

Defects and the optical band gap of ZnO nanoparticles prepared by a grinding method

Phuriwat Jitti-a-porn^a, Sumetha Suwanboon^{a,*}, Pongsaton Amornpitoksuk^b and Orasa Patarapaiboolchai^a

^aDepartment of Materials Science and Technology, Faculty of Science, Prince of Songkla University, Hat Yai, Songkhla, 90112, Thailand

^bDepartment of Chemistry and Center for Innovation in Chemistry, Faculty of Science, Prince of Songkla University, Hat Yai, Songkhla, 90112, Thailand

Zinc oxide (ZnO) nanoparticles with different sizes and shapes were prepared by a grinding method. Phase identification was carried out by XRD, the results showed that all samples exhibited a wurtzite structure. The particle shapes were determined by SEM. A spherical structure changed to a flower shape when the OH⁻ concentration increased. The optical band gap was evaluated by measurements of the optical absorption with a UV-Vis spectrophotometer. The optical band gap was dependent strongly on the defect concentration in the ZnO. In this study, the presence of the flower-like structure gave rise to a reduction of the optical band gap due to the increase of oxygen vacancies that could be confirmed by the EPR measurements.

Key words: Grinding method, ZnO, Optical properties, Defects, EPR.

Introduction

Owing to a wide band gap (3.37 eV) and a large exciton binding energy (60 meV), ZnO materials have received considerable attention for many applications such as rubber additives [1], gas sensors [2], optical devices [3] and antimicrobials [4]. These broad applications of ZnO materials depend mainly upon their microstructures, for example; crystallite size, particle size, orientation and shape. To obtain an appropriate microstructure, the most recent challenging research is to produce small sized ZnO particles, with few agglomerates and also a narrow size distribution. At present, ZnO nanoparticles with different sizes and shapes can be prepared by hydrothermal [5], decomposition [6], precipitation [7] and grinding methods [2]. It is not only the method of synthesis, but also the presence of a capping agent that can affect the particle size and shape. A number of capping agents have been investigating, for example, polyvinylpyrrolidone (PVP) [8], triethanolamine (TEA) [9], monoethanolamine (MEA) [10], cetyltrimethylammonium bromide (CTAB) [2] and polyethylene glycol (PEG) [11]. To date, there have been few reports that deal with the effect of CTAB on the preparation of ZnO nanoparticles by a grinding method, but there have been no reports that present the effect of PVP on controlling the morphology of ZnO nanoparticles. Sun *et al.* [2] could prepare ZnO nanorods with the assistance of CTAB. The as-prepared ZnO nanorods had a diameter of about 10–30 nm and lengths of 150–250 nm. In this study,

the preparation of ZnO nanoparticles with different sizes and shapes through a grinding method but using CTAB and PVP as capping agents is reported. We report the influence of both PVP and CTAB, because PVP is a cheap, bioclean, biocompatible reagent and it has excellent adsorption ability [12] whereas CTAB has many advantages such as having a very low content of impurities and is easily made into a clear, and biodegradable solution and reagent. Moreover, this method is convenient, environmentally friendly, inexpensive and efficient. Therefore, it is an appropriate way to fabricate many nanoscale devices with a low cost.

Experimental

Materials

The entire starting reagents; zinc acetate dihydrate ($\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$, Fluka), sodium hydroxide (NaOH, Carlo Erba), polyvinylpyrrolidone (PVP) ($(\text{C}_6\text{H}_9\text{NO})_n$, PVP K 30, Fluka) and cetyltrimethylammonium bromide (CTAB) ($(\text{C}_{16}\text{H}_{33})\text{N}(\text{CH}_3)_3\text{Br}$, Fluka) were used as received.

Grinding method

In a typical synthesis, 3.2, 6.4 and 12.8 g (0.08, 0.16 and 0.32 mol) NaOH were ground for 10 minutes each in a mortar and 8.78 g (0.04 mol) $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ was then added to the previously ground NaOH paste. After the mixtures were ground for 50 minutes, they were washed with 200 ml of distilled water in an ultrasonic bath. The samples obtained were filtered and washed again with acetone and finally dried at 60 °C for 1 h before calcining at 600 °C for 1 h in air.

