

Structural and Optical Properties of Nanocrystalline ZnO Powder from Sol-Gel Method

Sumetha Suwanboon

Materials Science Program, Faculty of Science, Prince of Songkla University, Hat Yai, Songkhla 90112, Thailand.

* Corresponding author, E-mail: ssumetha@yahoo.com

Received 2 May 2007

Accepted 31 Oct 2007

ABSTRACT: Nanocrystalline ZnO powders have been synthesized by using zinc acetate dihydrate and polyvinylpyrrolidone (PVP) as starting materials. The calcined powders in air at 600 °C for 1 hour have been characterized by XRD, indicating the wurtzite or hexagonal structure with crystallite size of about 45 nm. The TEM image gives the grain size of about 100 nm in diameter at 3×10^{-4} M PVP. The morphology of ZnO powders has been changed from platelet-like to rod shape with increase in PVP concentrations. The calcined ZnO powders have exhibited the direct optical band gap of about 3.222-3.237 eV and its photoluminescence has performed the UV emission peak at about 390 nm with small blue shift due to smaller grain size at higher PVP concentrations.

KEYWORDS: zinc oxide, PVP, sol-gel, optical properties, photoluminescence.

INTRODUCTION

Recently, nanocrystalline powders with a uniform size and shape have shown interesting properties particularly nanocrystalline of metal oxides, due to its numerous important properties such as catalytic, electrical and optical properties. Among them, ZnO is one of candidate materials which has been attracting attention because of its wide band gap energy of about 3.37 eV. Therefore, ZnO is an important material for room temperature UV lasers and short-wavelength optoelectronic device^{1,2}. Furthermore, ZnO with its good electrical and optical properties can be used in many applications such as photoconductors, integrated sensors and transparent conducting oxide electrodes^{3,4}.

Up to now, a number of chemical routes have been used to synthesize nanocrystalline ZnO powders such as hydrothermal method⁵, spray pyrolysis⁶ and sol-gel method⁷. Among these methods, sol-gel shows many advantages over other techniques such as its simplicity and low equipment cost. Therefore, in this study we had concentrated the effect of PVP concentration on controlling the structural and optical properties of nanocrystalline ZnO powders by sol-gel method.

MATERIALS AND METHODS

All the chemical reagents used in this experiment are analytical grade and they were used without further purification. In a typical procedure, 2.1949 g zinc

acetate dihydrate ($\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$) was first dissolved in 50 mL distilled water (0.2 M) with continuous stirring until homogeneous solutions were obtained. Various amounts (0, 4, 8 and 12 g or 0, 1×10^{-4} , 2×10^{-4} and 3×10^{-4} M) of PVP (M.W. 40,000) were then added into zinc precursor solutions so as to elucidate the role of PVP concentration in controlling the shape and size of ZnO powders. Finally, 1.6 g NaOH that was dissolved in 50 mL distilled water (0.8 M) was slowly added to the PVP-modified zinc precursor solutions. The white precipitates were achieved and were then vigorously stirred at ambient temperature for 1 hour before filtering, rinsing with distilled water, drying at 60 °C and calcining at 600 °C in air for 1 hour.

The phase identification of calcined powders was characterized by the X-ray diffraction (XRD) method using $\text{CuK}\alpha$ radiation with a conventional $\theta - 2\theta$ goniometer (X'Pert MPD, Philips). Fourier transformed infrared (FTIR) spectrum of calcined powder was recorded by FT-IR spectrophotometer (Equinox55, Bruker) in the range of 4000-400 cm^{-1} . The shape and grain size of calcined powders were evaluated with scanning electron microscopy (SEM, JSM-5800 LV, JOEL) and transmission electron microscopy (TEM, JEM-2001, JOEL). The transmittance was measured in the range of 200-800 nm by a UV-VIS spectrophotometer (UV-2401, Shimadzu) and photoluminescence measurement was performed by a luminescence spectrometer (LS/55, Perkin Elmer) equipped with a Xenon discharge lamp.

RESULTS AND DISCUSSION

Structural Properties

The FT-IR spectrum of synthetic ZnO powder (Figure 1) presented main absorption bands due to O-H stretching of hydroxyl group at 3439 cm^{-1} , asymmetric and symmetric C=O stretching of zinc acetate at 1643 and 1515 cm^{-1} , O-H bending of hydroxyl group at 567 cm^{-1} and Zn-O stretching of ZnO at 430 cm^{-1} . These data are similar to the result in another report⁸.

