



## Polychromatic Source Excitable and Enhanced Green Photoluminescence of ZnO Nanoparticles Dispersed in High Molecular Weight Polymer Matrix

Mikrajuddin

Department of Physics, Bandung Institute of Technology  
Jl. Ganesa 10 Bandung 40132, Indonesia

**Abstract.** Composite of zinc oxide (ZnO) nanoparticles in polyethylene glycol (PEG) has been produced by mixing the as prepared ZnO colloid with a solution of PEG in ethanol. ZnO colloid was produced by hydrolyzing zinc acetate in ethanol solution. The produced composite exhibits a wide band excitation spectra compared to ZnO colloid to allow the excitation using a wide range excitation wavelength for producing high green luminescence intensity. Since ZnO nanoparticles were trapped in a matrix of polymer (solid phase) no further growing as well as agglomeration process took place (as observed in ZnO colloid) so that the shape and positions of excitation and luminescence spectra were time independent. Heating the prepared composite results an increase in the luminescence intensity due the increase in the ZnO nanoparticles concentration in the heated composites.

**Keywords:** *excitation spectra, luminescence spectra, polyethylene glycol, zinc oxide colloid, zinc oxide nanoparticles*

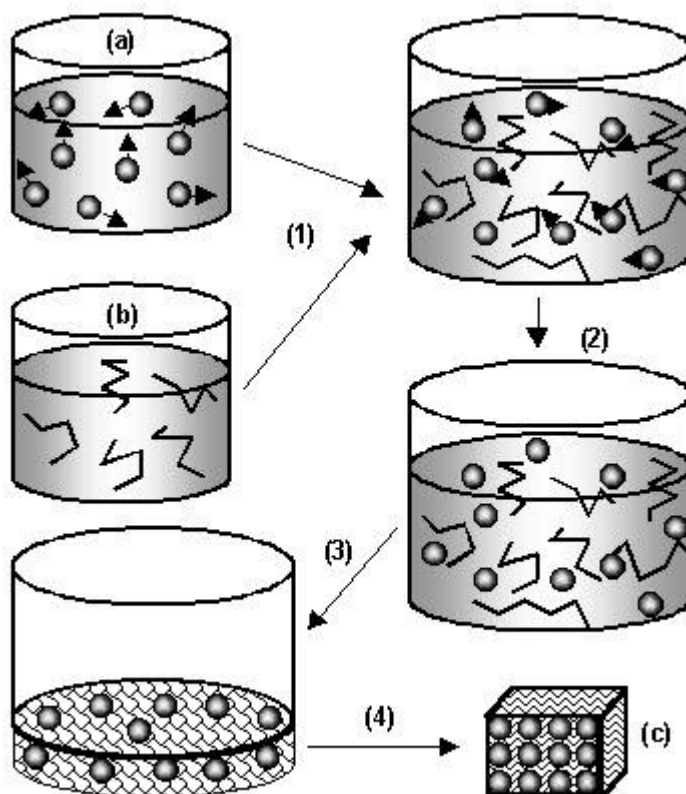
### 1. Introduction

As a wide gap semiconductor, ZnO has potential applications as a transparent electrode<sup>[1]</sup> for photovoltaic and electroluminescent devices and as a promising material for ultraviolet light emitting devices.<sup>[2]</sup> It presents interesting optical, acoustical and electrical properties which meet wide applications in the field of electronic,<sup>[3,4]</sup> optoelectronic,<sup>[5,6]</sup> and sensor.<sup>[3,7,8]</sup> ZnO nanoparticles are now being extensively investigated by a lot of researchers for nanotechnology applications. It exhibits a strong

luminescence at 500 nm, which is understood in term of electron transition from conduction band edge to a trap state located around the center of gap.<sup>[9]</sup>

