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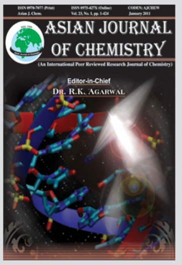

Shape-Controlled Synthesis of Zinc Oxide Spherical Structures by Microwave-Assisted Chemical Aqueous Refluxing Process†

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Large-scale and monodispersed zinc oxide spherical structures with different morphologies have been synthesized by a facile microwave-assisted chemical aqueous approach at reflux, using zinc acetate dihydrate, triethanolamine and deionized water as starting materials in the absence of the surfactants and organic solvent. By controlling the concentration of triethanolamine, the microwave irradiation time and the temperature of refluxing reaction, shape transformation of ZnO spherical structures could be achieved. The crystal structure and morphology of products were characterized by XRD, FT-IR, FESEM, EDS and TEM. The possible formation mechanisms for the shape transformation of ZnO crystals were proposed, as were considered to be three steps including triethanolamine-dominated hydrolysis process, Ostward ripening process and corrosion dissolution process. The present synthetic route is facile and controllable and gives a large-scale yield, indicating the products may be useful materials for optoelectronic nanodevices.

Key Words: Semiconductors, Zinc oxide, Chemical synthesis, Microwave irradiation.

INTRODUCTION

Controlling the size, shape and assembly of inorganic nanostructures are of fundamental and technological interest because it provides effective strategies for tuning the electronic, magnetic, optical, optoelectronic and catalytic properties of materials. As a direct wide band gap (3.37 eV) semiconductor with a large excitation binding energy (60 meV), zinc oxide (ZnO) is an important semiconductor transition-metal-oxide and has potential applications in fabricating nanometer-scale electronic devices possessing various interesting functions[1], such as catalytic, electrical and optoelectrical fields[2] and even for assembling complex three-dimensional (3D) nanoscale systems[3]. 3D spherical structures, including solid spheres, porous spheres and hollow spheres, have been intensively investigated because of their unique attributes, which derived from their special morphologies in lower light scattering at surfaces, higher packing densities as well as the highest symmetry[4,5].

Microwave-assisted chemical synthesis technique acts as the green and low-carbon method has been used extensively to generate novel materials with unusual properties as well as much smaller sizes and higher surface areas[6-12]. In this work, we demonstrate the successful preparation of the large-scale and monodispersed ZnO nanospheres with different morphologies *via* microwave-assisted chemical aqueous process at reflux using zinc acetate dihydrate, triethanolamine (TEA) and deionized water as starting materials in absence of any additives. To our best of knowledge, there are no systematic studies on the correlation between ZnO crystal morphology structure and the reaction conditions in literature. In addition, possible formation mechanisms of ZnO spherical structures were proposed.

EXPERIMENTAL

Zinc acetate dihydrate ($Zn(CH_3COO)_2·2H_2O$) and triethanolamine (TEA, $C_6H_{15}NO_3$) purchased from Shanghai Chemical Reagents Co., Shanghai, China, are of analytical grade and are used as received without further purification. The solvent used for the reaction is deionized (DI) water.

General procedure: In a typical experimental procedure, 10 mL $Zn(CH_3COO)_2·2H_2O$ aqueous solution (0.1 M) was added with stirring into 50 mL TEA aqueous solution (0.3 M, the molar ratio of Zn^{2+}:TEA was 1:15.) in a 100 mL conical flask and being stirred continuously for 20 min. The precursor

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solution containing conical flask was transferred into a MAS-II apparatus and was irradiated with microwave irradiation under stirring with 1000 r/min at the refluxing temperature of 80 ºC for 10 min. After the reaction was completed, the bottom solution was cooled naturally under ambient conditions for overnight and then the ivory white precipitate occurred. The precipitate was filtered with a microporous membrane with pores of 0.45 µm in diameter, washed with deionized water and anhydrous ethanol for several times to remove the impurities and then dried in a vacuum at 60 ºC for 6 h. The product was collected and labeled as sample B for further characterization. Based on the experimental conditions of sample B, series of control experiments were performed with changing each reaction condition while maintaining the other parameters unchanged. Hence when the molar ratios of Zn^{2+}:TEA were 1:5 and 1:30, the products labeled as sample A and C were obtained, respectively. The sample D and E were prepared with the condition of the reaction time prolonged to 0.5 h, as well as the refluxing temperature elevated to 100 ºC, respectively.

