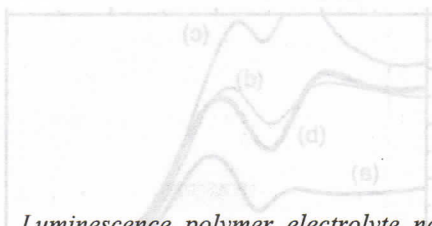


# EFFECT OF POLYMER MOLECULAR WEIGHT ON THE LUMINESCENCE PROPERTIES OF NANOCOMPOSITE ZINC OXIDE/POLYETHYLENE GLYCOL



M. Abdullah<sup>\*)</sup>

## Abstract

Luminescence polymer electrolyte nanocomposites (Zinc oxide/polyethylene glycol: Lithium ions) have been synthesized using different molecular weight of polymer. Changing the molecular weight produced no effect of the crystallinity of ZnO nanoparticles if similar molarity of ethylene glycol unit were used. However, the use of high molecular weight of polymers tended to reduce the size of nanoparticles, which implied to the enhancement in the luminescence spectra due to increasing in the particle number concentration. TEM picture of sample prepared using PEG of molecular weight of 500,000 exhibited a particle size of 5 nm, which was close to the value predicted by Warren-Scherer formula or size dependent band gap.

**Key words:** nanocomposite; luminescent polymer electrolytes; zinc oxide; polyethylene glycol

## Introduction

Zinc oxide (ZnO) presents interesting optical, acoustical and electrical properties, which meet wide applications in the field of electronic (Lin, *et al.*, 1995; Ramachalam, *et al.*, 1995), optoelectronic (Vanheusden, *et al.*, 1996; Nanto, *et al.*, 1981) and sensors (Lin, *et al.*, 1995; Weissenrieder and Muller, 1997). As a wide gap semiconductor ZnO has potential applications as transparent electrode (Izaki and Omi, 1996) for photovoltaic and electroluminescent devices and as a promising material for UV light emitting devices (Tang, *et al.*, 1998). This material produces high photoluminescence (PL) intensity peaks at around 380 nm and 530 nm (Dijken, *et al.*, 2000). Optical phonon confinement in nanocrystallites ZnO has been observed based on the shift of Raman peaks (Rajalakshmi, *et al.*, 2000).

In the previous reports we described an *in-situ* method for preparing nanocomposites polymer electrolytes containing ZnO nanoparticles (Abdullah, *et al.*, 2002; Abdullah, *et al.*, 2003). ZnO nanoparticles were grown directly in the polymer matrix and precursor material containing alkali ions, which did not participate in the formation of nanoparticles were used. Because ZnO nanoparticles emit luminescence, luminescence polymer electrolyte nanocomposites in which nanoparticles serve as luminescence centers could be produce.

However, the properties of the composites by varying the molecular weight of polymer have not been investigated. Here we report the luminescence properties of the composite by varying the molecular weight of polymer. During mixing, the viscosity of polymer solution increases with increasing the

molecular weight, so it is expected to affect the properties of the produced composites.

## Experiment

### Materials

Zinc acetate dihydrate ( $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ ) (Wako Pure Chemicals). Lithium hydroxide hydrate ( $\text{LiOH} \cdot \text{H}_2\text{O}$ ) (Wako Pure Chemicals). Ethanol ( $\text{C}_2\text{H}_5\text{OH}$ ) 99.5% (Kanto Chemicals). Polyethylene glycol, PEG ( $\text{H}[-\text{OCH}_2\text{CH}_2-]_n\text{OH}$ ) (Wako Pure Chemicals), with  $n = 2 \times 10^4$ ,  $5 \times 10^5$ ,  $2 \times 10^6$ , and  $4 \times 10^6$ .