Among several methods for preparation ZnO nanoparticles, a sol-gel process is relatively simple.<sup>[10]</sup> It allows the production of a large amount of ZnO colloid with particle size around 3 nm within a few minutes. However, the fresh colloid that exhibited a prominent PL peak at around 500 nm, suffered a significant red shift caused by increase in cluster size when aged over several days.<sup>[10,11]</sup> A shift from 500 nm to 560 nm was observed when the colloid is aged over a few days.<sup>[10]</sup> The excitation source wavelength must be carefully selected since the excitation spectra is very narrow, i.e., the width at half maximum (WHM) is only around 10 nm. It creates a serious problem if only a fixed wavelength or non-monochromic sources are available. Finally, the concentration of ZnO nanoparticles in colloid must be very low to avoid a rapid crystalline growth due to agglomeration that can make the quantum properties of the ZnO particles disappear quickly. Therefore, the “quantum” luminescence intensity of ZnO in colloid is usually very low.

Here we report an approach to overcome the above mentioned problems as illustrated in Fig. 1. (1) An as growing ZnO colloid consisting of precursor solution and ZnO nanoparticles performing a Brownian motion was mixed with a solution of high molecular weight polymer (HMWP). The mixing process reduced the Brownian motion of nanoparticles since nanoparticles were trapped between polymer chains. It then lowered the probability of nanoparticles collisions to form agglomerates. As an HMWP, we used polyethylene glycol (PEG) 20,000. (2) At a certain time after mixing, the mixture was put in an ice bath. (3) The mixture was then washed and filtered. (4) The filtrant was dried to produce a concentrated ZnO nanoparticles distributed in solid polymer matrix.



**Figure 1.** Schematic of sample preparation: (1) mixing of as grown colloid (a) with a solution of HMWP (b); (2) Cooling the mixture in an ice bath; (3) washing and removing the solvent; (4) drying in oven to produce solid composite (c).

This approach revealed several advantages. (1) It allowed the extraction of ZnO nanoparticles from the solvent easily by filtering. Since the size of ZnO nanoparticles produced by this method was less than 5 nm (diameter), it was difficult to extract such particles by simple filtering methods since the pore sizes of filter were relatively larger compared to particle sizes (usually in submicrometer or higher). By trapping the particles in the polymer, the extraction of particles became easier by simply filtering

the polymer. (2) Since the polymer volume was very low compared to that of solvent in ZnO colloid, the concentration of particles redistributed in polymer after drying the filtrant was higher than in the colloid. Thus, for equal volume, the PL intensity of ZnO/polymer was higher than that of colloid. (3) Since polymer was solid at room temperature, the particles were stable in their positions in polymer matrix to exhibit a time independent PL spectra, in the contrary to the ZnO colloid that showed a significant red shift by aging. (4) PEG is relatively simpler for further processing, such as the melting point is relatively low, dissolves in water, can be used to form thin film, and so on. (5) We also identified that mixing of as growing colloid with HMWP disturbed the growing process of ZnO nanoparticles to lead to the broadening of size distribution. As a result, a broad excitation peak that allowed the use of even polychromatic excitation source was obtained. Although there are a number of reports on the growing of nanoparticles in polymer matrix,<sup>[12-15]</sup> however, in our knowledge, similar report on the dispersing of ZnO nanoparticles in HMWP was not available, in particular that relates to the enhancement of PL intensity and producing polychromatic source excitable ZnO composites. This approach is also potential for producing luminescent polymer electrolyte nanocomposites.<sup>[16-21]</sup>

