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MICROWAVE-ASSISTED SYNTHESIS AND CHARACTERIZATION OF ROSE-LIKE AND FLOWER-LIKE ZINC OXIDE NANOSTRUCTURES

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Hexagonal zinc oxide was synthesized by 180 W, 20 min microwave heating of 1:5 and 1:12.5 mole ratios of zinc chloride and sodium hydroxide as starting materials in aqueous solution system. The products were characterized using X-ray diffraction (XRD), scanning and transmission electron microscopy (SEM, TEM), and Fourier transform infrared (FTIR) and Raman spectroscopy. Rose-like particles of nanoplates and flower-like particles of nanorods of hexagonal zinc oxide with optical phonon E_2 vibration mode at 440 cm^{-1}, and the stretching modes of Zn–O at 426 and 565 cm^{-1} were detected.

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1. Introduction

Semiconducting nanostructured materials, such as nanorods, nanowires, nanotubes and nanobelts, have very interesting physical and chemical properties, as compared to their corresponding bulks [1,2]. Zinc oxide (ZnO) is a 3.37 eV wide band gap semiconductor with a 60 meV large exciton binding energy [3-6]. It is very useful in a wide range of applications, such as solar cells, chemical and biological sensors, UV lasers, optoelectronics, and surface acoustic waveguides [3,4]. Recently, one-dimensional (1D) structured ZnO has attracted much interest for applications in light-emitting diodes, transparent conductors and electrodes, piezoelectric and pyroelectric devices and UV photodiodes [5-7]. There are a number techniques used to synthesize ZnO, such as sonochemistry [3], refluxing method [4], sol-gel [8] and hydrothermal process [7]. However, the researchers have been attempted in the novel, simple and mild routes for the preparation of ZnO using a wet chemistry method because they are well expected to be available for preparation of large-scale products.

Microwave radiation as a heating method has been used for a number of applications in chemistry, and is generally rapid, simple and effective. It has been developed and is widely used in many areas such as the preparation of inorganic complexes, oxides and chalcogenides, organic reactions, plasma chemistry, analytical chemistry and catalysts. The use of microwave radiation in preparing of materials has been reported in recent years. Comparing to the conventional method, microwave heating is a very promising route due to its unique effects, such as rapid volumetric heating, higher reaction rate, reaction selectivity, product yields and energy saving [3, 9-12].

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Water is a high dipole moment liquid that makes it to be good solvent for microwave-assisted synthesis. The movement and polarization of molecules under the rapid changing of electromagnetic field of the microwave reactor may result in transient, anisotropic micro-domains and localized high temperatures for accelerating the reaction rate, which facilitates the anisotropic growth of rose-like and flower-like structured zinc oxide [9].

In 2007, Shin et al. [4] reported on how to synthesize the flower-shaped ZnO nanostructures composing of hexagonal ZnO nanorods, from zinc acetate dihydrate and sodium hydroxide as source materials in 100 ml de-ionized water by refluxing at 90 ^{o}C for 30 min. In the present research, the synthesis of zinc oxide with rose-like and flower-like structures from zinc chloride and sodium hydroxide at different mole ratios by 180 W microwave heating for 20 min is reported.

2. Experimental procedure

To synthesize zinc oxide with rose-like structure, zinc chloride ($ZnCl_2$) and sodium hydroxide (NaOH) were used as starting materials. A mole ratio of [$ZnCl_2$]:[NaOH] = 1:5 was dissolved in 100 ml de-ionized water in a round bottom flask. The solution was then transferred into a microwave oven and heated at 180 W for 20 min with the reaction temperature of approximately 80 ^{o}C. When the reaction was complete, the white products were collected, washed for several times with de-ionized water and absolute ethanol, and dried at 80 °C for 24 h. The procedure was repeated but the 1:12.5 mole ratio of [$ZnCl_2$]:[NaOH] was used.

