothermal process.

SAED patterns of the products produced by the 1:10 and 1:20 molar ratios of $Zn(NO_3)_2{\cdot}6H_2O$:NaOH (Figs. 3c and 4c) appeared as systematic arrays of spots, showing that atoms were arranged in single crystal lattice. These patterns were indexed [22], and specified as wurtzite ZnO of the JCPDS database no 36-1451 [20]. Both of them have the same zone axes of [–110], showing the direction of electron beams used for these analyses. Their simulated patterns (Figs. 3d and 4d) [19] with lattice vectors (a*, b* and c*) in the [100], [010], and [001] directions are in systematic arrays, and in good accordance with the results obtained by these interpretations. Thus the products were really proved to be wurtzite ZnO.

When $Zn(NO_3)_2{\cdot}6H_2O$ and NaOH were dissolved in water, $Zn(OH)_2$ colloids formed. Concurrently, some $Zn(OH)_2$ decomposed into Zn^{2+} and OH^-. When the concentration of these ions reached the supersaturated values, ZnO nuclei started to form. During the sonothermal process, some $Zn(OH)_2$ could

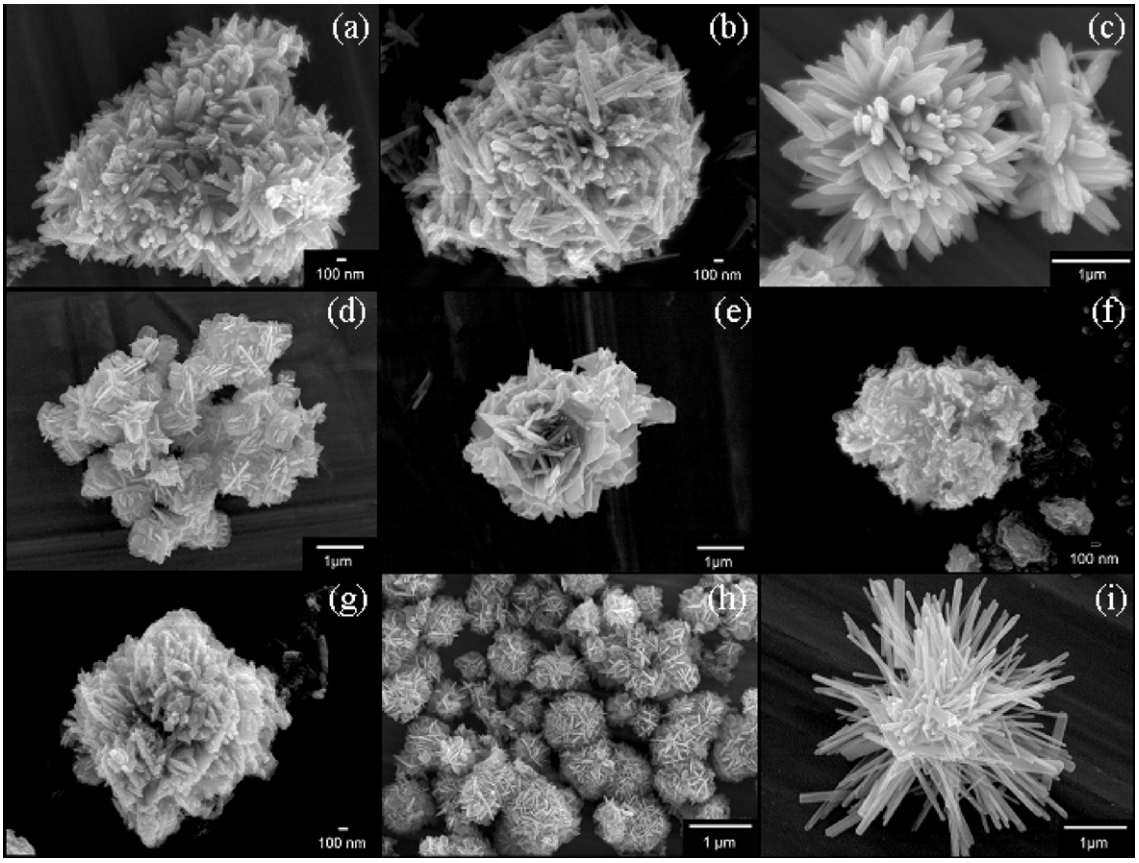

Fig. 2. SEM images of ZnO produced from the solutions containing (a-c) 1:10 molar ratio $Zn(NO_3)_2{\cdot}6H_2O$:NaOH, and 2 g, 5 g and 10 g PEG20000 for 5 h, (d, e) 1:10 molar ratio $Zn(NO_3)_2{\cdot}6H_2O$:NaOH and 10 g PEG20000 for 1 h and 3 h, (f, g) 1:10 molar ratio $Zn(NO_3)_2{\cdot}6H_2O$:NaOH, and 10 g PEG6000 and 10 g PEG10000 for 5 h, and (h, i) 1:5, and 1:20 molar ratios of $Zn(NO_3)_2{\cdot}6H_2O$:NaOH and 10 g PEG20000 for 5 h, respectively.

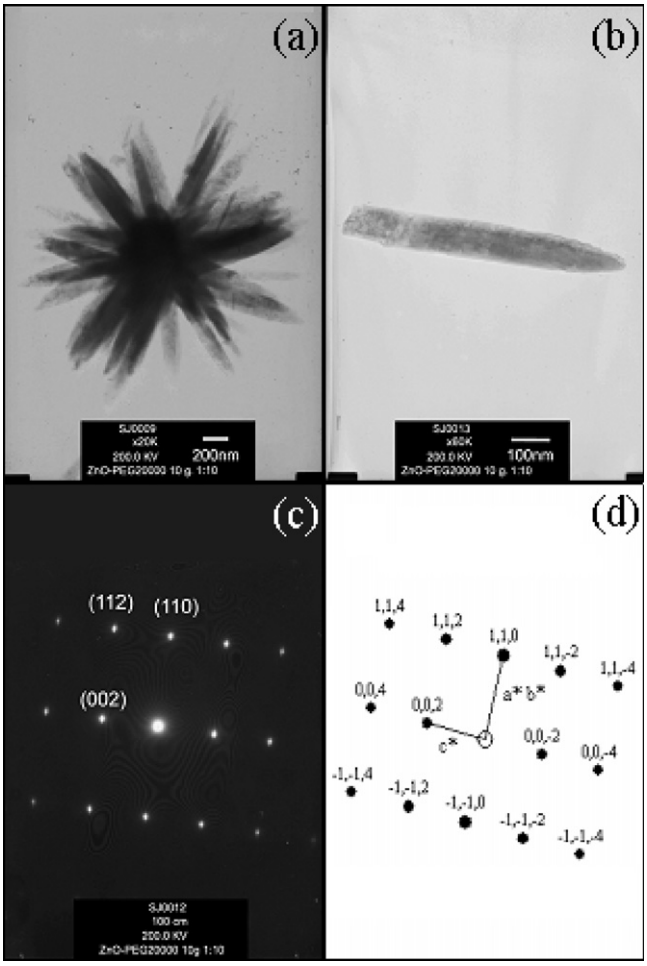

Fig. 3. (a, b) TEM images, and (c, d) SAED and simulated patterns of ZnO nanospears in flower-shaped clusters, produced from the solution containing 1:10 molar ratio $Zn(NO_3)_2{\cdot}6H_2O$:NaOH and 10 g PEG20000 for 5 h.