### Method

A solution of zinc acetate dihydrate in ethanol (0.1M) was distilled at 80 °C to produce 40 vol.% of a hygroscopic solution and 60 vol.% of unused condensate (Spanhel and Anderson, 1991). The lithium hydroxide dihydrate was dissolved in ethanol separately (0.14 M). PEG 0.5 g was dissolved in 40 ml of the lithium hydroxide solution at a temperature of 50 °C and stirred until homogeneous gel-like mixture was obtained. This solution was then mixed with 20 ml hygroscopic solution of zinc acetate. Several hours after mixing, the mixture then dried in oven at 40 °C for three days to produce ZnO nanoparticles dispersed in polymer matrix. The sample used were (a) PEG  $2 \times 10^4$ , (b) PEG  $5 \times 10^5$ , (c) PEG  $2 \times 10^6$ , and (d) PEG  $4 \times 10^6$ .

### Characterizations

X-ray diffraction (XRD) patterns were recorded using a Rigaku Denki RINT2000 instrument with  $\text{Cu-K}_\alpha$  source. Excitation and luminescence spectra were recorded using a Shimadzu RF-5300PC

<sup>\*)</sup> Departemen Fisika, ITB, Jl. Ganeca 10 Bandung 40132, Indonesia  
Department of Chemical Engineering, Hiroshima University,  
Higashi-Hiroshima, 739-8527, Japan, E-mail : din@hiroshima-u.ac.jp

spectrophotometer with xenon laser source. Scanning electron micrographs (SEM) were recorded using Hitachi S-5000 (20 kV). Transmission electron micrographs (TEM) were recorded using Hitachi H-7000FA (100 kV).

### Results and Discussion

Figure 1 shows the XRD patterns (with respect to  $2\theta$ ) of samples (a) to (d). We see some peaks of ZnO, i.e.,  $\langle 100 \rangle$ ,  $\langle 002 \rangle$ ,  $\langle 101 \rangle$ ,  $\langle 102 \rangle$ ,  $\langle 110 \rangle$ ,  $\langle 103 \rangle$ , and  $\langle 112 \rangle$  reflections. The peaks are clearly observed at high reflection angles (above  $2\theta = 50^\circ$ ). A low reflection angle, the PEG peaks also appeared. The intensity of ZnO peaks seemed to be independent of the PEG molecular weight. Since, the same weight of PEG were used, so that the molarities of ethylene glycol unit ( $[H[-OCH_2CH_2-]_nOH]$ ) are similar in all samples. We also observed the XRD peaks of samples prepared with PEG  $5 \times 10^5$  but different in weight (different in molarity of ethylene glycol units), and observed the ZnO peak intensities tended to decrease with increasing the weight of PEG used. These results indicated that, the ZnO crystallinity depends on the molarity of ethylene glycol units instead of PEG molecular weight.

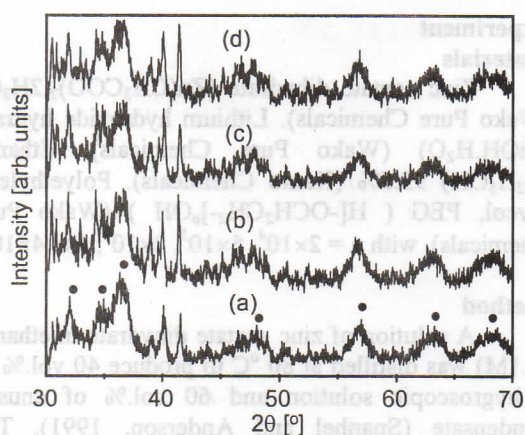


Figure 1. The XRD patterns of samples prepared using different PEG molecular weights: (a)  $2 \times 10^4$ , (b)  $5 \times 10^5$ , (c)  $2 \times 10^6$ , and (d)  $4 \times 10^6$ . The reflection peaks from left to right are  $\langle 100 \rangle$ ,  $\langle 002 \rangle$ ,  $\langle 101 \rangle$ ,  $\langle 102 \rangle$ ,  $\langle 110 \rangle$ ,  $\langle 103 \rangle$ , and  $\langle 112 \rangle$ .