The final products were characterized and recorded on a Philips X'Pert MPD X-ray diffractometer (XRD) equipped with a graphitic monochromator of Cu K_α radiation (λ = 0.1542 nm), using a scanning rate of 0.02 deg/s over the 2θ range of 20^{o} - 60^{o}. FTIR spectra were recorded on Perkin Elmer Spectrum RX FTIR Spectrometer with KBr as a diluting agent and operated in the range of 400-4,000 cm^{-1} with the resolution of 4 cm^{-1}. Raman vibrations of the products were detected by a HORIBA JOBIN YVON T64000 Raman spectrometer with 50 mW and 514.5 nm wavelength Ar laser. Field-emission scanning electron microscopic (FE-SEM) images were taken by a JEOL JSM-6335F operated at 15.0 kV beam energy. Transmission electron microscopic (TEM) images, and selected area electron diffraction (SAED) pattern were taken on a JEOL JEM-2010, employing at an accelerating voltage of 200 kV.

3. Results and discussion

The crystallization and phase of the products were characterized by XRD as shown in Fig. 1. All the diffraction peaks of (100), (002), (101), (102) and (110) crystallographic planes were indexed and specified as the pure hexagonal phase of ZnO - in accordance with those of the JCPDS database no 36-1451 [13]. The lattice constants were calculated from the relation between plane spacing equation for hexagonal structure and Bragg's law for diffraction [14], and are summarized in Table 1. They are in accordance with those of the JCPDS database [13].

Table 1. Lattice constants of ZnO synthesized in the solutions containing 1:5 and 1:12.5 mole ratios of [$ZnCl_2$]:[NaOH].

Lattice constant (Å)	JCPDS no 36-1451 [13]	[$ZnCl_2$]:[NaOH] mole ratio	
		1:5	1:12.5
a = b	3.2498	3.2492	3.2439
c	5.2066	5.0876	5.2130

The wurtzite hexagonal ZnO belongs to the C^4_{6v} space group with two formula units per primitive cell, and all atoms occupy in the 2b sites of the C_{3v} symmetry [4,15,16]. Group theory calculation shows six different vibration modes of $\Gamma = A_1 + 2B_1 + E_1 + 2E_2$. The A_1, E_1 and E_2 modes are Raman active. The A_1 and E_1 vibration modes are infrared active as well, and split into longitudinal and transverse optical (LO and TO) components [4,15-17]. Raman spectra of the products are shown in Fig 2. Sharp strong peaks are at 440 cm^{-1}, which are attributed to the optical phonon E_2 mode and the characteristic Raman active peaks for the wurtzite hexagonal ZnO phase. Furthermore, two very small peaks at 331 and 386 cm^{-1} were also detected in the spectra, and are assigned to be the E_{2H} - E_{2L} (multi phonon process) and A_{1T} modes, respectively. Additionally, very suppressed and weak peaks at 582 cm^{-1} were specified as the E_{1L} modes in the Raman scattering - caused by the impurities and structural defects of the synthesized products, such as oxygen anion vacancies and zinc cation interstitials [4,15-17].

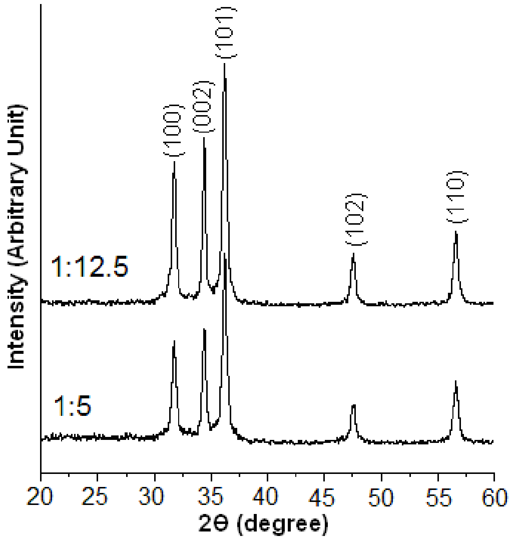

Fig. 1. XRD spectra of ZnO synthesized in the solutions containing 1:5 and 1:12.5 mole ratios of [$ZnCl_2$]:[NaOH].

