

Influence of solvents on the growth of zinc oxide nanoparticles fabricated by microwave irradiation

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Abstract. A simple and rapid process has been developed for preparation of nanometer-sized ZnO powders via microwave irradiation, by which ZnO powders with an average particle size of 10-12 nm and narrow size distribution can be synthesized in a short time. We have synthesized ZnO nanoparticles by precipitation from zinc acetate ($\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 6\text{H}_2\text{O}$) in different solvents: distilled water, absolute ethanol ($\text{C}_2\text{H}_5\text{OH}$), and isopropanol ($\text{C}_3\text{H}_7\text{OH}$). The ZnO nanopowders structure was characterized by X-ray powder diffraction (XRD). Raman scattering studies confirm that the as-synthesized nanopowders are of high crystalline quality. High-resolution transmission electron microscopy analysis reveals that the ZnO nanopowders have a perfect crystallinity. Photoluminescence have been observed. Thus, microwave irradiation can be an attractive method for industrial production of nanopowders

Keywords: ZnO, Nanopowder, Growth, Microwave technique, HRTEM, Optical property.

1. Introduction

In recent years, great interests are focused on nanostructured zinc oxide (ZnO) because of its wide direct band gap, high exciton binding energy and promising applications for UV-lasers with low threshold [1], surficial acoustic devices [2], transistors and biosensors [3] in nanoscale. The stable structure of ZnO is wurtzite, in which four of oxygen atoms in tetrahedral coordination surround each atom of zinc.

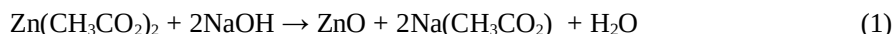
Synthesis of ZnO is often accomplished by sputtering, chemical vapor deposition and sol-gel techniques.

In this paper, we report on the influence of solvents on the synthesis of ZnO nanoparticles from zinc acetate at temperature about 70°C. The investigation of the influence of the solvents allows finding out a means to control over the ZnO nanoparticle size and size distribution, which is essential for changing optical, electrical, and magnetic properties of nanoparticles for specific applications. Microwave-solvothermal synthesis has many advantages such as faster, simpler and more efficient than other methods [6,9].

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2. Experimental

The ZnO nanoparticles were prepared by precipitation from solution using $\text{Zn}(\text{CH}_3\text{CO}_2)_2$ and NaOH. The overall reaction for the synthesis of ZnO nanoparticles from Zn(II) acetate can be written as follows



The used solvents included distilled water, absolute ethanol (Merk 99%) and isopropanol (Merk 99%). The solvents were used as received without further purities.

For typical preparation, 1 mmol of zinc acetate dihydrate $\text{Zn}(\text{CH}_3\text{CO}_2)_2 \cdot 2\text{H}_2\text{O}$ was dissolved in 80 ml of solvent in covered flask under vigorous stirring at 50°C. After cooling to room temperature, 8 ml of the transparent zinc salt solution was added into 64 ml of the pure solvent. A 0.02 M NaOH solution was prepared by adding sodium hydroxide to the pure solvent in a covered flask under vigorous stirring at 60°C. After cooling to room temperature, 8 ml of the sodium hydroxide solution was added into 20 ml of the pure solvent. The sodium hydroxide solution was then added into the zinc acetate solution under vigorous stirring to give a total volume of 100 ml with 0,1 mmol of zinc acetate and 0,16 mmol of NaOH. From the overall reaction it follows that the synthesis is carried out with a 25% excess of Zn(II). The resulting solution was then placed in a conventional microwave oven. The microwave power was set to 150 W. The reaction time was 5 minutes. During the microwave irradiation the temperature of the solution reached up 70°C. After 5 minutes, the transparent solution yields white products, which was washed several times with absolute ethanol and distilled water. Finally the products were dried at 70°C for 4 hours.

The morphologies and structures of the products were investigated by SEM (JEOL-J8M5410 LV), TEM (JEOL JEM 1010, Japan), X-ray diffractometer (Bruker-AXSD5005). Raman scattering spectra at room temperature in the energy region between 100 and 1000 cm^{-1} were recorded by a micro-Raman spectrograph LABRAM-1B equipped with a He-Ne laser ($\lambda = 632,817 \text{ nm}$) with a power of 11 mW. High-resolution transmission electron microscopy (HRTEM) images were obtained on a JEOL – 2010 TEM. The photoluminescence (PL) measurement at room temperature was carried out on a 325 nm He-Cd laser. A UV-vis spectrophotometer (UV-2450PC Shimadzu) was used to record the UV-visible absorption spectra.