In order to investigate the effect of the capping agents, 10.6667 g (0.267 mmol) PVP or 7.2892 g (0.02 mol) CTAB

*Corresponding author:
Tel : +66-74-28-8250
Fax: +66-74-28-8395
E-mail: ssuwanboon@yahoo.com

were ground with 0.08, 0.16 and 0.32 mol NaOH paste before adding 8.78 g (0.04 mol) $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ for each experiment and prepared as above.

Characterization

The crystal structure of all calcined ZnO nanoparticles were investigated using an X-ray diffractometer (XRD, X'Pert MPD, Philips). The shape and size of the ZnO nanoparticles were determined with a scanning electron microscope (SEM, JSM-5800 LV, JOEL). The optical absorption spectra were recorded on a UV-Vis spectrophotometer (UV-2401, Shimadzu). The defect characteristic of the ZnO nanoparticles was examined by electron paramagnetic resonance (EPR) at the X band (9.8 GHz) (Bruker E 500 CW spectrometer).

Results and Discussion

Structural properties

Fig. 1 shows the XRD patterns of ZnO nanoparticles prepared by grinding using various conditions. The diffraction peaks of all samples were identified as having a hexag-

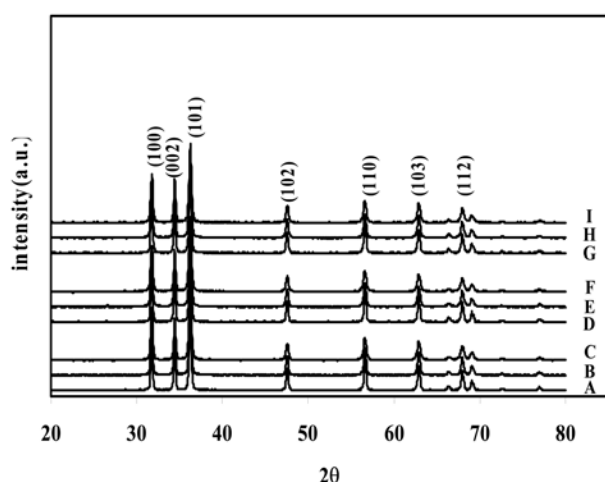


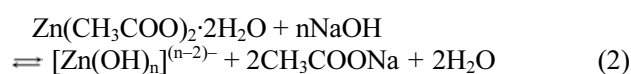
Fig. 1. XRD patterns of ZnO samples prepared using various conditions.

onal or wurzite structure in accordance with the JCPDS Card no. 36-1451. It was obvious that there were no extra peaks of a secondary phase such as $\text{Zn}(\text{OH})_2$ appearing in the diffraction patterns. Therefore, it could be said that only a single ZnO phase formed after calcining the samples in air at 600 °C for 1 h. By applying the Debye-Scherrer formula [7], the average crystallite size (D) was obtained by measurement of the broadening of the diffraction lines:

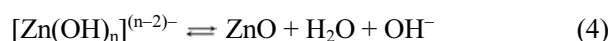
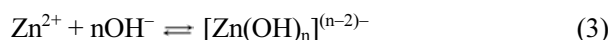
$$D = \frac{0.9\lambda}{\beta \cos \theta} \quad (1)$$

where λ is the wavelength of CuK_α radiation (1.5406 Å), β is the full-width at half-maximum of the peaks and θ is the Bragg angle corresponding to the peaks in the XRD patterns. The crystallite size of ZnO nanoparticles as a function of NaOH concentration is presented in Table 1.

