# Synthesis of a stable sol of ZnO nanoparticles by low-temperature heating of Zn(OH)<sub>2</sub> in ethylene glycol containing Zn<sup>2+</sup> ions

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Stable sols with a homogeneous dispersion of ZnO nanoparticles were prepared by heating zinc hydroxide  $(Zn(OH)_2)$  precipitate in an ethylene glycol solution of zinc nitrate hexahydrate  $(Zn(NO_3)_2 \cdot 6H_2O)$  at 308 K. The formation of ZnO nanoparticles occurred within 1 h when the mixed solution of Zn(OH)\_2 precipitate and 0.05 mol/L of the ethylene glycol solution of zinc nitrate hydrate was heated at 308 K. The obtained sol was homogeneous, and no aggregation of the ZnO nanoparticles was observed. The formation process of ZnO nanoparticles in the mixed solution of Zn(OH)\_2 and the 0.05 mol/L ethylene glycol solution of zinc nitrate hexahydrate was examined by measuring changes in the UV–VIS spectra of the obtained sol and the XRD patterns of the particles separated from the sol. Strong absorption due to the electron transition between the band gap of ZnO appeared during heating at 308 K for 1 h. When the heating time decreased, the shift in the absorption edge to a shorter wavelength was observed. This shift in the absorption edge would be related to changes in the particle size during the formation process of ZnO nanoparticles. Furthermore, the photoluminescence spectra of the obtained ZnO nanoparticles were examined. The intensity of photoluminescence increased with increases in the concentrations of zinc nitrate hydrate in the ethylene glycol solution.

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#### 1. Introduction

Zinc oxide (ZnO) is an important oxide semiconductor due to its wide band gap and large exciton binding energy. The optical and electrical properties of ZnO have been applied to various devices such as the electrodes of dye-sensitized solar cells, gas sensors, and short-wavelength photonic devices.<sup>1)-3)</sup> Furthermore, the photoluminescent characteristics of ZnO particles have been intensively investigated in order to develop highly efficient EL and LED devices.<sup>4),5)</sup> These characteristics of ZnO particles greatly depend on the defect structure in the ZnO lattice.<sup>6)</sup> For example, the oxygen vacancies in the ZnO lattice produce donor levels with electrons functioning as carriers. It is considered that the presence of interstitial Zn atoms and oxygen vacancies is related to the photoluminescent characteristics.<sup>7)-9)</sup> The effects of lattice defects on the ZnO nanoparticle surface on the optical and electrical characteristics become more important as the size of the ZnO nanoparticles decreases. The band gap energy of ZnO nanoparticles whose particle size is less than 20 nm depends on their particle size.<sup>10</sup> This dependence is known as the quantum size effect. Accordingly, in order to regulate the characteristics of ZnO particles, the development of ZnO nanoparticle preparation methods and the control of particle size are very important issues. Moreover, the ZnO nanoparticles can be used for ZnO film preparation as a source of coating solution.

Various methods for preparing ZnO nanoparticles have been reported. In particular, solution processes have been intensively investigated since they are environmentally friendly. Leung et al. have prepared ZnO nanorods by heating a mixed solution of zinc

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nitrate and hexamethylenetetraine at 323 K.<sup>11</sup>) Uthirakumar et al. have obtained nanocrystalline ZnO particles by heating the methanol solution of zinc acetate hydrate at 333 K for 10 h.<sup>12</sup>) Koshizaki et al. prepared the sol with ZnO nanoparticles using pulsed laser ablation in aqueous solution.<sup>13</sup>) The solution processes can be carried out at low temperature, and the reaction conditions are environmentally friendly. They therefore have many advantages as compared with other vapor deposition processes and physical processes. The solution processes are suitable for preparing a stable sol with a dispersion of ZnO nanoparticles that can be used for preparing thin ZnO films.