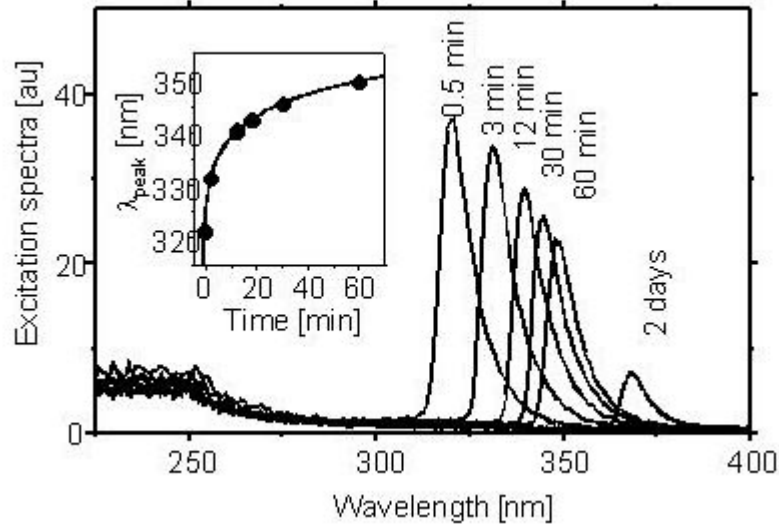
## 2. Experiment

Materials used in this experiments were Zinc Acetate Dihydrate,  $(\text{CH}_3\text{COO})_2\text{Zn}\cdot 2\text{H}_2\text{O}$ , Lithium Hydroxide Monohydrate,  $\text{LiOH}\cdot \text{H}_2\text{O}$  and Polyethylene Glycol (PEG),  $\text{H}(\text{OCH}_2\text{CH}_2)_n\text{OH}$  from Wako Pure Chemicals, and Ethanol (99.5%) from Kanto Chemicals. All chemicals were used as received. The production of ZnO colloid is similar to that reported elsewhere.<sup>[11]</sup> An amount of 4.39 g  $(\text{CH}_3\text{COO})_2\text{Zn}\cdot 2\text{H}_2\text{O}$  was put in 200 mL of ethanol and heated under stirring in distillation equipment at temperature of 80 °C to result about 120 mL of condensate and 80 mL of hygroscopic solution. The time required was around 3 hours.  $\text{LiOH}\cdot \text{H}_2\text{O}$  1.176 g was put in 120 mL ethanol and stirred tens of minutes until all granular dissolved. PEG (Mw = 20,000) 8 g was put in 100 mL of ethanol and then heated several minutes under stirring at temperature around 60 °C until all meshes dissolved. Hygroscopic solution of  $(\text{CH}_3\text{COO})_2\text{Zn}\cdot 2\text{H}_2\text{O}$  4 mL was mixed with 6 mL of  $\text{LiOH}\cdot \text{H}_2\text{O}$  solution and shacked at a certain time. This mixture

(contains growing ZnO nanoparticles) was then mixed with solution of PEG, kept at temperature around 40 °C and shaken around 30 seconds, after that put in ice bath. The mixture transformed into solid state as the temperature went down below the room temperature. Ethanol 90 mL was then added into the solid mixture to result 100 mL mixture. This mixture was then filtered. Then filtrant from the first filtering process was washed with 100 mL ethanol and filtered again to remove the rest precursor materials. The second filtrant was dried at 40 °C under atmospheric condition and air environment during 12 hours. Another colloid of ZnO as comparison was also made by mixing 8 mL hygroscopic solution of  $(\text{CH}_3\text{COO})_2\text{Zn} \cdot 2\text{H}_2\text{O}$  and 12 mL  $\text{LiOH} \cdot \text{H}_2\text{O}$  solution. Luminescence spectra were observed at room temperature using Shimadzu RF-5300PC Spectrophotometer with a Xenon laser source.