Under the experimental condition investigated, the precursor used ($\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$) was in a crystalline form and contained hydration water. Furthermore, NaOH also contains small quantities of water which are sufficient to act as a solvent, also it was found that the precursors ($\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ and NaOH) possess hygroscopicity. Upon grinding the precursors and as the reaction progresses, this water is released from the crystals and it becomes available to act as a solvent. Thus, the reaction involving the formation of ZnO particles could be expressed as follows:



or



For each of the systems, the crystallite size of ZnO particles decreased as a function of NaOH or OH^- concentration. It is well-known that the formation of crystals involves a nucleation and a growth process. Particles of a smaller size are usually obtained when the rate of nucleation is

Table 1. Information on the ZnO nanoparticles prepared under various conditions

code	NaOH (mole)	capping agent (mole)		crystallite size (nm)	E_g (eV)	E_0	particle shape
		PVP	CTAB				
A	0.08	-	-	41	3.226	0.086	spherical
B	0.16	-	-	39	3.200	0.101	spherical
C	0.32	-	-	37	3.149	0.148	flower
D	0.08	2.67×10^{-4}	-	40	3.230	0.084	spherical
E	0.16	2.67×10^{-4}	-	38	3.201	0.115	spherical + small rod
F	0.32	2.67×10^{-4}	-	36	3.176	0.161	flower
G	0.08	-	0.02	39	3.230	0.077	spherical
H	0.16	-	0.02	38	3.204	0.118	spherical + small rod
I	0.32	-	0.02	36	3.182	0.158	flower

faster than that of their growth. In this study, more ZnO nuclei could be formed more quickly as the OH^- concentration was increased, giving rise to the formation of smaller crystallite sizes.

The effects of PVP and CTAB, were to produce a smaller crystallite size at the same amount of OH^- concentration used. This is because CTAB and PVP could adsorb onto the surface of the ZnO particles and could thus inhibit the diffusion of growth species from the surrounding solute atoms onto the surface of the growing particles (diffusion-limited growth). So, the growth rate of the ZnO crystals was inhibited [8].

It is well-known that the interaction between the surface of solid particles and capping agent are significantly dependent upon the surface chemistry of the solid, the type of capping agent, the type and concentration of precursors, solvent and temperature. For this reason, different particle shapes occurred when different NaOH concentrations were utilized. It was observed that the spherical-like particles changed to a flower-like shape when the NaOH concentration was increased. Based on the reactions involved, the $\text{Zn}(\text{OH})_4^{2-}$ species with different rates of growth for planes was found to be formed as $v_{(0001)} > v_{(\bar{1}010)} > v_{(\bar{1}011)} > v_{(000\bar{1})}$ and acted as a growth unit under a strong alkaline solution or high OH^- concentration. Therefore, the particles preferred to grow along the c -axis due to its highest growth velocity [13]. In contrast, the $\text{Zn}(\text{OH})_2$ species acted as a growth unit at low OH^- concentration. In this case, the growth rate along the (0001) plane of the ZnO nuclei is much slower than that of the other planes [14]. Thus, producing the spherical-like shape as shown in Fig. 2.

Optical properties

It is well-known that UV absorption is related to the electronic transition from filled valence states to empty conduction states. Therefore, the optical band gap can be defined as the difference between the valence band and conduction band in momentum space. The optical band gap is dependent upon the particle shape, particle size and defect concentration in the crystal. Therefore, the optical band gap of all samples was estimated from the well-known relationship for a transition [15]:

$$\alpha E = A(E - E_g)^{n/2} \quad (5)$$

where $E (=hc/\lambda)$ is the photon energy, α is an absorption coefficient, A is a constant and $n = 1$ (due to the ZnO being a direct transition).

Fig. 3(a) shows the extrapolation of the straight line down to $\alpha E = 0$ (where $E = E_g$) for all samples with the results shown in Table 1. It has been observed that the optical band gap of ZnO nanoparticles decreased or shifted to a higher wavelength as a function of NaOH concentration in each system even though their crystallite size decreased. In this study, the reduction of the E_g values or red-shift in the band gap could be explained by the enhancement of oxygen vacancies [16, 17] that were created in large numbers