The authors have reported that zinc hydroxide  $(Zn(OH)_2)$  is a good precursor for synthesis of zinc compounds using the solution process. For example, we have shown that the heating of zinc hydroxide Zn(OH)<sub>2</sub> in hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) aqueous solution at 348 K for 2 h forms a stable sol with dispersion of zinc peroxide (ZnO<sub>2</sub>) nanoparticles.<sup>14),15)</sup> The authors have also reported that ZnO nanoparticles can be obtained by the heating of Zn(OH)<sub>2</sub> in ethylene glycol.<sup>16)</sup> In recent years, the development of a solution process for controlling the electrical and optical properties of ZnO nanoparticles has become very important. In the present study, the heat treatment of Zn(OH)<sub>2</sub> in ethylene glycol solution at low temperatures near room temperature was examined to obtain stable sols with a dispersion of ZnO nanoparticles. This low-temperature heating process of Zn(OH)2 is very simple since it only involves keeping solutions at constant temperature. The simple low-temperature preparation method of ZnO nanoparticles with photoluminescent (PL) characteristics by heating Zn(OH)2 in ethylene glycol containing Zn(NO3)2·6H2O was examined. The details of the formation process of the ZnO nanoparticles were also investigated.

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# 2. Experiments

# 2.1 Preparation of ZnO nanoparticles

The ZnO nanoparticles were prepared as follows: One hundred milliliters of NH3 aqueous solution (0.1 mol/L) was added to 100 ml of an aqueous solution (0.1 mol/ L) of Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O. The obtained Zn(OH)<sub>2</sub> precipitate was then separated by centrifugation at 3000 rpm. for 5 min. The obtained Zn(OH)<sub>2</sub> was dispersed into distilled water and was again separated by a centrifuge. This procedure was repeated 3 times, and the coexisting and adsorbed ammonium ions and nitrate ions in the precipitate were removed. The average molar ratio of the obtained Zn(OH)2 precipitate against Zn(NO<sub>3</sub>)<sub>2</sub> in the precursor solution was 0.55. Hereinafter, this Zn(OH)<sub>2</sub> precipitate is referred to as "Zn(OH)<sub>2</sub>-P". All of the obtained Zn(OH)<sub>2</sub> precipitate (Zn(OH)<sub>2</sub>-P) was then dispersed in 100 mL of ethylene glycol, and a mixture of the Zn(OH)<sub>2</sub>-P and ethylene glycol was obtained. The mixture was an opaque solution and was heated at 308 K for 24 h in a closed Pyrex glass vessel. After the heating process, a homogeneous stable sol without precipitate was obtained, and the average concentration of ZnO in the sol was 0.055 mol/L.

In order to control the characteristics of the ZnO nanoparticles, another synthetic process was examined. An ethylene glycol solution of zinc nitrate hydrate (Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O) was prepared, and the concentrations of zinc nitrate hydrate in the ethylene glycol solution ranged from 0 mol/L to 0.1 mol/L. All of the Zn(OH)<sub>2</sub> precipitate (Zn(OH)<sub>2</sub>–P) obtained by the same synthetic process described in the previous paragraph was dispersed into the ethylene glycol solution of zinc nitrate hydrate. The mixed solution was then heated at 308 K for 24 h so that the homogeneous sol without precipitates was also obtained. Hereinafter, the obtained sol is referred as "Z–Sol–[Zn<sup>2+</sup>] in the used ethylene glycol solution". For example, when the Zn(OH)<sub>2</sub>–P was dispersed into the 0.01 M ethylene glycol solution of zinc nitrate hydrate and heated at 308 K for 24 h, we refer to the obtained sol as Z–Sol–0.01 mol/L.

The particles in the obtained sol (Z-Sol) were homogeneously dispersed, and the precipitation did not form easily. Therefore, to separate the particles from the sol, 100 mL of 0.1 mol/L NH<sub>3</sub> aqueous solution was added to the sol (Z-Sol). The ZnO nanoparticles in the Z-Sol were aggregated and precipitated. When 100 mL of 0.1 mol/L NH<sub>3</sub> aqueous solution was added to the 100 mL of 0.1 mol/L ethylene glycol solution of zinc nitrate hydrate, no precipitation occurred. Accordingly, in the case that 0.1 mol/ L NH<sub>3</sub> aqueous solution was added to the Z–Sol, the precipitates were the particles in the Z-Sol. The obtained precipitate was then separated by centrifugation at 3000 rpm for 5 min, and the precipitate was dried at 348 K for 12 h. Hereinafter, the particles in the dried precipitates are referred as "Z-Par-[Zn<sup>2+</sup>] in the used ethylene glycol solution". Preparation of the solutions in for all the synthetic processes was carried out in a room where the temperature was 298 K. All of the chemicals used in this preparation were of reagent grade (Wako Pure Chemical Industries, Ltd.).