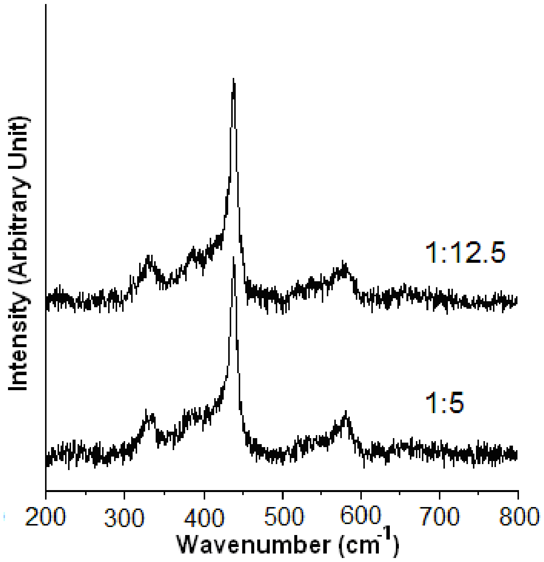

Fig. 2. Raman spectra of ZnO synthesized in the solutions containing 1:5 and 1:12.5 mole ratios of [$ZnCl_2$]:[NaOH].

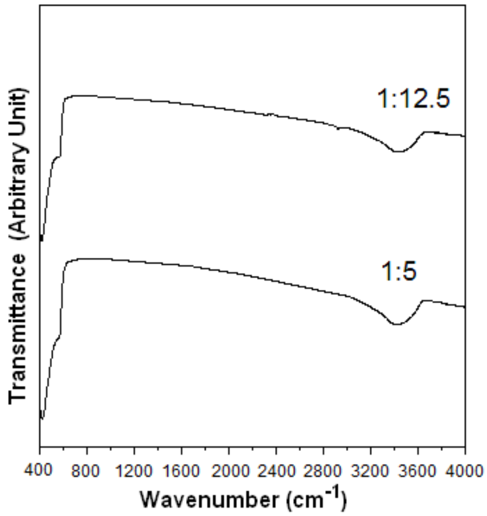

Fig. 3. FTIR spectra of ZnO synthesized in the solutions containing 1:5 and 1:12.5 mole ratios of [$ZnCl_2$]:[NaOH].

FTIR spectra of the products are shown in Fig. 3. The broad absorption bands at 3,013-3,633 cm^{-1} are the O–H stretching vibration of adsorbed water on ZnO surface. The strong absorption bands at 426 and 565 cm^{-1} are ascribed as the stretching modes of Zn–O [7,18].

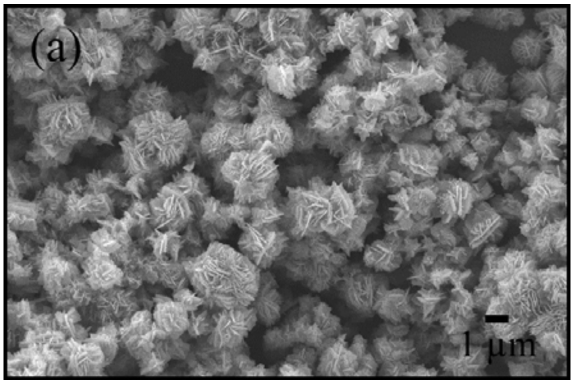

Fig. 4a

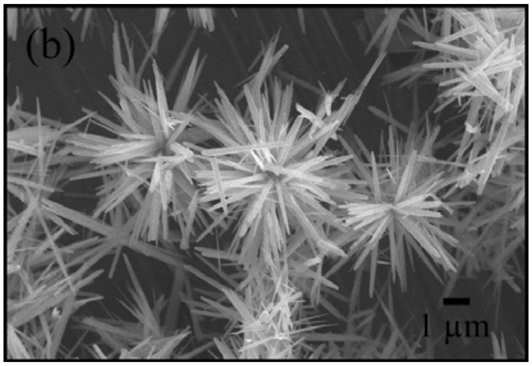

Fig. 4b

Fig. 4. SEM images of ZnO synthesized in the solutions containing (a) 1:5 and (b) 1:12.5 mole ratios of [$ZnCl_2$]:[NaOH].