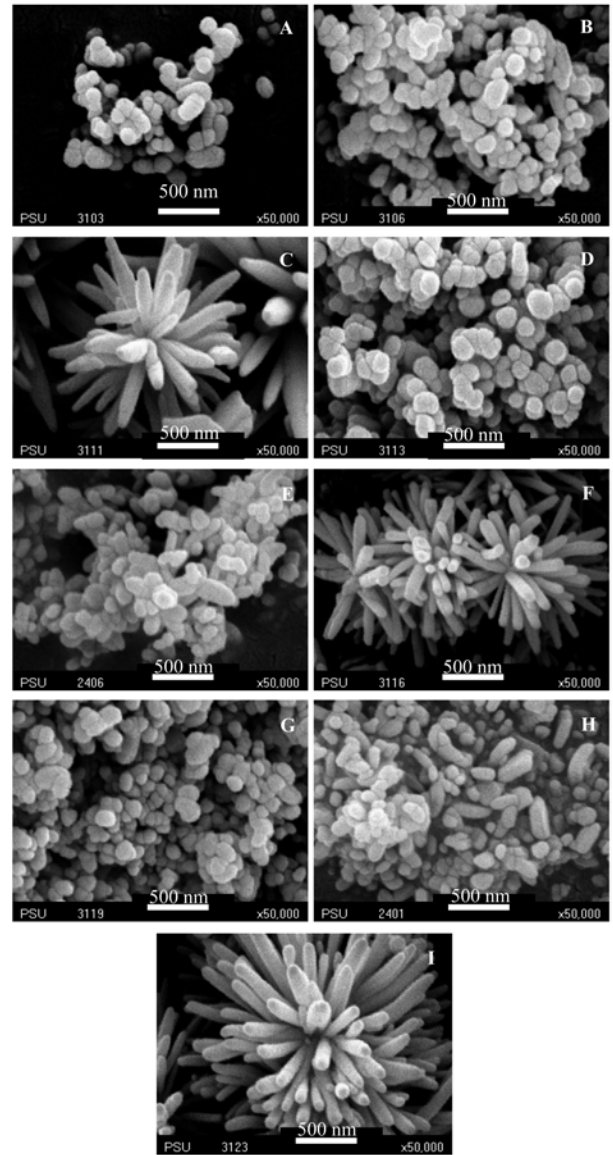


Fig. 2. SEM images of ZnO nanoparticles prepared under various conditions (see Table 1 for specimen codes).

in the calcined ZnO nanoparticles. It is to be noted that the defects or the nature of the disorder in the system brought about a localized energy level inside the band gap or discrete states. This is well-known as the band tailing effect [18]. In general, the absorption coefficient just below the band edge ($E < E_g$) should vary exponentially with the photon energy according to the relationship:

$$\alpha E = \alpha_0 \exp(E/E_0) \quad (6)$$

where α_0 is a constant and E_0 is an empirical parameter depending on the defect concentration, temperature and the structural disorder. The E_0 could be evaluated from the reciprocal of the slope of the linear part from the $\ln(\alpha)$ vs. E curve ($E < E_g$) as presented in Fig. 3(b). The red-shift in the band gap is caused by the increase of E_0 as presented in Table 1 owing to the increase of oxygen vacancies.