3. Results and discussion

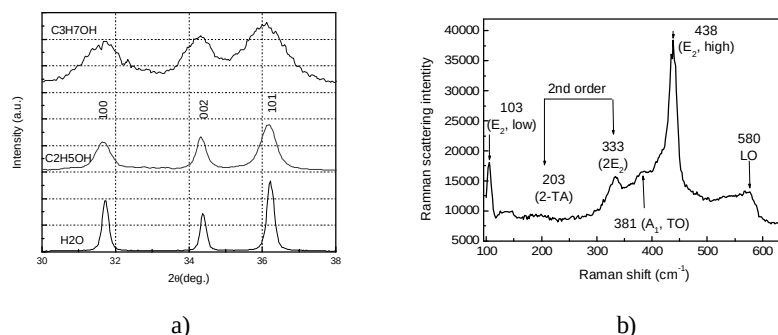


Fig. 1. (a) X-ray diffraction patterns of ZnO nanoparticles prepared in different solvents: distilled water, absolute ethanol, and isopropanol. (b) Typical room-temperature micro-Raman spectrum of the sample synthesized in isopropanol.

Figure 1(a) shows X-ray diffraction patterns of ZnO nanoparticles prepared in different solvents. As indexed in the figure, all the diffraction peaks match those of wurtzite ZnO with lattice constants of $a = 3.250 \text{ \AA}$ and $c = 5.207 \text{ \AA}$. The strong diffraction peaks appear at 31.8° , 34.3° , and 36.5° , which correspond to (100), (002), and (101) planes of wurtzite ZnO, respectively. It should be pointed that in the XRD patterns except the diffraction peaks of ZnO, no peak of additional phase observed.

The mean particle sizes have been estimated using the Scherrer's formula [5]:

$$d = \frac{0.9l}{b \cos q} \quad (2)$$

where l is the wavelength for the $K_{\alpha 1}$ component of the employed copper radiation ($1.54056 \text{ \AA}$), b is the corrected full width at half maximum (FWHM) and q is the Bragg's angle, and they average 59.6 , 28.4 and 11.3 nm across, respectively, for the three samples prepared with distilled water, absolute ethanol and isopropanol. These values agreed well with TEM observations (Fig. 3) of the ZnO nanopowders.

Fig. 1(b) shows a micro-Raman scattering spectrum of the sample synthesized in isopropanol. ZnO has a wurtzite crystal structure and belongs to C_{6v} group. According to the group theory analysis, the $A_1 + E_1 + 2E_2$ modes are Raman active. The two higher peaks at 103 and 438 cm^{-1} can be assigned to E_2 modes, characteristic of the wurtzite lattice. The much weaker peak at 379 cm^{-1} is attributed to the transverse optical modes of A_1 . The other two weaker and broader peaks at 203 and 333 cm^{-1} can be assigned to the secondary Raman scattering arising from zero-boundary phonons 2-TA (M) , and $2\text{-}E_2 \text{ (M)}$, respectively [10]. The presence of the $E_1 \text{ (LO, } 580 \text{ cm}^{-1})$ mode of oxygen deficiency indicates that there are oxygen vacancies in our ZnO nanoparticles. The XRD and Raman spectra reveal good crystal quality.

The EDS elemental analysis is shown in Fig. 2. This result indicates that ZnO nanoparticles were only composed of zinc (Zn) and oxygen (O). This suggested the high purity of the ZnO nanopowders.

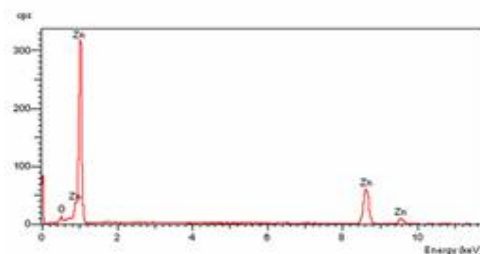


Fig. 2. Typical energy dispersion spectrum of ZnO nanopowders.

The morphology and structure of the ZnO powders were further investigated by TEM. Figure 3 shows TEM images with a low magnifier of ZnO nanoparticles prepared in different solvents. It is clearly seen that, the ZnO nanoparticles prepared in different solvents have completely different sizes and shapes.