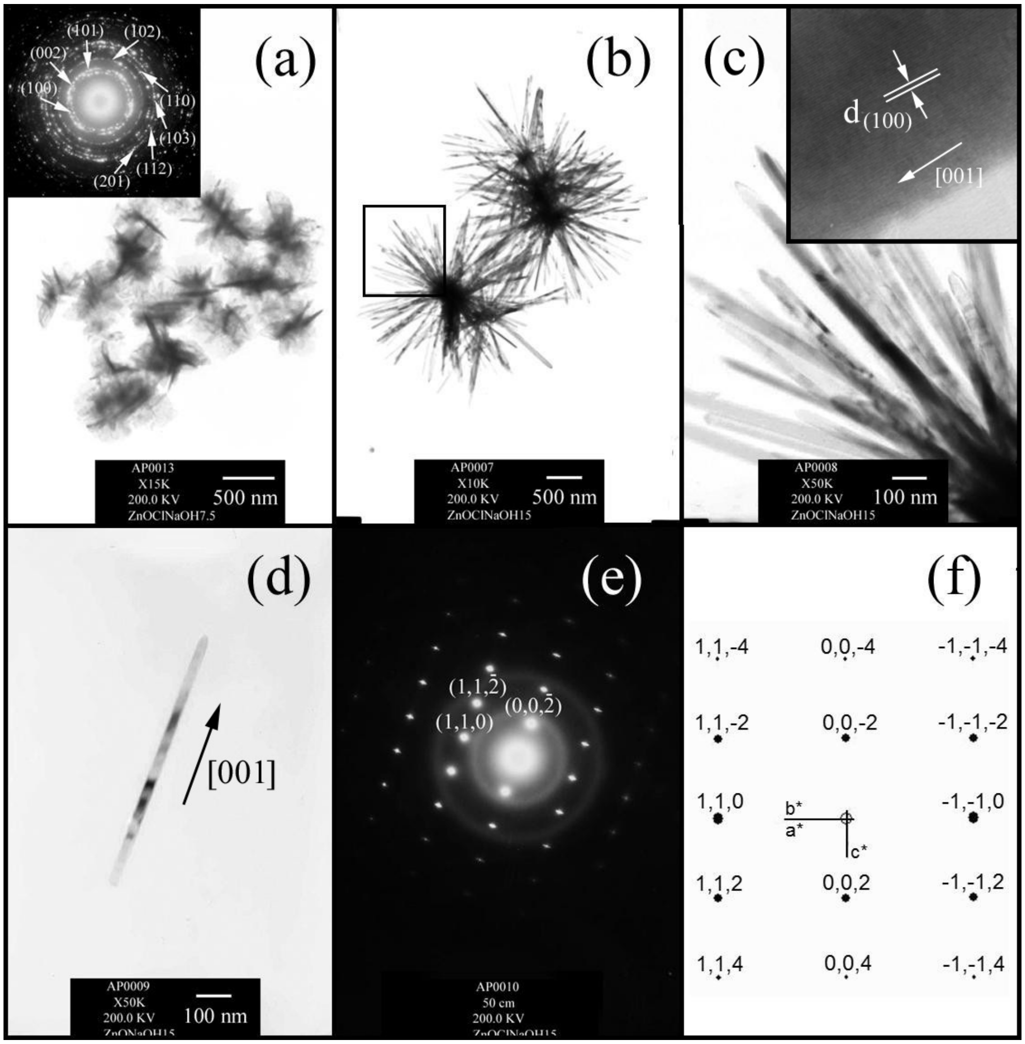

Fig. 5. TEM and HRTEM images, and SAED patterns of ZnO synthesized in the solutions containing (a) 1:5, and (b-e) 1:12.5 mole ratios of [$ZnCl_2$]:[NaOH]. (f) Simulated electron diffraction pattern of (e).