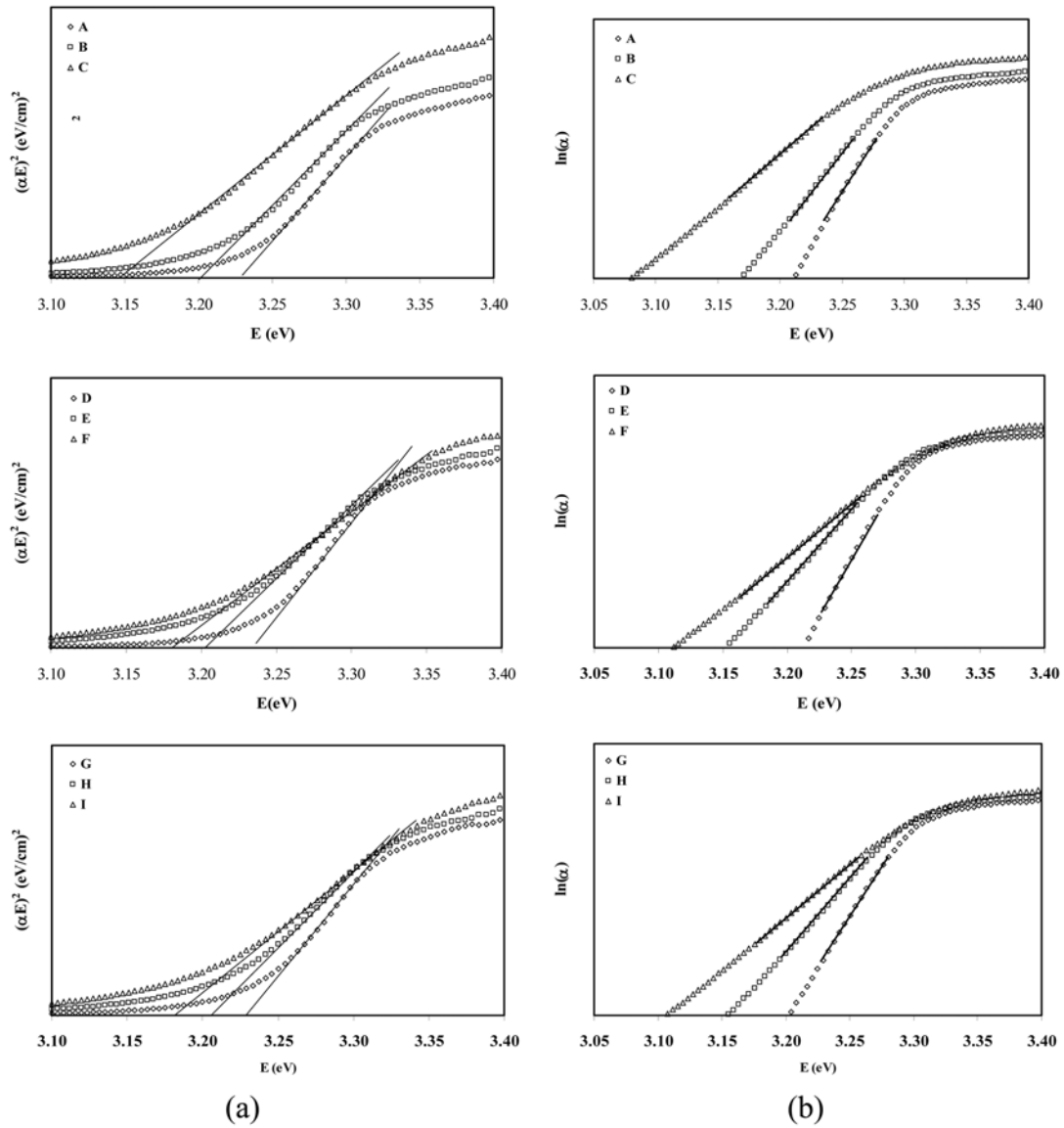


Fig. 3. (a) Evolution of the $(\alpha E)^2$ vs. E curves and (b) plots of $\ln(\alpha)$ vs. E of all ZnO Samples (see table 1 for specimen codes).

Electron paramagnetic resonance (EPR) measurements were used to investigate the paramagnetic defects in materials. The first-order differential EPR spectrum of a calcined ZnO nanoparticle is presented in Fig. 4.

The EPR spectrum shows a single sharp line at a Landé factor $g \sim 1.9592$. This resonance signal was attributed to the singly ionized oxygen vacancy (V_O^+) defects [19]. Moreover, the presence of the oxygen vacancies was also evident from the expansion of the c -axis parameter from 5.2199 to 5.2220 and 5.2241 Å when the particle shape of ZnO was altered from being spherical to a mixed spherical-like and small rod-like and to a flower-like shape, respectively [17]. Therefore, it could be summarized that the flower-like structure prepared by the grinding method produced a higher oxygen vacancy concentration than that of the spherical-like shape, giving rise to a reduction in the band gap as mentioned in the previously.

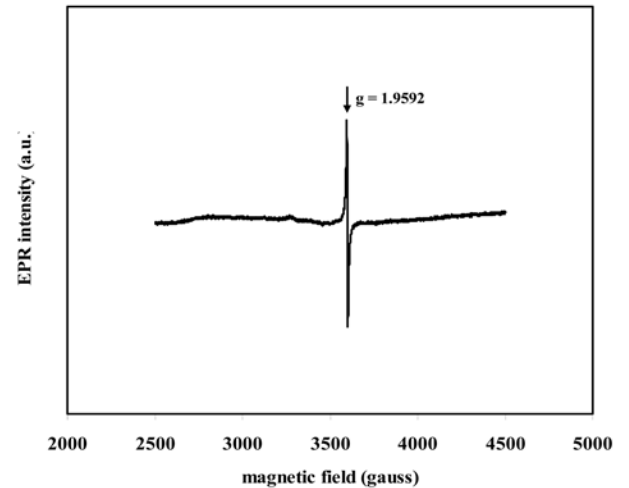


Fig. 4. EPR signal of sample I.