Detection method: The mircowave-assisted chemical aqueous synthesis method was proceeded on a MAS-II microwave synthesis/extraction reaction workstation (work frequency 2.45 GHz, power adjustable range 0-1000 W, Shanghai Sineo Microwave Chemistry Technology Co., Shanghai, China). The crystal structure was measured on an X-ray diffraction meter (XRD) using standard CuK_α radiation (MXPAHF, 18 KW, λ = 1.5418 Å). The morphology of the products was determined on a field emission scanning electron microscope (Sirion-200) with the energy dispersive X-ray spectrometry (EDS) attached and a transmission electron microscope (TEM, HITACHI H-7650), repectively. The quality and composition of the samples were characterized by the Fourier transform infrared spectroscopy (FTIR-8400s) in the range of 4000-400 cm^{-1}.

RESULTS AND DISCUSSION

The XRD pattern and the EDS result of sample B were given in Fig. 1. As shown in Fig. 1a, all the diffraction peaks in the pattern can be indexed according to the values in the standard card (JCPDS Card No. 5-664), which has wurtzite crystal structure with calculated lattice constants of a = 3.24 6 Å, c = 5.21 2 Å and the hexagonal symmetry belonging to the $P6_3mc$ (No. 186) space group. No diffraction peaks from any other impurities were detected. On the basis of the full width at half-maximum (FWHM) of ZnO (101) diffraction peaks, the average crystalline size of the nanoparticles composing the nanostructures calculated according to the Scherrer equation were determined to be about 21 nm. The XRD patterns of the rest samples were analogous to sample B. It could be confirmed that pure and high crystalline ZnO nanoparticles were successfully synthesized by the microwave-assisted aqueous process. The EDS result of sample B (Fig. 1b) exhibited the presence of Zn, O and Al elements, in which Al come from aluminium stage when prepared the sample for FESEM observation. The spectrum revealed that atomic ratio of Zn to O was about equal to 1:1, which was consistent with stoichiometric ZnO and confirmed XRD analysis.

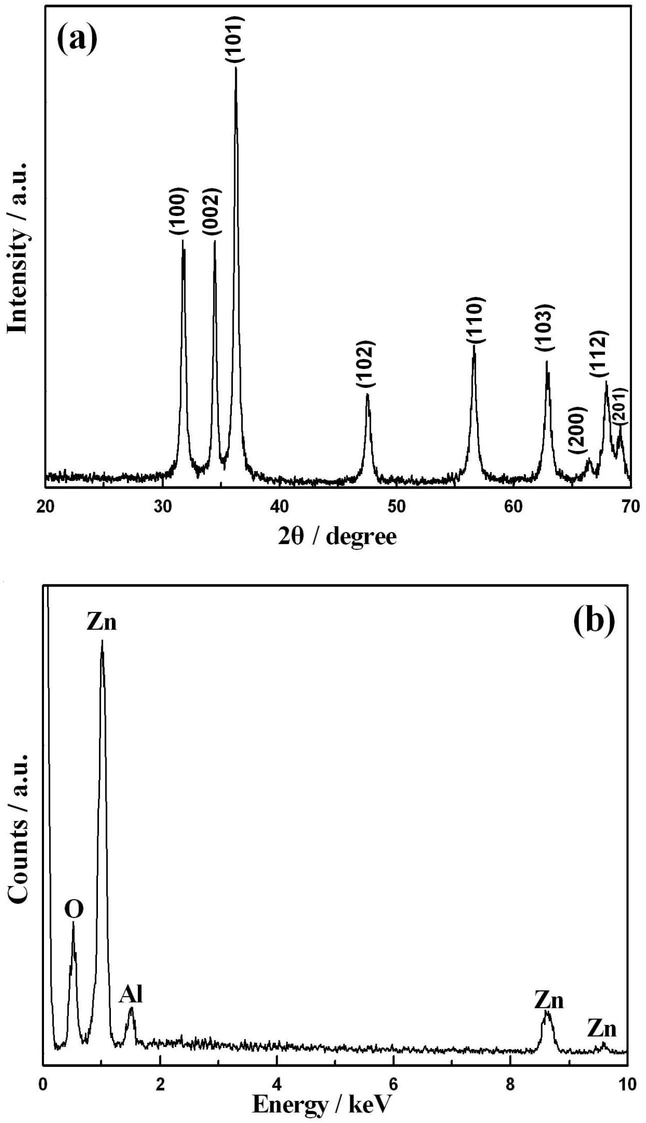
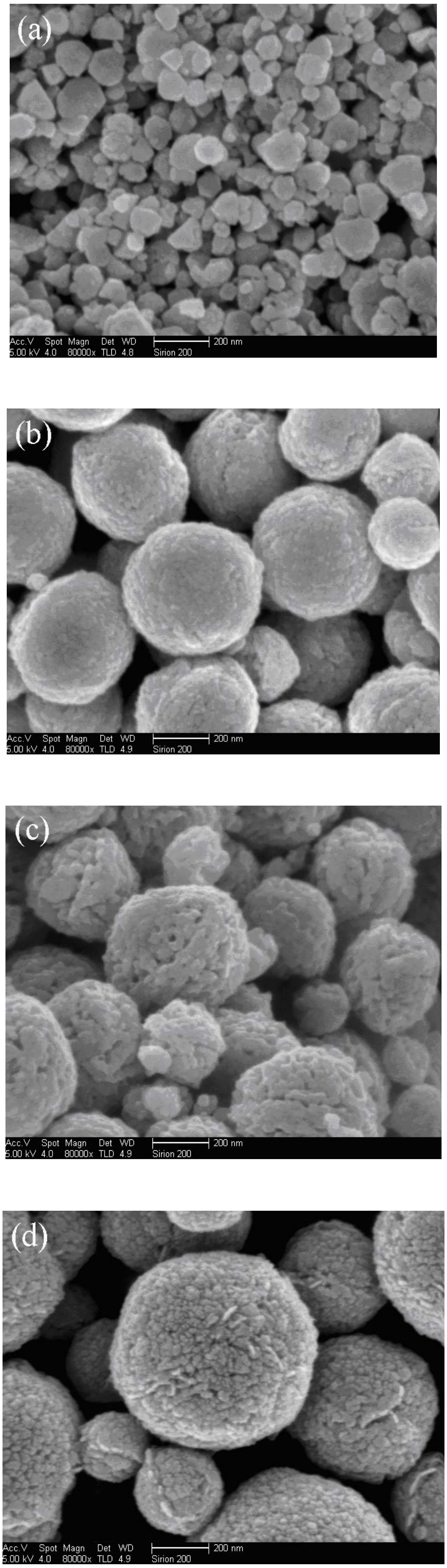