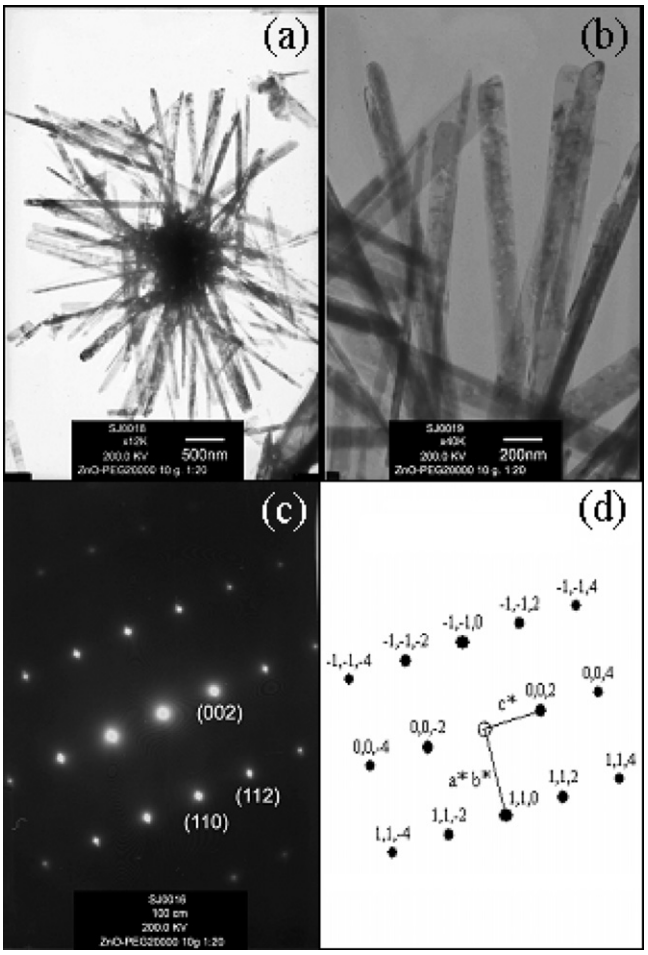

Fig. 4. (a, b) TEM images, and (c, d) SAED and simulated patterns of ZnO long nanorods in clusters, produced from the solution containing 1:20 molar ratio $Zn(NO_3)_2{\cdot}6H_2O$:NaOH and 10 g PEG20000 for 5 h.

react with OH^- ions to form $[Zn(OH)_4]^{2-}$ growth units [5].

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

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

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

$$Zn(OH)_2 + 2OH^- \rightarrow [Zn(OH)_4]^{2-} \quad (\text{growth units}) \quad (4)$$

Due to the concentration gradient, growth units diffused towards the nearby ZnO nuclei and adsorbed onto the active sites to form particles. These were influenced by the concentration of growth units, distribution of active sites, nucleation and crystal growth rates. In the solutions containing less amount of NaOH and PEG, low MW of PEG, and short reaction time, active sites and growth units were insufficient to form spear-shape particles [5,23]. Hence nanoplates in clusters were produced. When the solutions contained more NaOH or PEG, higher MW of PEG, or the reaction time was increased, the growth units and active sites became more concentrated. Thus the anisotropic growth process was promoted. At this stage, the reaction proceeded to produce nanospears, gathered together in the shape of flowers. Sharp tips of the nanospears were caused by the growth rates (R) of different crystallographic planes: $R(001) > R(-10-1) > R(-100) > R(-101) > R(00-1)$. The growth rate of the (001) plane was the most rapid. Hence, the (001) plane faded away during the sonothermal processing, and sharp tips were developed. At the other extremes, the growth rate of the (00-1) plane was the slowest, and the tips were planar [5,23]. During processing, ZnO nuclei gradually grew into nanoplates in ordinary clusters and nanospears in flower-shaped clusters – controlled by the MW and amount of PEG, amount of NaOH, and length of time. In the solution containing excessive NaOH, the nanospears with sharp tips changed into the long nanorods with the oval tips – dominated by the basicity of the solution. At this stage, growth rate of the (001) plane could be slow down, so that the tips of the nanorods were oval shape.

4. Conclusions

ZnO nanoplates and nanospears gathering together in the ordinary and flower- shaped clusters were successfully produced by the sonothermal method. By increasing the length of time, NaOH contents, and both the MW and amount of PEG, they still retain their phase, but not for the morphologies - they

changed from nanoplates in clusters to nanospears with sharp tips gathering together in the shape of flowers, and the nanospears further changed to nanorods with oval tips.

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