#### 2.2 Characterization

The structure of the obtained powder (Z–Par) was characterized by X-ray diffraction (XRD) (Cu K $\alpha$  40 kV, 100 mA, MXP– 18, Bruker AXS K. K.). The particle shape was observed by field emission scanning electron microscopy (FE–SEM : JSM–6330, JEOL Ltd.) after Os coating. The ultraviolet-visible (UV–VIS) spectra of the obtained ZnO sol (Z–Sol) were measured with a wavelength range from 300 nm to 800 nm (JASCO Co., U– best210). In order to investigate the formation process of ZnO nanoparticles in the mixed solution of the Zn(OH)<sub>2</sub>–P and ethylene glycol solution of zinc nitrate hydrate, the dependence of the UV–VIS absorption spectra of the solution on the heating time was examined. The temperature of the mixed solution of Zn(OH)<sub>2</sub>–P and ethylene glycol solution of zinc nitrate hydrate was kept at 308 K, and 1.0 mL of the mixed solution was isolated from the solution once every hour and poured into a quartz glass cell to measure the UV–VIS absorption spectrum. The photoluminescence spectra were measured using a Shimadzu Co., RF– 5300PC photoluminescence spectrometer. The optical source was a Xe lamp (150 W), and the band width of the excitation beam was 3.0 nm. Raman spectroscopy (JASCO NRS1000) was also used to characterize the ZnO nanoparticles.

#### 3. Results and discussion

# 3.1 Characterization of ZnO nanoparticles obtained by heating Zn(OH)<sub>2</sub> in ethylene glycol solution of zinc nitrate hydrate

Figure 1 shows the XRD patterns of the particles (Z-Par) prepared by drying the precipitates formed by mixing 100 mL of the Z-sol and 100 mL of 0.1 M NH<sub>3</sub> aqueous solution. All of the XRD peaks in Figs. 1(a), (b), and (c) can be assigned to the ZnO lattice. The precipitates (Z-Par) were formed by aggregation of the particles in the Z-Sol. The heating of Zn(OH)2-P in ethylene glycol at 308 K then resulted in the formation of ZnO particles. In order to estimate the crystallite size of the obtained ZnO particles,  $\beta \cos \theta$  was plotted against  $\sin \theta$ , where  $\beta$  is the net width of the diffraction peak at one-half its maximum height and  $\theta$  is the diffraction peak angle. The values of  $\theta$  and  $\beta$  of the diffraction peaks of the plane (1 0 0), (0 0 2), (1 0 1), (1 0 3), and (1 1 2) were used for the  $\sin\theta - \beta \cos\theta$  plots. The crystallite size was calculated from the intercept  $\varepsilon$  of the plot by using the equation 0.9  $\lambda \epsilon$ . When the concentrations of zinc nitrate hydrate in the ethylene glycol solution used for heating Zn(OH)2-P were 0 mol/ L, 0.01 mol/L, and 0.1 mol/L, the crystallite sizes of the Z-Par-0 mol/L, Z-Par-0.01 mol/L, and Z-Par-0.1 mol/L were 20 nm, 17 nm, and 14 nm, respectively. Thus, the crystallite size of the Z-Par decreased with increases in the zinc nitrate hydrate concentrations in the ethylene glycol solution. The Zn<sup>2+</sup> ions and NO<sub>3</sub><sup>-</sup> ions in the ethylene glycol affected the nucleation frequency of ZnO particle formation so that the crystallite size of each ZnO particle decreased. Furthermore, it is considered that the pH condition in the ethylene glycol solution also affected the nucleation frequency and the particle growth rate.

Figure 2 shows the FE-SEM images of the ZnO particles (Z-



Fig. 1. XRD patterns of the particles (Z–Par). The particles were: (a) Z–Par–0 mol/L, (b) Z–Par–0.01 mol/L, and (c) Z–Par–0.05 mol/L.