Fig. 1. XRD pattern (a) and the EDS result (b) of ZnO products of sample B

The morphologies of ZnO samples A-E were presented in Fig. 2. As shown in FESEM image (Fig. 2b) and TEM image (Fig. 2f), the products of sample B are consisted of uniform shaped and monodispered solid spheres with the diameters ranging from 200-400 nm. The surfaces of spheres are not smooth but rough, showing uncountable protrusive nanostructures resulted from self-assembly of nanoflakes which can be seen clearly at the edge of spheres in TEM image (Fig. 2f). By controlling the concentration of TEA, the microwave irradiation time and the reaction temperature at reflux, shape transformation of ZnO nanostructures are further observed by FESEM. When the molar ratio of Zn^{2+}:TEA was decreased to 1:5 (sample A), irregular quasi-spherical nanoparticles with about 40 nm in diameter were generated (Fig. 2a). If the molar ratio of Zn^{2+}:TEA was increased to 1:30 (sample C), peach nut-like spheres with diameters of 100-400 nm were formed (Fig. 2c), in which the surface was decorated by numerous porous with around 10 nm in diameter. While prolonging irradiation time to 0.5 h (sample D), solid spheres were changed to pompon-like spheres as shown in Fig. 2d. The size of pompon-like spheres (sample D) is obviously bigger