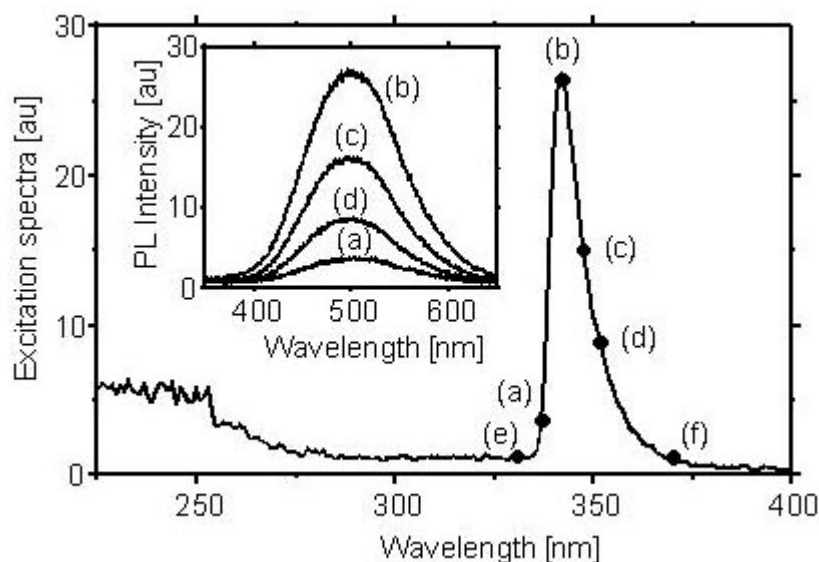
### 3. Results and Discussion

Figure 2 shows the time dependent excitation spectra of ZnO colloid (0.1 M) detected at a wavelength of 500 nm. It shifted quickly towards long wavelengths region as the aging period increased. The time dependent excitation spectra peak position displayed in the figure inset could be well fitted with  $\lambda_{\text{peak}} = 325t^{0.0176}$  nm, where  $t$  is in minute.<sup>[20]</sup> Interband transition of electrons from valence band to conduction band resulted this spectrum. The red shift indicated the decrease in the band gap opening as time increased, caused by a growing process of nanocrystallites.<sup>[9-11]</sup> By assuming the total spectra was a superposition of excitation spectra of individual particles and since the total spectra was very narrow, one expected the particle sizes were nearly monodisperse.



**Figure 2.** Time dependence of excitation spectra of ZnO colloid detected at 500 nm. Inset is the time dependence of the position of the peak of excitation spectra both in linear and logarithmic scale. Those observed data can be well fitted using a relation  $\lambda_{\text{peak}} = 325 t^{0.0176}$  [nm] with  $t$  is denoted in minutes.

Careful selection of the excitation source wavelength must be done to generate high PL intensities because the width of ZnO colloid excitation spectra was very narrow. This problem has paid a little attention from the previous reports, in which a fixed excitation wavelength was used to generate PL spectra of ZnO colloids, independent of aging periods.<sup>[9,10]</sup> Only excitation source wavelength equal to the peak of excitation spectra generates a maximum PL intensity. The WHM of ZnO colloid excitation spectra is generally less than 10 nm. Excitation source wavelength outside this range produces only weak PL intensities. As shown in Fig. 3, various excitation wavelengths were used for ZnO colloid aged over 18 minutes. The corresponding PL spectra are displayed in the figure inset. It is clear that the PL intensities using a source wavelength outside this range such as (e) and (f) are very weak (almost not observable).

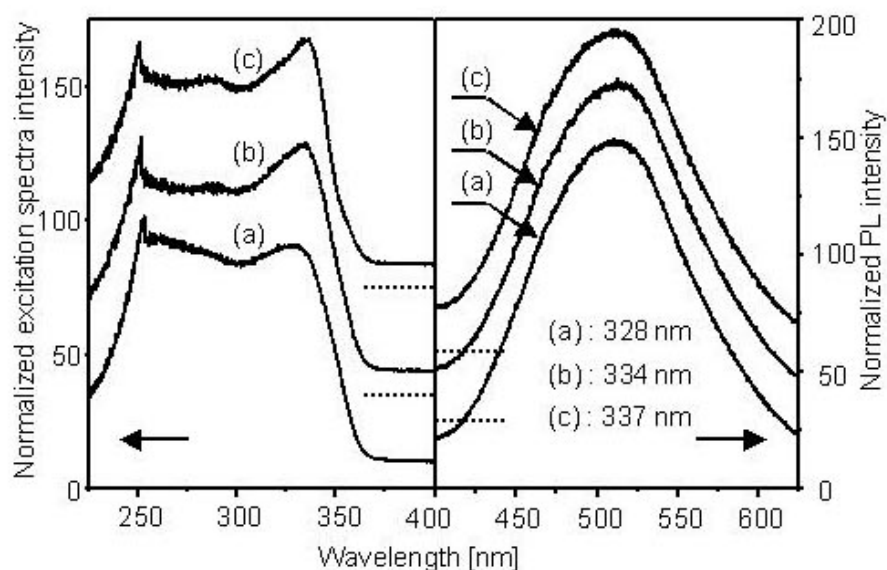


**Figure 3.** Excitation spectra of 18 minutes aged colloid detected at 500 nm. Inset is the photoluminescence spectra of the corresponding colloid using some excitation wavelengths around the peak of excitation spectra (denoted by symbols in the plot of excitation spectra).