Par) obtained by heating  $Zn(OH)_2$  in the ethylene glycol solution of zinc nitrate hydrate at 308 K for 24 h. The average particle size of the ZnO particles shown in Fig. 2(a) was 21.2 nm. In the case that the  $Zn(OH)_2$ -P was heated in 0.05 mol/L of the ethylene glycol solution of zinc nitrate hydrate, the average diameter of the obtained ZnO nanoparticles (Z-Par-0.05 mol/L) was 15.1 nm. These average particles sizes almost agreed with the crystallite size calculated from the XRD peak width in Fig. 1. The average particle size depended on the concentrations of zinc nitrate hydrate in the ethylene glycol.

# 3.2 Formation process of ZnO nanoparticles when Zn(OH)<sub>2</sub> was heated in the ethylene glycol solution of zinc nitrate hydrate

We will first discuss the formation process of the ZnO nanoparticles in response to heating the Zn(OH)2-P in ethylene glycol alone. The XRD pattern of the particles (Z-Par) obtained by heating the Zn(OH)<sub>2</sub>-P in ethylene glycol at 308 K are shown in Fig. 3. Figure 3(a) shows the XRD pattern of the Zn(OH)<sub>2</sub>–P. In Fig. 3(a), the heating time was 0 h. There is no sharp peak, and the XRD pattern has a very broad peak between  $2\theta = 15^{\circ}$  and  $2\theta = 40^{\circ}$ . Accordingly, the Zn(OH)<sub>2</sub> precipitate (Zn(OH)<sub>2</sub>-P) without the heating treatment at 308 K was amorphous. The XRD patterns of the particles (Z-Par) obtained by heating the Zn(OH)<sub>2</sub>-P in ethylene glycol at 308 K for 2 h, 4 h, 6 h, 8 h, and 12 h are shown in Figs. 3(b), (c), (d), (e), and (f). When the heating time was 2 h and 4 h, the XRD patterns of the obtained powders also had a very broad peak in the range of  $2\theta$  from  $15^{\circ}$  and 40°, and no sharp diffraction peaks were observed, as shown in Fig. 3(b) and (c). Accordingly, the particles obtained by heating the Zn(OH)2-P in ethylene glycol for 2 h and 4 h also consisted of an amorphous phase. In contrast, the diffraction peaks in Figs. 3(d), (e), and (f) can be assigned to ZnO. In Fig. 3(d), the  $(1\ 0\ 0)$ peak intensity of the ZnO crystallite is compared with the intensity around  $2\theta = 27^{\circ}$  of the amorphous phase. According to this result, the obtained particles were likely a mixture of the amorphous phase and ZnO particles with some degree of crystallization when the heating time was 6 h. Furthermore, when the heating time was 8 h and 12 h, the intensities of the XRD peaks corresponding to ZnO were quite high as compared with the intensity of the amorphous phase. Accordingly, it can be concluded that a heating time of Zn(OH)2-P in ethylene glycol of more than 8 h is sufficient to obtain ZnO nanoparticles with crystallinity.

In order to examine the formation process of the ZnO nanoparticles, changes in the UV-VIS absorption spectra of the obtained sol (Z-Sol) with increases in the heating time were examined. The formation of a ZnO lattice can be identified by the appearance of strong optical absorption due to the electron transition between the band gap. Then, changes in the ZnO nanoparticle size can also be detected by measuring the shift in wavelength of the absorption edge due to the band gap transition. In many cases, an absorption spectrum with less wavelength dependence corresponded to a relatively muddy solution, and the scattering of light caused a decrease in the transparency and an increase in the value of absorbance. Figure 4 shows the UV-VIS absorption spectra of the sol obtained by heating the Zn(OH)2-P in ethylene glycol at 308 K. The optical absorption spectrum of ethylene glycol with the dispersion of the Zn(OH)<sub>2</sub>–P at 308 K before the heating at 308 K is shown in Fig. 4(a). In this spectrum, for which the heating time was 0 h, there is no strong absorption peak, as the XRD pattern shown in Fig. 3(a) indicates that the obtained particles were amorphous. The value of the optical absorption from 0.89 to 1.18 in the wavelength range



### 100nm

Fig. 2. FE–SEM images of the ZnO nanoparticles (Z–Par). The nanoparticles were : (a) Z–Par–0 mol/L and (b) Z–Par–0.05 mol/L.