To predict the mean crystalline size ( $D$ ) based on XRD pattern we using Scherrer-Warren formula (Bailar, *et al.*, 1973; Mikrajuddin, *et al.*, 2001)

$$D = K \lambda / [\Delta(2\theta) \cos \theta] \quad (1)$$

with  $\lambda$  is the X-ray wavelength (for Cu-K $\alpha$  = 1.5418 Å),  $\Delta(2\theta)$  is the width of half maximum, and  $K = 0.9$  (Kaelble, 1967). We select  $\langle 110 \rangle$  peak of sample (b)

since it is relative clear. We measured  $\Delta(2\theta) \approx 0.038$  rad, and  $2\theta \approx 57^\circ$  or  $\theta \approx 28.5^\circ$ . We thus predicted the diameter of ZnO nanoparticles of around  $D \approx 4$  nm

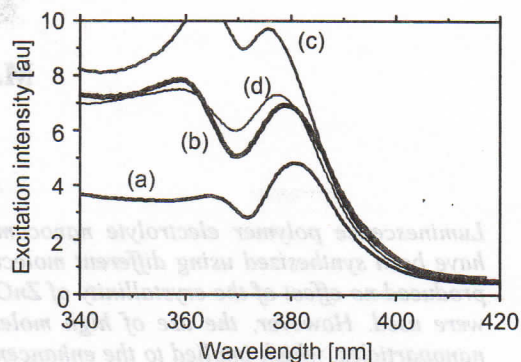


Figure 2. The excitation spectra of samples prepared using different PEG molecular weights: (a)  $2 \times 10^4$ , (b)  $5 \times 10^5$ , (c)  $2 \times 10^6$ , and (d)  $4 \times 10^6$ , which detected at 530 nm.

Figure 2 shows the excitation spectra (measured at room temperature) of samples (a) to (d) detected at wavelength of 530 nm. Initially, the intensity increased from samples (a) to (c) and the decreased for sample (d). The change in these intensities was not well understood. Each spectrum contains two peaks. The long wavelength peak is attributed by electron transition from the top of valence band to the exciton state (electron-hole pair) with energy located slightly below the bottom of conduction band. The short wavelength peak is attributed to the electron transition from the top of valence band to the bottom of conduction band (band gap transition) (Abdullah, *et al.*, 2003).

The peaks of the excitation spectra shifted slightly to the left (blue shift) by increasing the PEG molecular weight form sample (a) to (c), and then slightly shifted right from sample (c) to (d). It is well known that the band gap of particle in nanometer size depends of the particle size. The band gap opening increases with decreasing particle size due to quantum confinement of electron in nanoparticles. The relation between band gap and particle size can be calculated using a simple equation (Dijken, *et al.*, 2000)

$$E_g(R) = E_g(\infty) + h^2/8\mu R^2 - 1.8e^2/4\pi\epsilon\epsilon_0 R \quad (2)$$

with  $E_g(R)$ , band gap of nanoparticle with radius  $R$ ,  $E_g(\infty)$  band gap of bulk material,  $h$  Planck constant,  $e$  electron charge,  $\epsilon$  dielectric constant of material,  $\epsilon_0$  permittivity of vacuum, and  $\mu$  reduced mass satisfying

$$1/\mu = 1/m_e + 1/m_h \quad (3)$$

with  $m_e$  and  $m_h$  are the effective masses of electron and hole, respectively. For zinc oxide we have  $E_g(\infty) = 3.4$  eV,  $m_e = 0.31m_o$  and  $m_h = 0.8m_o$ , with  $m_o = 9.1 \times 10^{-31}$  kg is the mass of free electron,  $\epsilon = 6$  [18].  $E_g(R)$  is calculated using the band gap peak position of excitation spectrum using a relation  $E_g(R) = hc/\lambda_{bp}$ , with  $\lambda_{bp}$  is the wavelength of band gap peak. The values of  $\lambda_{bp}$  for four samples are 364.8 nm, 360.4 nm, 359.3 nm, 363.2 nm, from samples (a), (b), (c), and (d), respectively. Therefore, the predicted particle diameter in four samples are 7.7 nm, 6 nm, 5.8 nm, 7 nm, respectively for sample (a), (b), (c), and (d).