The WHM of a PL spectra excited using a source wavelength equal to the peak of excitation spectra was around 120 nm. The shift of the PL spectra position during aging over several hours was only about 40 nm so that, we can say all the PL spectra almost coincided, at least visually. Henceforth, one observed no significant color change when the colloid was excited using different excitation source wavelength during aging over several hours. Indeed, we observed visually the green PL only shifted from near blue to near yellow when aged over several hours.

If the ZnO colloid aged over a certain period was excited using a wide band UV source, only spectrum related to its excitation spectra was absorbed to generate the PL spectra. If ZnO colloid with different aged period were mixed and assumed that the sizes of particles were not changed by mixing and the mixture was then excited using a wide band UV source,

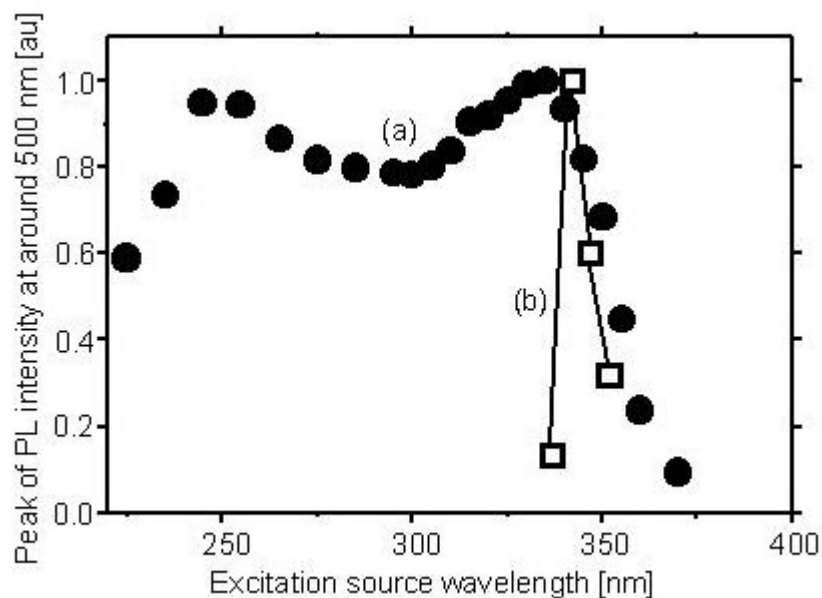
each component would absorb the spectrum related to their own excitation spectra. Since the PL spectra of all aged colloids almost coincided (almost same in color), one obtained an almost additional PL intensity contributed by those components. This technique allowed to obtaining a wide band UV (polychromatic) excitable ZnO composite.



**Figure 4.** Left: the excitation spectra of samples: (a) **A**, (b) **B**, and (c) **C** detected at 500 nm. Right: the PL spectra of samples: (a) **A**, (b) **B**, and (c) **C** using excitation wavelengths corresponding to the peak of their excitation spectra, i.e. 328 nm, 334 nm, and 337 nm for samples **A**, **B**, and **C**, respectively.