Fig. 3. XRD patterns of the particles (Z–Par) that were prepared by drying the precipitates formed by mixing 100 mL of 0.1 M NH<sub>3</sub> aqueous solution and 100 mL of Z–Sol–0 mol/L. The heating times of the mixture of  $Zn(OH)_2$ –P and ethylene glycol were : (a) 0 h (Zn(OH)\_2–P), (b) 2 h, (c) 4 h, (d) 6 h, (e) 8 h, and (f) 12 h.



Fig. 4. UV–VIS absorption spectra of Z–Sol–0 mol/L obtained by heating  $Zn(OH)_2$ –P in ethylene glycol at 308 K. The heating times of the mixture of  $Zn(OH)_2$ –P and ethylene glycol were were: (a) 0 h, (b) 2 h, (c) 4 h, (d) 6 h, (e) 8 h, and (f) 12 h.

from 450 nm to 300 nm corresponded to the scattering of light. The optical absorption spectrum of ethylene glycol with dispersion of the  $Zn(OH)_2$ –P at 308 K for 2 h is shown in Fig. 4(b). In this spectrum, there is also no strong absorption peak. The value of the optical absorption from 0.91 to 1.22 in the wavelength range from 450 nm to 300 nm also corresponds to the scattering of light. The absorption spectrum shown in Fig. 4(c) also has no strong absorption peak due to the electron transition of the ZnO

band gap. This result is in agreement with the XRD pattern in Fig. 3(c). On the other hand, a strong absorption around 330 nm does appear in the absorption spectrum shown in Fig. 4(d). This strong absorption corresponded to the electron transition of the ZnO band gap, and the formation of ZnO nanoparticles did occur in response to heating the Zn(OH)2-P in ethylene glycol at 308 K for 6 h. Furthermore, as shown in Fig. 3(d), the XRD pattern of the particles obtained by heating for 6 h had XRD peaks that can be assigned to ZnO. The XRD result in Fig. 3 is in agreement with the results of the UV-VIS absorption spectra. Figures 4(e) and (f) show the UV-VIS absorption spectra of the sol obtained by heating the Zn(OH)<sub>2</sub>-P in ethylene glycol at 308 K for 8 h and 12 h, respectively. When the wavelength was larger than 320 nm, the optical absorption was increased with increases in the heating time. It is considered that this increase in absorbance corresponds to light scattering due to formation of the aggregated structure of ZnO nanoparticles. The formation of precipitate was also not observed. Therefore, aggregation of the ZnO nanoparticles occurred as well as ZnO nanoparticle formation when the heating time was more than 6 h.

The effect of the addition of zinc nitrate hydrate to the ethylene glycol solution on the dispersion of ZnO nanoparticles in the obtained sol was examined. The UV-VIS absorption spectra of the Z-Sol with a dispersion of ZnO nanoparticles are shown in Fig. 5. The UV-VIS absorption spectrum of the Z-Sol obtained by heating the Zn(OH)<sub>2</sub>-P in ethylene glycol without zinc nitrate hydrate is shown in Fig. 5(a). The value of optical absorbance ranged from 2.2 to 3.6 when the wavelength was from 300 nm to 450 nm. In this case, the obtained solution was an opaque sol. Then, the observed optical absorbance was due to light scattering. In contrast, the UV-VIS absorption spectrum of Z-Sol-0.005 mol/L obtained by heating Zn(OH)2-P in the ethylene glycol solution of 0.005 mol/L zinc nitrate hydrate is shown in Fig. 5(b). The optical absorbance around 400 nm was ca. 0.4. This value was lower than that shown in Fig. 5(a), and no precipitate was observed, meaning that the obtained sol was almost clear and that little light scattering was observed. Furthermore, a steep increase in optical absorbance was observed at around 360 nm. This increase in the optical absorbance corresponded to the electron transition from the valence band to the conduction band of ZnO. Accordingly, the heat treatment of Zn(OH)<sub>2</sub>-P in the 0.005 mol/L ethylene glycol solution of zinc nitrate hydrate at 308 K for 24 h formed the sol (Z-Sol-0.005 mol/L) with a homogeneous dispersion of ZnO nanoparticles. The addition of