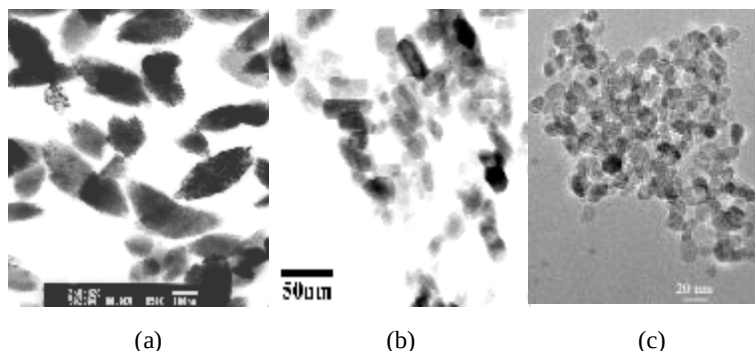


Fig. 3. TEM images of ZnO nanoparticles prepared in different solvents: a) distilled water; b) absolute ethanol; and c) isopropanol.

When we use distilled water as a solvent, ZnO nanoparticles has ellipse shape and large size with size of larger axis is about 100 nm and size of the other axis is about 40 nm. In addition, the size distribution is not very narrow. With ethanol as solvent, the obtained nanostructure has rod form with length is about 45 nm and radius is about 20 nm. However, when isopropanol is used as a medium to create nanoparticles, we obtain spherical particles with radius of 10-12 nm. Furthermore, nanoparticles prepared in isopropanol have more homogenous size and shape.

TEM gives us more details about microstructure of the ZnO nanopowders prepared in isopropanol, as shown in Fig. 4. The nanopowders are of good transparency for the electron beam. The particles appeared to be well separated from each other. Fig. 4a shows the morphologies of ZnO nanoparticles containing mainly spherical particles typically with diameters ranging from 10 to 15 nm. Fig. 4b shows the selected area electron diffraction (SAED) pattern of the produced nanopowder. The SAED pattern shows ring pattern without any additional spots and rings of secondary phases revealing their highly crystalline ZnO wurtzite structure. Three fringe patterns were observed with plane distances of 2.79, 2.58 and 2.44 Å in the electron diffraction pattern which corresponds to 100, 002 and 101 planes of pure wurtzite hexagonal structure of ZnO. The fringe spacing is about 0.28 nm, corresponding to the (100) crystal planes of ZnO (Fig. 4c). The SAED of a single ZnO nanoparticle reveals that the ZnO product exhibits a single-crystal structure, which is in good agreement with the XRD data.

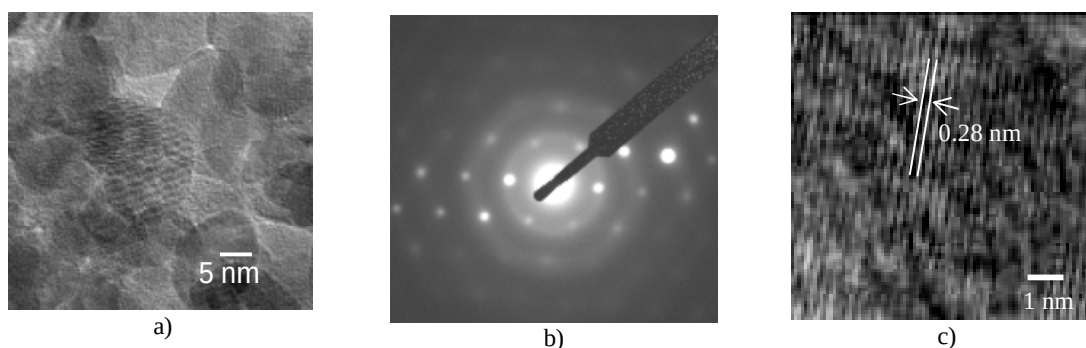


Fig. 4. (a) Magnified TEM image of ZnO nanopowder prepared in isopropanol, (b) corresponding electron diffraction pattern, and (c) HR-TEM image of single ZnO nanoparticle showed (100) crystalline planes .

Coarsening involves the growth of larger crystals at the expense of smaller crystals and is governed by capillary effects. Since the chemical potential of a particle increases with decreasing particle size, the equilibrium solute concentration for a small particle is much higher than that for a large particle. The resulting concentration gradients lead to transport of solute (e.g., metal ions) from the small particles to the larger particles. The rate law for this process, derived by Lifshitz, Slyozov, and Wagner (LSW) [4], is given by

$$\bar{r}^3 - \bar{r}_0^3 = kt \quad (3)$$

where $\bar{r}$ is the average particle radius, $\bar{r}_0$ is the average initial radius, k is the rate constant, and t is time. The rate constant k is given by [4]

$$k = \frac{8\gamma V_m^2 c_{r=\infty}}{54\pi h a N_A} \quad (4)$$

where γ is the surface energy, V_m is the molar volume, $c_{r=\infty}$ is the equilibrium concentration at a flat surface (i.e., the bulk solubility), h is the viscosity of the solvent (in room temperature, $h_{\text{water}} = 8.94 \times 10^{-4} \text{ Pa.s}$, $h_{\text{absolut ethanol}} = 10.74 \times 10^{-4} \text{ Pa.s}$ and $h_{\text{iso propanol}} = 19.45 \times 10^{-4} \text{ Pa.s}$ [4]) and a is the solvated ion radius.