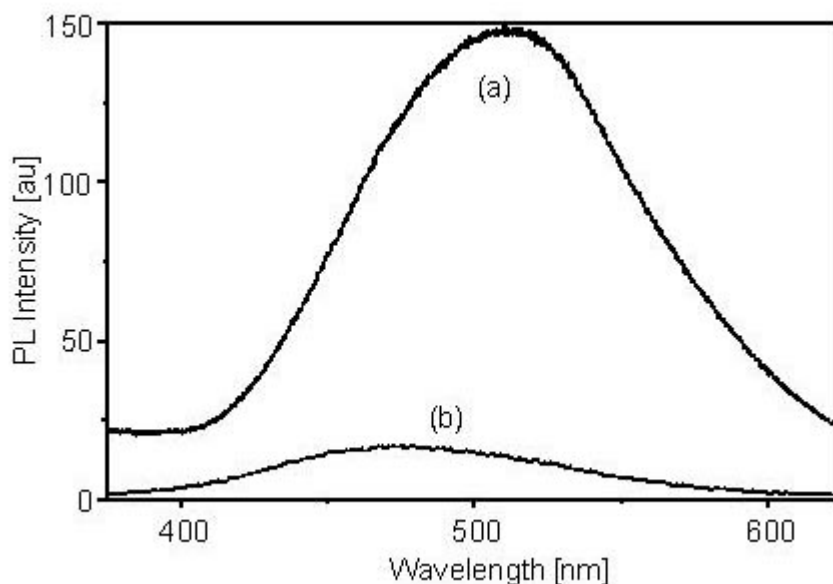
Obtaining a mixed ZnO colloid from components having different aged periods is equivalent to obtaining ZnO colloid with a broad size distribution. This can be realized by mixing ZnO colloid with a PEG solution. Instead of water, we used ethanol as solvent for PEG to avoid any mismatching with solvent in colloid that might affect the PL properties of ZnO nanoparticles. Although this polymer does not dissolve in ethanol at low temperatures, it dissolves in ethanol at temperatures above 50 °C

(forming gel-like mixture). Fortunately we also found that the mixture transformed suddenly into solid state as temperature went below room temperature. The combination of mixture solidification and cooling process greatly reduce further growing process due to the decrease in Brownian motion and chemical reaction rates.



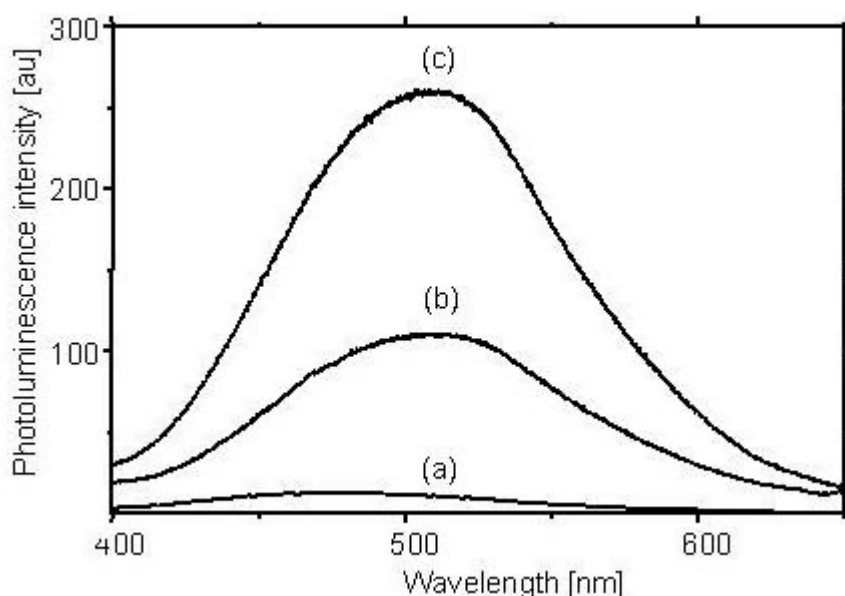
**Figure 5.** The dependence of the peak of photoluminescence spectra on the excitation wavelength for : (a) sample A and (b) 18 minutes aged colloid.

Figure 4 shows the excitation and PL spectra of samples prepared by mixing ZnO colloid aged over: (A) 30 second, (B) 12 minutes, and (C) 1 hour with PEG solution. The peaks of PL spectra are located at around 500 nm, with a bit red shift for long aged colloids. The peak of excitation spectra is broader than for colloids.