Fig. 5. UV–VIS spectra of Z–Sol obtained by heating  $Zn(OH)_2$ –P in the ethylene glycol solution of zinc nitrate hydrate at 308 K for 24 h. The sols used for the UV–VIS absorption spectra measurement were : (a) Z–Sol–0 mol/L, (b) Z–Sol–0.005 mol/L, and (c) Z–Sol–0.05 mol/L.

zinc nitrate hydrate to the ethylene glycol solution greatly improved the dispersion of the formed ZnO nanoparticles in the sol. Figure 5(c) shows the UV–VIS spectrum of the sol (Z–Sol– 0.05 mol/L). The optical absorbance around 400 nm was 0.15, which is lower than that shown in Fig. 5(b). Accordingly, the obtained sol also had a homogeneous dispersion of ZnO nanoparticles. In this spectrum, a steep increase in optical absorption due to the electron transition between the band gap of ZnO was also observed around 360 nm.

**Figure 6** shows the XRD patterns of the particles in the Z–Sol–0.05 mol/L prepared by heating the  $Zn(OH)_2$ –P in ethylene glycol solution of the zinc nitrate hydrate for various heating time. Figure 6(a) shows the XRD pattern of the  $Zn(OH)_2$ –P. There was no sharp peak in this XRD pattern in Fig. 6(a). However, as shown in Figs. 6(b) and (c), the XRD patterns of the particles separated from the sol obtained by heating  $Zn(OH)_2$ –P in a 0.05 mol/L ethylene glycol solution of zinc nitrate hydrate for 1 h and 2 h at 308 K had peaks that can be assigned to the ZnO lattice. Accordingly, the heating of  $Zn(OH)_2$ –P in 0.05 mol/L of the ethylene glycol solution of zinc nitrate hydrate at 308 K for 1 h was sufficient to obtain ZnO particles. This heating time was shorter than that need for the heating of  $Zn(OH)_2$ –P in ethylene glycol alone.

Figure 7 shows the UV–VIS absorption spectra of the Z–Sol– 0.05 mol/L obtained by heating  $\text{Zn}(\text{OH})_2$ –P in the 0.05 mol/L



Fig. 6. XRD patterns of the particles (Z–Par–0.05 mol/L) prepared by drying the precipitates formed by mixing 100 mL of 0.1 M NH<sub>3</sub> aqueous solution and 100 mL of Z–Sol–0.05 mol/L which was prepared by heating at 308 K for various heating times. The heating times were: (a) 0 h (Zn(OH)<sub>2</sub>–P), (b) 1 h, and (c) 2 h.



Fig. 7. UV–VIS absorption spectra of Z–Sol–0.05 mol/L obtained by heating  $Zn(OH)_2$ –P in the 0.05 mol/L ethylene glycol solution of zinc nitrate hydrate at 308 K. The heating times were: (a) 0 h, (b) 1 h, (c) 2 h, (d) 4 h, (e) 6 h, (f) 8 h, (g) 12 h, and (h) 24 h.