Since the amount of precursors used to make four samples were similar, the total amount of the produced ZnO material should be similar in four samples. Therefore, sample containing smaller ZnO particles has larger ZnO nanoparticles number concentration. The particle size of ZnO in four samples decreases from sample (a), (b), (d), and (c), so that the particle number concentration increases from samples (a), (b), (d), and (c). This result is in consistent with the increase in the excitation intensities from samples (a), (b), (d), and (c).

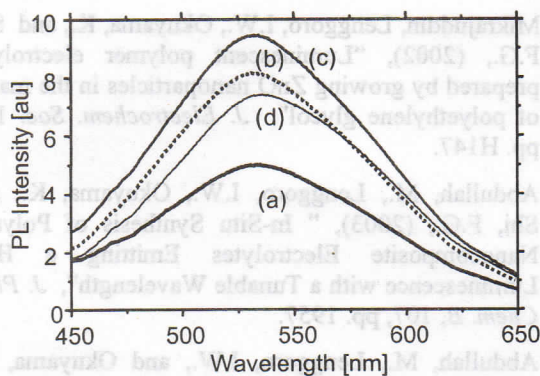


Figure 3. The photoluminescence spectra of samples prepared using different PEG molecular weights: (a)  $2 \times 10^4$ , (b)  $5 \times 10^5$ , (c)  $2 \times 10^6$ , and (d)  $4 \times 10^6$ , excited with wavelengths coincided with the band gap peaks in the excitation spectra.

Figure 3 is the photoluminescence spectra of samples (a) to (d) excited using wavelengths coincided with the band gap peaks in the excitation spectra. The positions of photoluminescence peaks were at around 533 nm, attributed to the transition of electron from exciton state to a deep level located in the band gap. The intensity of samples changed according to the change in the intensity of excitation spectra, to indicate that the particle number concentration responsible to the intensity.

The energy of exciton state measured from the bottom of conduction band is [19]

$$E_{exc} = (\mu/m_o\epsilon^2) \times 13.6 \text{ eV} \quad (4)$$

Using  $m_e = 0.31m_o$ ,  $m_h = 0.8m_o$ , and  $\epsilon = 6$ , one has  $E_{exc} = 82$  meV. The position of band gap and exciton peaks in four samples were: (a) (364.8 nm, 380.9 nm), (b) (360.4 nm, 378.7 nm), (c) (359.3 nm, 377.2 nm), and (d) (363.4 nm, and 375.8 nm). The exciton binding energy for four samples then 144 meV, 166 meV, 164 meV, and 113 meV, for samples (a), (b), (c), and (d), respectively. These values are higher than predicted using Eq. (4) of about 82 meV. However, in fact, there are many parameters suggested for ZnO materials. For example, if the values of  $m_e = 0.24 m_o$ ,  $m_h = 0.45 m_o$ , and  $\epsilon = 3.7$  (Monticone, *et al.*, 1998). The calculated predicted exciton binding energy of 155 meV, very close to the measurement data.

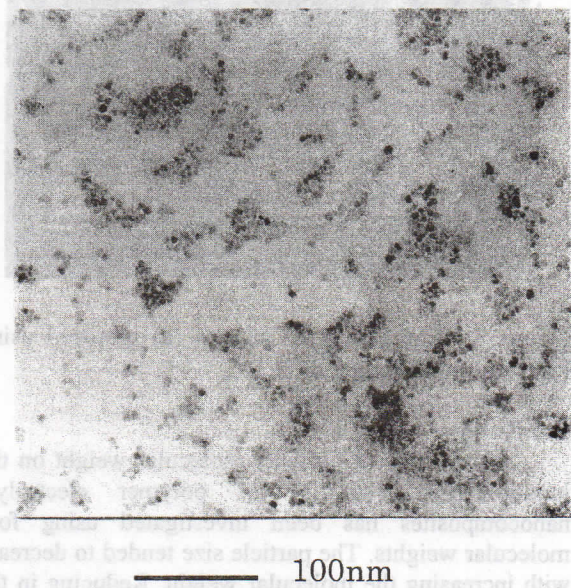


Figure 4. TEM picture of sample (b) prepared using PEG molecular weight of  $5 \times 10^5$ .