**Figure 6.** Photoluminescence spectra of (a) sample **A** excited using a wavelength of 328 nm and (b) 70 second aged colloid excited using a wavelength of 321 nm.

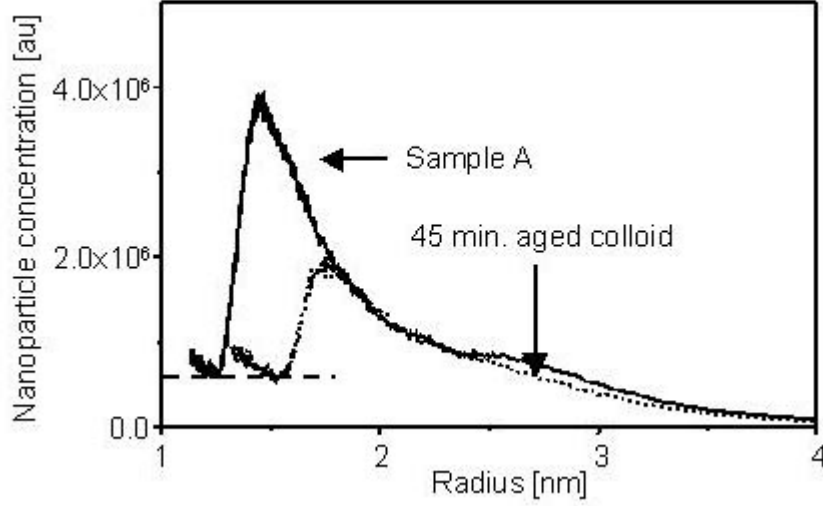
Figure 5 displays the excitation wavelength dependent of the 500 nm PL of sample **A**. Similar data for 18 minutes aged ZnO colloid is also displayed as comparison. For sample **A**, the width of excitation spectra is very wide. The sample was excitable with a source wavelength spreading from about 225 nm to 350 nm (around 125 nm range) with the peak of PL intensity above 50% of the largest one. It means that the composite was excitable even using a polychromatic UV source. In the contrary, the PL intensity above 50% of the largest one of the ZnO colloid was excitable only in the range of about 10 nm, so that the use of monochromatic excitation source was essential.



**Figure 7.** Effect of heating on the photoluminescence intensity of sample **A**: (a) the luminescence of 70 second aged colloid as comparison, (b) the luminescence of sample **A** before heating and (b) the luminescence of sample **A** after heating.

Figure 6 compares the PL spectra intensities of sample **A** and 70 seconds aged colloid. The colloid was placed in a glass bottle, while the sample was placed in a dark. The excitation beam cross sections on the colloid and sample **A** were almost similar. The PL intensity of ZnO in polymer was around five times larger than in colloid. This indicated the density of ZnO particles in the polymer was greater than in the colloid. The dried sample looked like a porous material. When it was heated until melt and then cooled, it became denser since several pores found in unheated sample were removed. The total volume of sample was then reduced such that the density of ZnO particles increased. The PL intensity of heated samples was around 2.5 of that of unheated samples as displayed in Fig. 7. There were other reports on the enhancement of PL intensity of ZnO nanoparticles such as Excimer laser irradiation of a sol-gel-derived precursor,<sup>[22]</sup> doping with terbium,<sup>[23]</sup> and heat treatment at high

temperatures.<sup>[24]</sup> Our approach, however, seemed to be relatively simpler and processable at low temperatures and allowing the total enhancement of PL intensity around 12 times.



**Figure 8.** The calculated size distribution of nanoparticles in sample A and in 45 minutes aged colloid. Sample A was excited using wavelength of 253 nm, while the 45 min. aged colloid was excited using wavelength of 240 nm.