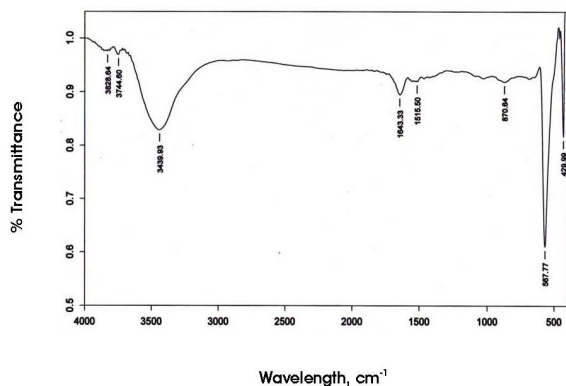


Fig 1. FT-IR spectrum of nanocrystalline ZnO powder.

In this part, we studied the role of PVP concentrations in controlling the size and shape of nanocrystalline ZnO powders which were calcined at $600\text{ }^{\circ}\text{C}$ in air for 1 hour. The XRD patterns presented good crystallinity in the whole ranges of PVP concentrations. These peaks corresponded to the (100), (002), (101), (102), (110), (103), (200), (112) and (201) planes of ZnO in the wurtzite structure (Figure 2) correspondence with JCPDS (card number

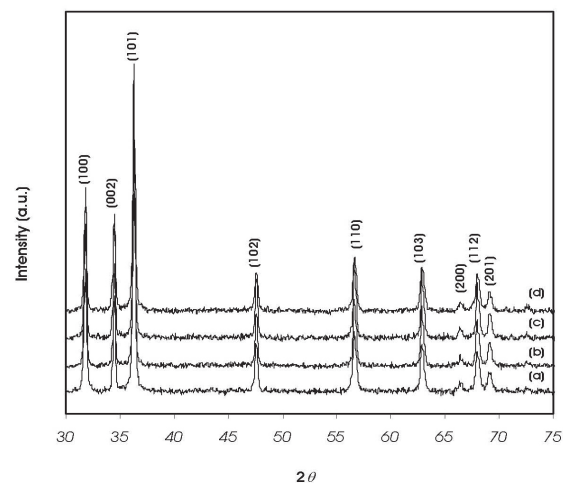


Fig 2. XRD patterns of nanocrystalline ZnO powders modified with (a) no PVP, (b) 1×10^{-4} M, (c) 2×10^{-4} M and (d) 3×10^{-4} M, respectively.

36-1451). The crystallite size of nanocrystalline ZnO powders which was calculated by Scherrer's formula⁹ [$D = 0.9 \lambda / \beta \cos \theta$, where D is crystallite size, λ is the wavelength of the x-rays, β is the full-width at a half-maximum intensity of the peak and θ is the diffraction angle], gave the values of about 49, 56, 48 and 45 nm at 0, 1×10^{-4} , 2×10^{-4} and 3×10^{-4} M PVP, respectively. Therefore, it had been concluded that PVP plays two important roles in this system. First, the PVP could promote the reaction of Zn^{2+} ions with NaOH to form $\text{Zn}(\text{OH})_2$ by generating the OH^- groups in solution, observing from the increasing pH of the solutions. This phenomenon promoted more reaction and grain growth. The PVP, secondly, acts as stabilizer or capping agent when the concentration was higher than 1×10^{-4} M. Therefore, the PVP can encapsulate the generated particles at higher concentrations, giving rise to the suppression of the grain growth. In this study, the morphology of nanocrystalline ZnO powders was changed from platelet-like with grain size of about 150 nm to rod shape with a diameter size of about 100 nm at 3×10^{-4} M PVP (Figure 3) because of the adsorption of protonated PVP species on (100) negative plane so the grains can grow in $\langle 001 \rangle$ direction¹⁰. The grain size

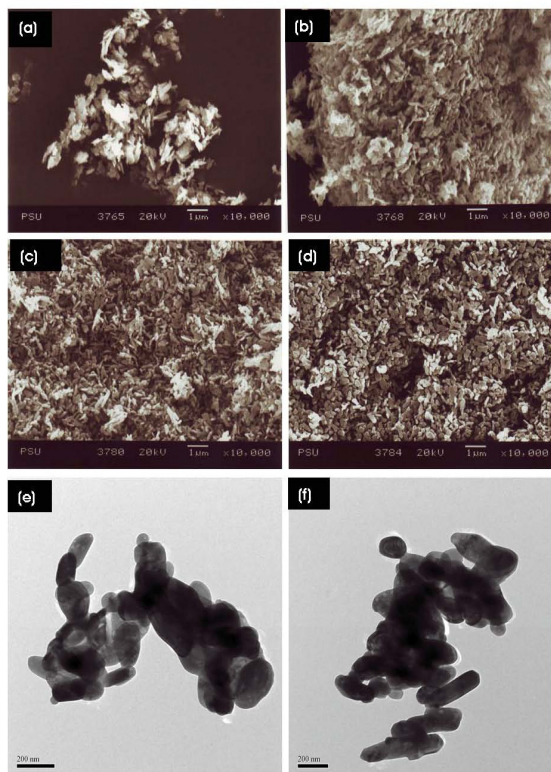


Fig 3. SEM images of nanocrystalline ZnO powders modified with (a) no PVP, (b) 1×10^{-4} M, (c) 2×10^{-4} M and (d) 3×10^{-4} M, as well as the TEM images at (e) no PVP and (f) 3×10^{-4} M, respectively.