The morphologies of the products were characterized using SEM and TEM. Fig. 4a shows the rose-like structured zinc oxide synthesized in the solution containing 1:5 mole ratio of [$ZnCl_2$]:[NaOH]. The ZnO particles were composed of a number of nanoplates in spherical clusters, similar to roses. By increasing the mole ratio of [$ZnCl_2$]:[NaOH] from 1:5 to 1:12.5, morphology of the product was changed into flower-like structure (Fig. 4b), composed of a number of nanorods grown from ZnO cores. Fig. 5 shows TEM and HRTEM images and SAED patterns of the products. Morphology of the product synthesized using 1:5 mole ratio of [$ZnCl_2$]:[NaOH] (Fig. 5a) was rose-like structure of zinc oxide nanoplates, clustered in groups similar to roses. Selected area electron diffraction (SAED) pattern appears as randomly and continuously bright spots of diffraction rings with the same center, indicating that the product was composed of a number of hexagonal ZnO nanocrystals [13] with crystallographic axes oriented in different directions. By increasing of [$ZnCl_2$]:[NaOH] mole ratios from 1:5 to 1:12.5, the rose-like structure of nanoplates was transformed into the flower-like structure of zinc oxide nanorods, as shown in Fig. 5b and c. TEM image at high magnification (Fig. 5c) shows that the flower-like structure was produced by the systematic gathering of several sharp-tipped hexagonal ZnO nanorods. HRTEM image (inserted in Fig. 5c) shows the (100) lattice plane lying parallel to the

[001] growth direction of ZnO nanorod. An individual nanorod of hexagonal ZnO (Fig. 5d) is about 600 nm long and about 30 nm in diameter. It indicates that the individual nanorod of flower-like zinc oxide has a preferential growth along the [001] direction or the c-axis. Its SAED pattern (Fig 5e), which has the [-110] direction as zone axis, were composed of the (110), (11-2), and (00-2) crystallographic planes. They were specified that the product was hexagonal ZnO [13]. This SAED pattern was in accordance with electron diffraction simulated using CaRIne Crystallography software version 3.1 [19], as shown in Fig. 5f. The sizes of the rose-like flowers were 281-633 nm with the petals of 134-300 nm wide and 30-71 nm thick. But for the flower-like structure of nanorods, their sizes were 1,932-2,450 nm with the rods of 883-1,264 nm long and 23-65 nm in diameter.

The present research shows that different molar ratios of [$ZnCl_2$]:[NaOH], influenced to the nucleation and growth processes, play a significant role in synthesizing the products with different morphologies. Generally, ZnO has a hexagonal crystal system with $P6_3mc$ space group. Its crystal structure is hexagonal closed packing of Zn atoms, surrounded by four oxygen atoms, forming $Zn\text{-}O_4^{6-}$ tetrahedrons with the vertex pointing to the positive direction of the polar c-axis, and the corresponding base of the tetrahedrons aligning in the (00-1) face. ZnO is a polar crystal, of which zinc and oxygen atoms are alternatively arranged along the c-axis. It possesses the positive and negative faces of the crystal, due to the asymmetric distribution of Zn and O atoms along the mutual polar axis, allowing the anisotropic growth of the crystals along the [001] direction. The top is Zn-terminated (001) face, and the bottom is oxygen-terminated (00-1) face. It should be noted that the negative hydroxyl ions have the strong influence on the growth units and interfaces; especially, the positive Zn terminated and negative O terminated faces. Thus, sodium hydroxide was used in the present research to control the morphologies of the as-synthesized products [3,20].

4. Conclusions

Zinc oxide was successfully synthesized by 180 W microwave heating for 20 min using 1:5 and 1:12.5 molar ratios of zinc chloride to sodium hydroxide as starting materials. The products were rose-like and flower-like structures of zinc oxide, when [$ZnCl_2$]:[NaOH] mole ratios of 1:5 and 1:12.5 were respectively used. Each of the rods grew along the [001] direction. The common peak of the optical phonon E_2 mode was detected at 440 cm^{-1} with the stretching modes of Zn–O at 426 and 565 cm^{-1}. The present research proved that microwave heating is a simple and fast method used for synthesizing the crystalline solids.

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