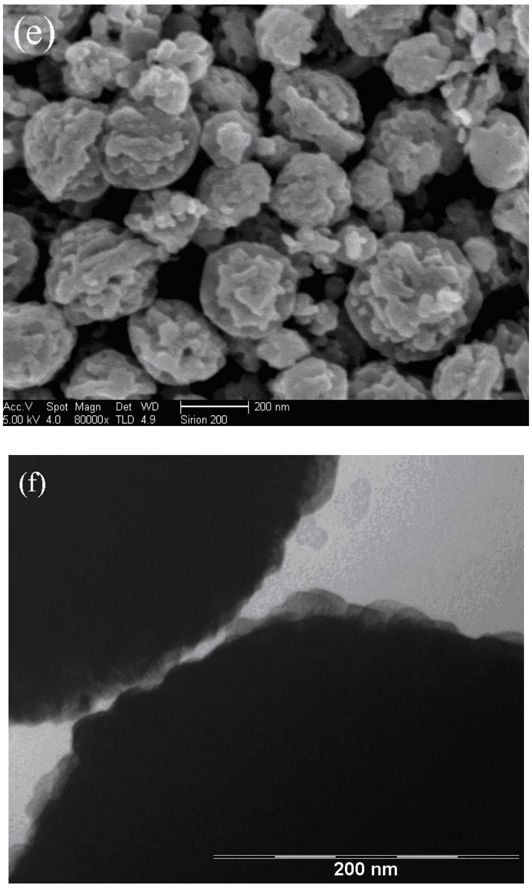


Fig. 2. FESEM images (a-e) and TEM image (f) of the as-obtained ZnO products

than that of sample B, as well as the protrusive nanostructures. It suggests that the building blocks (nanoflakes) grow continuously along with the reaction time. When the reaction temperature at reflux was elevated to 100 ºC (sample E), the products was composed of misshaped spherical structures in major with rough surface and partly scattered irregular nanoparticles (Fig. 2e).

The composition and quality of the as-prepared products were analyzed by the FTIR spectroscopy in the range of 4000-400 cm^{-1}. The representative resultant spectrum of sample B is shown in Fig. 3. There are significant spectroscopic bands at 470 cm^{-1}, corresponding to the characteristic of ZnO[13]. The broad absorption peak in the range of 3600-3200 cm^{-1} is attributed to vibration of the hydroxyl groups. The peaks which are located at 2918 and 2974 cm^{-1} are due to symmetric and asymmetric C-H bonds, respectively. The bands at 1635 and 1406 cm^{-1} resemble the asymmetric and symmetric C=O stretching mode of vibrations in acetate groups. The absorption at 1047 cm^{-1} can be assigned to symmetric C-N stretching vibration. According to the FTIR curve, it can be confirmed that the surface of ZnO crystals may be adsorbed with CH_3COO^- ions and TEA molecules.

The microwave irradiation can accelerate the reactions by means of material-wave interactions. With the microwave irradiation, the heating phenomenon occurs *via* the interaction of the dipole molecules with the high frequency electromagnetic radiation[14]. Microwaves are tuned so that polar molecules absorb microwaves into rotational energy levels accusing

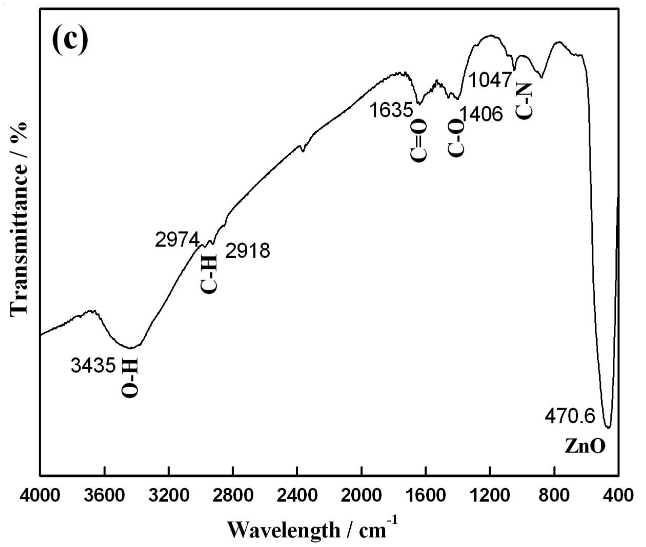


Fig. 3. FTIR spectrum of the as-grown ZnO products of sample B

molecular motion and heating[15]. The movement and polarization of ions under the rapidly changing electromagnetic field in the microwave chamber may result in transient and localized high temperatures for the reaction system, facilitating the growth and formation of various ZnO nanostructures[10-12].

Based on the above reaction pathway and the experimental results, we propose the following possible growth processes for the shape transformation of ZnO samples. In aqueous solutions, TEA not only can provide alkaline environment by hydrolyzing in water, but also act as modification agent through fabricating the strong complex ion of TEA with Zn^{2+} [16,17]. During the heating process, the Zn^{2+} reacts with the decomposition products of TEA, then $Zn(OH)_4^{2-}$ complexes decompose to produce zinc oxide. The brief chemical reactions for the formation of ZnO spherical structures could be formulated as follows[16]:

$$N(CH_2CH_2OH)_3 + H_2O \rightarrow (HOCH_2CH_2)_3NH^+ + OH^- \quad (1)$$

$$Zn^{2+} + 4OH^- \rightarrow Zn(OH)_4^{2-} \quad (2)$$

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

As can be concluded from the FTIR analysis, the strong complex ion $TEA \cdots Zn(OH)_4^{2-}$ may be formed in aqueous solution due to interaction between the hydroxyl ligands of TEA molecular and Zn^{2+} ions, which adsorbs to some extent onto the crystal surface of ZnO-(0001) crystals. It is understandable that the growth along the c-axis of ZnO crystal is greatly retarded while ZnO nanoflakes are apt to generate in the reaction system[18]. By controlling van der Waals force from TEA molecules and decreasing the high specific surface energy, nanoflakes turn to assemble orientedly to form nanoflake aggregates and have a tendency to fabricate spherical structures (Fig. 2a). The formation of ZnO crystals can be considered as TEA-dominated hydrolysis process, which is similar to the reported formation process of ZnO[18]. The TEA-dominated effect is naturally stronger as soon as the TEA concentration is higher. While the ratio of Zn^{2+}:TEA is up to 1:15, the uniform and geometrical ZnO spheres are obtained and the final particle size is limited by the surface energy (Fig. 2b). As prolonging irradiation time to 0.5 h, the building blocks (nanoflakes) grew larger and finally pompon-like spheres were produced through the process of Ostward ripening (Fig. 2d). When the molar ratio of Zn^{2+}:TEA was further increased to 1:30, larger numbers of OH$^-$ ions were generated according to eqn. 1. ZnO nanocrystals at the surface of preformed solid spheres were partly dissolved in the high alkaline solution and the reaction was expressed as follow[19,20]:

$$ZnO + OH^- \rightarrow ZnO_2^{2-} + H_2O \quad (4)$$

Hence the peach nut-like spheres with porous were formed at the highest TEA concentration (Fig. 2c). In addition, the increase of the temperature can obviously accelerate the reaction the eqns. 1 and 4. The preformed solid spheres were seriously eroded by OH$^-$ ions to finally result in misshaped spheres (Fig. 2e). Simultaneously, under the microwave irradiation, the newly produced ZnO_2^{2-} ions by eqn. 4 can continuously decompose to generate ZnO nuclei and grow into nanocrystals. It is an acceptable reason that there are some scattered irregular nanoparticles in the as-prepared products of sample E (Fig. 2e). In short, the formation of peach nut-like spheres with porous and misshaped spheres can be attributed to the process of corrosion dissolution. On the basis of above analysis, it is suggested that the possible shape evolution process of ZnO spherical structures are considered as three steps including TEA-dominated hydrolysis process, Ostward ripening process and corrosion dissolution process and a schematic diagram is illustrated in Fig. 4.

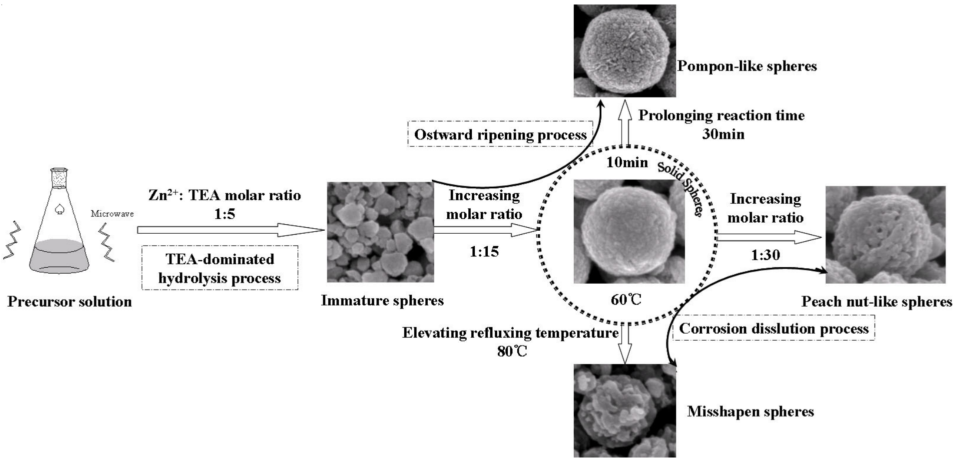


Fig. 4. Scheme of the shape transformation of ZnO spherical structures

Conclusion

In summary, we have demonstrated that series of ZnO spherical structures with different morphologies can be fabricated by a facile template-free microwave-assisted chemical aqueous method using zinc acetate dihydrate, triethanolamine and deionized water as starting materials. The crystallite size and shape of ZnO nanostructures can be controlled simply by varying the TEA concentration, the microwave irradiation time and the reaction temperature at reflux. The possible growth mechanisms of crystals were considered to be three steps including TEA-dominated hydrolysis process, Ostward ripening process and corrosion dissolution process. The synthetic method is facile and controllable and gives a large-scale yield, indicating the products may be useful materials for optoelectronic nanodevices.

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