From equation (4) it is apparent that the rate constant $k \sim h^{-1}$ if $c_{r=\infty}$ and γ are independent of the solvent. It's clearly seen that our experiment results agree well with LSW model.

Photoluminescence and absorption spectra of the ZnO nanoparticles prepared in isopropanol are shown in Fig. 5. A broad emission band centered at 528 nm was observed. This green emission band is attributed to the radiative recombination of photogenerated holes with electrons belonging to singly ionized oxygen vacancies in the surface and subsurface [9]. The observation of the green band emission stronger than that in the bulk ZnO indicates the existence of oxygen vacancies concentrated on nanoparticle surface.

The absorption spectrum of ZnO nanoparticles dispersed in ethanol solution is shown in the inset of Fig. 5. The optical band gap of ZnO nanoparticles was calculated from the measured absorption data of samples. Fig. 6 shows a plot of the square of the absorption coefficient α of ZnO nanoparticles versus photon energy. From the figure, the band gap value is found to be of 3.40 eV. Compared with bulk ZnO ($E_g = 3.37 \text{ eV}$), the blue shift observed in the ZnO nanostructures is due to the quantum size effect.

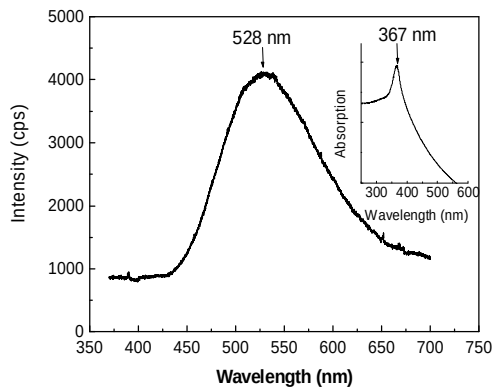


Fig. 5. The PL spectrum of the ZnO nanopowders. The inset shows UV-vis spectrum of the ZnO nanopowders.

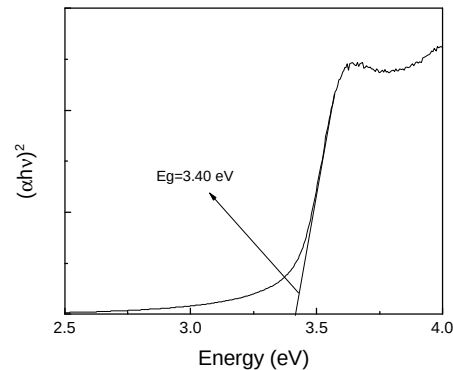


Fig. 6. Square of the absorption coefficient as a function of photon energy.

The average particle size in colloid can be obtained from the absorption onset using the effective mass model [4,7] where the band gap E_g (in eV) can be approximated by:

$$E_g = E_g^{bulk} + \frac{p^2 \hbar^2}{2er^2} \left(\frac{1}{m_e^*} + \frac{1}{m_h^*} \right) - \frac{1.8e}{4\pi\epsilon_0 r} - \frac{0.124e^3}{\hbar^2 (4\pi\epsilon_0)^2} \left(\frac{1}{m_e^*} + \frac{1}{m_h^*} \right)^{-1} \quad (5)$$

where E_g^{bulk} is the bulk band gap (eV), $\hbar$ is Plank's constant, r is the particle radius, m_e^* is electron effective mass, m_h^* is hole effective mass, m_0 is free electron mass, e is the charge on the electron, ϵ is the relative permittivity, and ϵ_0 is the permittivity of free space. Due to the small effective masses from ZnO ($m_e^* = 0.26 m_0$, $m_h^* = 0.59 m_0$, $e = 8.5$ [4,8]), band gap enlargement give us the expected particle size of about 9 nm.

4. Conclusion

The ZnO nanoparticles were prepared using microwave irradiation which is an easy and very fast method. XRD results showed that the obtained ZnO nanoparticles were composed of hexagonal wurtzite phase with very good crystallinity. For different solvents, the kinetics of coarsening was consistent with the Lifshitz-Slyozov-Wagner model. For the ZnO nanoparticles prepared in isopropanol, the size of 11.3 nm obtained by using Scherer formula was in good agreement with TEM results.

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