We observed no change in the excitation as well as the PL spectra of sample A after aged over 3 weeks, in the contrary with that observed in ZnO colloid.<sup>[10,11]</sup> This indicated that the dispersion of ZnO nanoparticles in polymer matrix stabilized the luminescence spectra of ZnO nanoparticles. This result has a significant technological implications such as for producing ZnO based fixed color displays or fluorescent biological labels.<sup>[25]</sup>

Size distribution of ZnO nanoparticles can be predicted by measuring their UV luminescence,<sup>[11]</sup> besides the common method based on transmission electron micrograph picture. The PL intensity can be expressed as

$$I_{PL} = \int W_{exc}(R) W_{PL}(\lambda, R) f(R) dR \quad [1]$$

where  $W_{exc}(R)$ ,  $W_{PL}(\lambda, R)$ , and  $f(R)$  are the excitation and fluorescence efficiencies and size distribution function, respectively.<sup>[11]</sup> In the case when  $m_h/m_e \leq 1.9$ ,  $1 \leq R/a_B \leq 5$ , with  $m_h^*$ ,  $m_e^*$ , and  $a_B$  are effective mass of hole, electron, and Bohr radius one can approximate

$$f(R) \propto I_{PL}(\lambda) \frac{1}{R} \left| \frac{d\lambda}{dR} \right| \quad [2]$$

Size dependence of  $\lambda$  is given by  $hc/\lambda = E_g + h^2/8\mu R^2 - 1.8e^2/4\kappa\epsilon_0 R$ , with  $E_g$  the band gap of bulk ZnO,  $h$  the Planck constant,  $1/\mu = 1/m_e^* + 1/m_h^*$ ,  $e$  the elementary charge, and  $\kappa$  the dielectric constant of ZnO.<sup>[9]</sup> For ZnO,  $m_e^* = 0.24m_e$ , and  $m_h^* = 0.45m_e$  were commonly used so that  $m_h^*/m_e^* = 1.88$ .<sup>[11]</sup> There is also another report on the effective masses of electron and hole, i.e.,  $m_e^* = 0.28m_e$ ,  $m_h^* = 0.50m_e$  so that  $m_h^*/m_e^* = 1.79$ .<sup>[9]</sup> However, this ratio is also  $\leq 1.9$ . The dielectric constant of ZnO is  $\kappa = 3.7$  and the Bohr radius is  $a_B = 1.25$  nm.<sup>[11]</sup> Thus, all conditions for applying equations [1] and [2] are satisfied by ZnO nanoparticles investigated here. We excited sample **A** using a wavelength of 253 nm and the 45 minutes aged colloid with a wavelength of 240 nm in order to generate UV luminescence. Figure 8 shows the size distribution of ZnO nanoparticles in sample **A** and in colloid aged over 45 minutes. We rescaled the height of curves to equalize the background levels (indicated by dashed horizontal line). It is clear that the concentration of particles in polymer is higher than in colloid as explain previously. It is also displayed that particle distribution in polymer is broader than in colloid such that able to receive wide band UV source to generate PL spectra, as also described previously. The average diameter of ZnO nanoparticles in sample **A** is around 3 nm, while in 45 minutes aged colloid is around 3.5 nm. This size is similar to that reported previously based on TEM picture<sup>[10]</sup> or XRD pattern.<sup>[26]</sup>

Our results provide several technological implications. One big problem faced by previous investigators is how to increase the concentration of nanoparticles without production another implication on the size distribution and luminescence spectra. The increase in particle concentration is hoped to increase photoluminescence intensity. Using the

present approach we proved that stable and high luminescence intensity of ZnO nanoparticles dispersed in polymer can be obtained.

#### 4. Conclusion

We have produced ZnO/HMWP composites by mixing the as prepared ZnO colloid with a solution of polyethylene glycol. The time independence of excitation as well as luminescence spectra were observed in the produced composite. Using the present approach we proved that stable and high luminescence intensity of ZnO nanoparticles dispersed in polymer can be obtained. In addition, using this approach, one can excite the ZnO nanoparticles composites to generate high luminescence intensity by just using a cheap fixed wavelength UV source or a polychromatic UV source, instead of strictly controlled UV source as usually used to generate photoluminescence of colloid. Finally, because ZnO nanoparticles are dispersed in PEG that has low melting point and good solubility in aqueous solution we can perform further processing easily depending on the field of applications.

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