Conclusions

ZnO nanoparticles prepared by a grinding method produced a hexagonal or wurtzite structure. The shape of the ZnO nanoparticles changed from being spherical to a flower-like structure when the NaOH concentration was increased. The crystallite size of the ZnO decreased as a function of the NaOH concentration and the crystallite size also decreased further when PVP or CTAB was added as a capping agent at the same NaOH concentration. The optical band gap was reduced when the small rod and flower-like structures formed because of the increase of oxygen vacancies in the crystal.

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References

1. S. Sahoo and A.K. Bhowmick, *J. Appl. Polym. Sci.* 106[5] (2007) 3077-3083.
2. Z.P. Sun, L. Liu, L. Zhang and D.Z. Jia, *Nanotechnology*. 17[9] (2006) 2266-2270.
3. C.W. Nahm, *Ceram. Int.* 35[2] (2009) 541-546.
4. L. Zhang, Y. Jiang, Y. Ding, M. Povey and D. York, *J. Nanopart. Res.* 9 (2007) 479-489.
5. F. Li, L. Hu, Z. Li and X. Huang, *J. Alloys Compd.* 465[1-2] (2008) L14-L19.
6. F. Rataboul, C. Nayral, M.J. Casanove, A. Maisonnat and B. Chaudret, *J. Organomet. Chem.* 643-644 (2002) 307-312.
7. S. Suwanboon, P. Amornpitoksuk, A. Haidoux and J.C. Tedenac *J. Alloys Compd.* 462[1-2] (2008) 335-339.
8. S. Suwanboon, *ScienceAsia*. 34[1] (2008) 31-34.
9. A. Kajbafvala, M.R. Shayegh, M. Mazloumi, S. Zanganeh, A. Lak, M.S. Mohajerani and S.K. Sadrnezhad, *J. Alloys Compd.* 469[1-2] (2009) 293-297.
10. S. Ilican, Y. Caglar, M. Caglar, F. Yakuphanoglu and J. Cui, *Physica E*. 41[1] (2008) 96-100.
11. M. Bitenc and Z.C. Orel, *Mater. Res. Bull.* 44[2] (2009) 381-387.
12. J. Zhang, H. Liu, Z. Wang and N. Ming, *J. Cryst. Growth*. 310[11] (2008) 2848-2853.
13. J. Liu and X. Huang, *J. Solid State Chem.* 179[3] (2006) 843-848.
14. Q. Ahsanulhaq, J.H. Kim, N.K. Reddy and Y.B. Hahn, *J. Ind. Eng. Chem.* 14[5] (2008) 578-583.
15. S. Dutta, S. Chattopadhyay, A. Sarkar, M. Chakrabarti, D. Sanyal and D. Jana, *Prog. Mater. Sci.* 54[1] (2008) 89-136.
16. S. Dutta, S. Chattopadhyay and D. Jana, *J. Appl. Phys.* 100 (2006) DOI: 10.1063/1.2401311.
17. S. Dutta, M. Chakrabarti, S. Chattopadhyay and D. Jana, *J. Appl. Phys.* 98 (2005) DOI: 10.1063/1.2035308.
18. S. Dutta, S. Chattopadhyay, M. Sutradhar, A. Sarkar, M. Chakrabarti, D. Sanyal and D. Jana, *J. Phys: Condens. Matter*. 19 (2007) DOI: 10.1088/0953-8984/19/23/236218.
19. N.O. Dantas, L. Damigo, F. Qu, R. Silva, P.P.C. Sartoratto, K.L. Miranda, E.C. Vilela, F. Pelegrini and P.C. Morais, *J. Non-Cryst. Solids*. 354[42-44] (2008) 4727-4729.