of nanocrystalline ZnO powder modified with PVP (M.W. 40000) in this study was smaller than that of the nanocrystalline ZnO powder modified with PVP (M.W. 1300000) and PVP (M.W. 8000) in other reports^{8,11}. However, it was observed that there was a difference between the size measurement by two methods like XRD and TEM. The reason is well known. In TEM, the grain size was measured by the difference between the visible grain boundaries while in the XRD method the measurement was extended to the crystalline region that diffracted x-ray coherently. So, the XRD method was a more stringent criterion and led to smaller size¹².

Optical Properties

In order to investigate the optical properties of nanocrystalline ZnO powders modified with PVP at various concentrations, the transmittance was measured as a function of wavelength in the range of 200-800 nm and the calcined ZnO powders performed in a highly transparent mode in visible region. In general, the wurtzite ZnO structure has a direct band gap and this direct interband transition could calculate from the relationship:

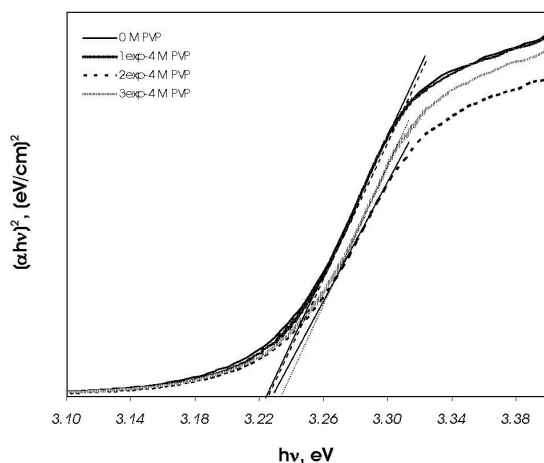
$$(\alpha h\nu)^2 = E_D (h\nu - E_{opt})$$

where α is the optical absorption coefficient [$\alpha = (1/t)\ln(1/T)$, where t is thickness and T is transmittance], h is the Planck's constant, ν is the frequency of the incident photon, E_D is a constant and E_{opt} is the direct band gap¹³.

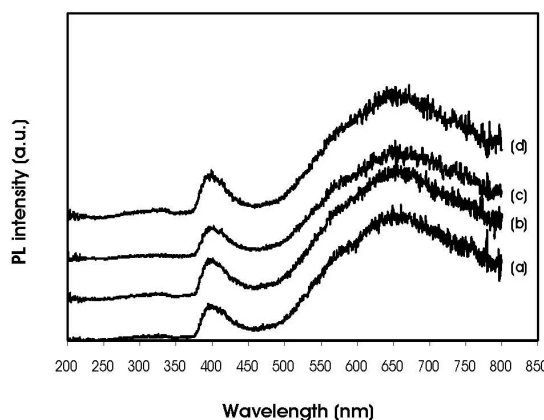
The values of direct band gap were obtained from the linear portion of the plot of $(\alpha h\nu)^2$ vs. $h\nu$ when extrapolating to zero. The nanocrystalline ZnO powders gave the direct band gap of about 3.222, 3.225, 3.230 and 3.237 eV at 0, 1×10^{-4} M, 2×10^{-4} and 3×10^{-4} M PVP, respectively (Figure 4(a)). The photoluminescence at room temperature of nanocrystalline ZnO powders modified with PVP at various concentrations was also measured. It was evident that there are two broad emission peaks in each spectrum (Figure 4(b)). The UV emission of nanocrystalline ZnO powder at 0 M PVP showed a peak at 390 nm. This emission originates from the recombination of free excitons through an exciton-exciton collision process¹⁴. Another peak at 640 nm is a yellow emission, this emission attributes to oxygen interstice¹⁵. Moreover, the UV emission peaks shifted to lower wavelength or higher energy (blue shift) as increasing the PVP concentrations or decreasing the grain size.

CONCLUSION

Nanocrystalline ZnO powders have been synthesized in an aqueous solution by simple method using zinc acetate dihydrate and PVP as precursors.