The energy of deep level can be calculated using  $E_{dl} = E_{vb-exc} - E_{pl}$ , with  $E_{pl}$  is energy of the peak of photoluminescence spectrum. For four samples, the locations of photoluminescence peaks were similar at around 533 nm, or with energy 2.328 eV.  $E_{vb-exc}$  is energy of exciton state measured from the top of valence band. This energy can be calculated from the exciton peak in Fig. 2.  $E_{vb-exc}$  for samples (a), (b), (c), and (d) are 3.257 eV, 3.276 eV, 3.289 eV, and 3.301 eV, respectively. Thus, the positions of deep level states in four samples are 0.929 eV, 0.948 eV, 0.961 eV, and 0.973 eV, respectively. Thus the positions of deep level in all samples are nearly similar at around 1 eV above the top of valence band (Abdullah, *et al.*).

The exact size of ZnO nanoparticles was determined using TEM. Figure 4 is the TEM picture of sample (b) as an example. The particle diameter was about 5 nm. The particle sizes are nearly homogenous to indicate the present method is

promising for producing monosize nanoparticles. This particle size is close to that predicted using Warren-Scherrer formula in E. (1) of about 4 nm and prediction using size dependent band gap Eq. (2) of about 7.7 nm. The differences appeared since these two formulas are approximation equations. SEM picture of sample (a) is shown in Fig. (5). The sample is not smooth, but contains some hill due to molecular folding.

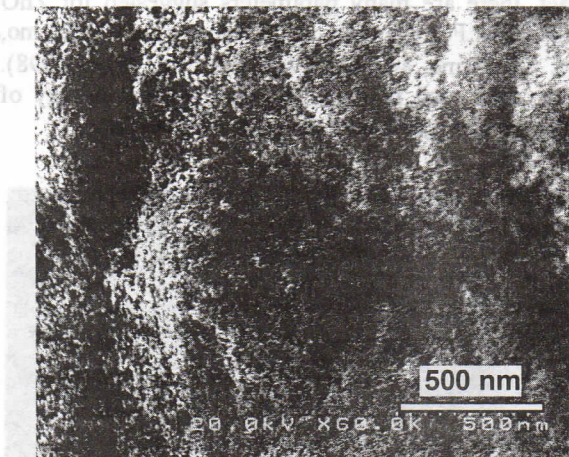


Figure 5. SEM picture of sample (a) prepared using PEG molecular weight of  $2 \times 10^4$ .

### Conclusion

The effect of polymer molecular weight on the luminescence properties of polymer electrolyte nanocomposites has been investigated using four molecular weights. The particle size tended to decrease with increasing the molecular weight. Reducing in the particles size increased the number concentration of particles, henceforth increases the luminescence intensity. The predicted particle sizes calculated using Warren-Scherer formula based on the XRD pattern, calculated using size dependent band gap based on the excitation spectra were comparable with the data given by TEM picture.

### References

- Lin, F.C., Takao, Y., Shimizu, Y., and Egashira, M., (1995), "Hydrogen-sensing mechanism of zinc oxide varistor gas sensors", *Sens. Actuators B* 25, pp. 843.
- Ramachalam, M.S., Rohatgi, A., Carter, W.B., Shaffer, J.P., and T.K. Gupta, T.K., (1995), "Photoluminescence Study of ZnO Varistor Stability", *J. Electron. Mater.* 24, pp. 413.
- Vanheusden, K., Seager, C.H., Warren, W.L., Tallant, D.R., and Voigt, J.A., (1996), "Correlation between photoluminescence and oxygen vacancies in ZnO phosphors", *Appl. Phys. Lett.* 68, pp. 403.
- Nanto, H., Minami, T., and Takata, S., (1981), "Photoluminescence in Sputtered ZnO Thin Films", *Phys. Status Solidi (a)* 65, pp. K131.

K. S. Weissenrieder K.S. and J. Muller, J., (1997), "Conductivity model for sputtered ZnO-thin film gas sensors", *Thin Solid Films*, 300, pp. 30.