(a)



(b)

Fig 4. (a) Plots of $(\alpha h\nu)^2$ vs. $h\nu$ for nanocrystalline ZnO powders modified with PVP at various concentrations when calcining at 600 °C in air for 1 hour and (b) room temperature photoluminescence of nanocrystalline ZnO powders modified with (a) no PVP, (b) 1×10^{-4} M, (c) 2×10^{-4} M and (d) 3×10^{-4} M, respectively.

These powders have been indexed as wurtzite or hexagonal structure with the smallest average crystallite size of about 45 nm and grain size (from TEM) of about 100 nm at PVP concentration of 3×10^{-4} M. The morphology has altered from platelet-like to rod shape when adding PVP into solution. The nanocrystalline ZnO powders have exhibited the direct optical band gap in the range of 3.222-3.237 eV in this study. Moreover, the photoluminescence at room temperature of ZnO powders performed the UV emission peak at 390 and 640 nm and the UV emission peaks shifted to higher energy or blue shift with increasing the PVP concentration or decreasing the grain size.

ACKNOWLEDGEMENTS

This work was supported by the Faculty of Science, Prince of Songkla University under a Seed Money Project fund. The use of facilities partly supported by Chemistry Department, Faculty of Science, Prince of Songkla University is also acknowledged.

REFERENCES

1. Bao D, Gu H and Kuang A (1998) Sol-gel-derived c-axis oriented ZnO thin films. *Thin Solid Films* **312**, 37-9.
2. Majumder SB, Jain M, Dobal PS and Katiyar RS (2003) Investigations on solution derived aluminium doped zinc oxide thin films. *Mat. Sci. Eng. B* **103**,16-25.
3. Huang Y, Liu M, Li Z, Zeng Y and Liu S (2003) Raman spectroscopy study of ZnO-based ceramic films fabricated by novel sol-gel process. *Mat. Sci. Eng. B* **97**, 111-6.
4. Xu J, Pan Q, Shun Q and Tian Z (2000) Grain size control and gas sensing properties of ZnO gas sensor. *Sensor. Actuat. B-Chem.* **66**, 277-9.
5. Pal U, Garcia, Santiago P, Xiong G, Ucer KB and Williams RT (2006) Synthesis and optical properties of ZnO nanostructures with different morphologies. *Opt. Mater.* **29**, 65-9.
6. Mohammad MT, Hashim AA and Al-Maamory MH (2006) Highly conductive and transparent ZnO thin films prepared by spray pyrolysis technique. *Mater. Chem. Phys.* **99**, 382-7.
7. Tang H, Yan M, Ma X, Zhang H, Wang M and Yang D (2006) Gas sensing behavior of polyvinylpyrrolidone-modified ZnO nanoparticles for trimethylamine. *Sensor. Actuat. B-Chem.* **113**, 324-8.
8. Maensiri S, Laokul P and Promarak V (2006) Synthesis and optical properties of nanocrystalline ZnO powders by a simple method using zinc acetate dihydrate and poly(vinyl pyrrolidone). *J. Cryst. Growth* **289**, 102-6.
9. Byeong KC, Dong HC, Yung SY and Seong JK (2006) Optical characterization of ZnO thin films deposited by sol-gel method. *J. Mater. Sci.: Mater. Electron.* **17**, 1011-5.
10. Caswell KK, Bender CM and Murphy CJ (2003) Surfactantless wet chemical synthesis of silver wires. *Nano Lett.* **3**, 667-9.
11. Lepot N, VanBael MK, Van den Rul H, D'Haen J, Peeters R, Franco D and Mullens J (2007) Synthesis of ZnO nanorods from aqueous solution. *Mater. Lett.* **61**, 2624-7.
12. Bandyopadhyay S, Paul GK, Roy R and Sen SK (2002) Study of structural and electrical properties of grain-boundary modified ZnO films prepared by sol-gel technique. *Mater. Chem. Phys.* **74**, 83-91.
13. Serpone N, Lawless D and Khairutdinov R (1995) Size effects on the photophysical properties of colloidal anatase TiO₂ particles: size quantization or direct transitions in the indirect semiconductor. *J. Phys. Chem.* **99**, 16646-54.
14. Kong YC, Yu DP, Zhang B, Fang W and Feng SQ (2001) Ultraviolet-emitting ZnO nanowires synthesized by a physical vapor deposition approach. *Appl. Phys. Lett.* **78**, 407- 9.
15. Vanheusden K, Warren WL, Seager CH, Tallant DR and Voigt JA (1996) Mechanisms behind green photoluminescence in ZnO phosphor powders. *J. Appl. Phys.* **79**, 7983-90.