Muller J. and Weissenrieder, K.S., (1994), "ZnO-Thin Film Chemical Sensors", *J. Anal. Chem.* 349, pp. 380.

Izaki M. and Omi, T., (1996), "Transparent zinc oxide films prepared by electrochemical reaction", *Appl. Phys. Lett.* 68, pp. 2439.

Tang, Z.K., Wong, G.K.L., Yu, P., Kawasaki, M., Ohtomo, A., Koinuma, H., and Segawa, Y., (1998), "Room-temperature ultraviolet laser emission from self-assembled ZnO microcrystallite thin films", *Appl. Phys. Lett.* 72, pp. 3270.

van Dijken, A., Meulenkaamp, E.A., Vanmaekelbergh, D., and Meijerink, A., (2000), "Identification of the transition responsible for the visible emission in ZnO using quantum size effects", *J. Lumin.* 90, pp. 123.

Rajalakshmi, M., Arora, A.K., Bendre, B.S., and Mahamuni, S., (2000), "Optical phonon confinement in zinc oxide nanoparticles", *J. Appl. Phys.* 87, pp. 2445.

Mikrajuddin, Lenggoro, I.W., Okuyama, K., and Shi, F.G., (2002), "Luminescent polymer electrolytes prepared by growing ZnO nanoparticles in the matrix of polyethylene glycol", *J. Electrochem. Soc.* 149, pp. H147.

Abdullah, M., Lenggoro, I.W., Okuyama, K., and Shi, F.G., (2003), "In-Situ Synthesis of Polymer Nanocomposite Electrolytes Emitting a High Luminescence with a Tunable Wavelength", *J. Phys. Chem. B*, 107, pp. 1957.

Abdullah, M., Lenggoro, I.W., and Okuyama, K., "Polymer Electrolyte Nanocomposites", will appear in *Encyclopedia of Nanoscience and Nanotechnology*, American Scientific Publisher, California.

Spanhel, L. and Anderson, M.A., (1991), "Semiconductor Clusters in the Sol-Gel Process: Quantized Aggregation, Gelation, and Crystal Growth in Concentrated ZnO Colloids", *J. Am. Chem. Soc.* 113, pp. 2826.

J. C. Bailar, A.F. Trotman-Dickenson, H.J. Emeleus, and S. R. Nyholm (Eds), (1973), *Comprehensive Inorganic Chemistry*, Vol. 3, 1st ed., Pergamon, Oxford.

Mikrajuddin, Iskandar, F., Shi, F.G., and Okuyama, K., (2001), "Stable Photoluminescence of Zinc Oxide Quantum Dots in Silica Nanoparticles Matrix Prepared by the Combined Sol-Gel and Spray Drying Method", *J. Appl. Phys.*, 89, pp. 6431; Mikrajuddin, Iskandar, F., and Okuyama, K., (July 5-6, 2001), "Powder Composite of ZnO/SiO<sub>2</sub> Nanoparticles with Stable Photoluminescence", *Int. Symp.*

*Nanoparticles: Aerosols and Materials*, July 5-6, 2001, Pusan, Korea.

E. F. Kaelble (Ed.), (1967), *Handbook of X-rays*, McGraw-Hill, New York.

Enright, B. and Fitzmaurice, D., (1996), "Spectroscopic Determination of Electron and Hole Effective Masses in Nanocrystalline Semiconductor Films", *J. Phys. Chem.* 100, pp. 1027.

Yu, P.Y. and Cardona, M., (1996), "*Fundamentals of Semiconductors*", Springer-Verlag, Berlin/Heidelberg, pp. 272.

Monticone, S., Tufeu, R., and Kanaev, A.V., (1998), "Complex Nature of the UV and Visible Fluorescence of Colloidal ZnO Nanoparticles", *J. Phys. Chem. B* 102, pp. 2854.

Abdullah, M., Morimoto, T., and Okuyama, K., "Generating blue and red luminescence from ZnO/polyethylene glycol nanocomposites prepared by in-situ method", *Adv. Func. Mater.*, in press