ethylene glycol solution of zinc nitrate hydrate at 308 K for various heating time. The absorption spectrum of the solution in which Zn(OH)<sub>2</sub>-P was dispersed in the ethylene glycol solution before the heating procedure at 308 K is shown in Fig. 7(a). The absorbance also corresponds to light scattering. The optical absorption spectrum of the sol obtained by heating Zn(OH)2-P in the ethylene glycol solution of zinc nitrate hydrate at 308 K for 1 h is shown in Fig. 7(b). Strong optical absorption was observed when the wavelength was less than 340 nm. This strong absorption corresponds to the electron transition from the valence band to the conduction band of ZnO. When the wavelength was longer than 340 nm, the optical absorbance was quite low and no precipitate was observed, indicating that the obtained ZnO particles were homogeneously dispersed in the solution without light scattering in this wavelength region. Accordingly, sol with a homogeneous dispersion of ZnO nanoparticles was successfully obtained by the heat treatment of Zn(OH)<sub>2</sub>-P in the 0.05 mol/L ethylene glycol solution of zinc nitrate hydrate at 308 K for 1 h, and this UV-VIS result agreed with the XRD results in Figs. 6(a)-(c). When the heating time increased from 1 h to 24 h, the wavelength of the UV-VIS absorption edge due to the band gap transition shifted to a longer wavelength. Meulenkamp has reported that there is a relationship between the absorption edge and the size of the ZnO nanoparticles.10),17),18) According to the reference, when the ZnO nanoparticles become larger than 1.0 nm, the absorption edge approaches 365 nm. When the particle size was 0.3 nm, the absorption edge was 330 nm. When the heating time decreased, the absorption edge of the band gap transition shifted to a shorter wavelength, as shown in Figs. 7(b)-(h). This phenomenon indicated that the size of the ZnO nanoparticles in the sol was smaller in response to the heat treatment at 308 K for a shorter heating time. Accordingly, since the clear sol was obtained by heating at 308 K for 1 h, the particle growth process of the ZnO nanoparticles could be observed by measuring the UV-VIS absorption spectra. When the wavelength was larger than 360 nm, no increase in optical absorption occurred with increases in the heating time and no aggregation or precipitation of the ZnO particles was observed when Zn(OH)2-P was heated in the ethylene glycol solution of zinc nitrate hydrate.

When  $Zn(OH)_2$ –P was dispersed into the ethylene glycol solution of zinc nitrate hydrate, the zinc nitrate hydrate dissolved in the ethylene glycol played an important role in the rapid formation of ZnO nanoparticles and in inhibiting aggregation of the nanoparticles. It is considered that one of the reasons for the rapid formation and inhibited aggregation of ZnO nanoparticles was the effect of the pH value of the ethylene glycol solution of zinc nitrate hydrate. The pH values of the 0.05 mol/L, 0.005 mol/L, and 0 mol/L ethylene glycol solutions were 4.1, 5.2, and 6.9, respectively. The weak acidic condition was found to be related to the quick cleavage and recombination of the hydroxo bridge bonds between Zn<sup>2+</sup> ions in the hydroxides, resulting in the rapid formation and homogeneous dispersion of ZnO nanoparticles.<sup>19</sup>

#### 3.3 Photoluminescence characteristics of the obtained ZnO nanoparticles

**Figure 8** shows the photoluminescent (PL) spectra of Z–Sol obtained by heating  $Zn(OH)_2$ –P in the ethylene glycol solution of zinc nitrate hydrate at 308 K for 24 h, with an excitation wavelength of 365 nm. As shown in Figs. 8(a)–(f), the peak wavelengths of the PL intensity ranged from 510 nm and 525 nm, and green luminescence was observed. The PL intensity increased when the concentrations of zinc nitrate hydrate increased from 0 mol/L to 0.1 mol/L. The amount of  $Zn(OH)_2$ –P dispersed into the

ethylene glycol solution was the same in each solution. The amounts of the ZnO nanoparticles that were precipitated from Z–Sol by adding 0.1 mol/L of NH<sub>3</sub> aqueous solution ranged from 0.04 mol to 0.06 mol. The PL intensity then did not depend on the amounts of ZnO nanoparticles in the Z–Sols. It is known that the broad visible emission of ZnO can be attributed to donor-acceptor pair recombination involving point defects such as oxygen vacancies and zinc interstitials.<sup>7)</sup> As the ZnO nanoparticles with the PL characteristics were obtained by heating Zn(OH)<sub>2</sub>–P in the ethylene glycol solution of zinc nitrate hydrate at 308 K, the ZnO nanoparticles contain some lattice defects.

In order to examine the defects in these ZnO nanoparticles, the Raman spectra were measured. **Figures 9**(a), (b), and (c) show the Raman spectra of the ZnO nanoparticles of Z–Par–0 mol/L, Z–Par–0.01 mol/L, and Z–Par–0.1 mol/L, respectively. The spectra in Figs. 9(a)–(c) exhibit a peak near 437 cm<sup>-1</sup>, a weak peak



Fig. 8. Photoluminescent spectra of Z–Sol. The sols used for the PL spectra measurement were : (a) Z–Sol–0 mol/L, (b) Z–Sol–0.001 mol/L, (c) Z–Sol–0.005 mol/L, (d) Z–Sol–0.01 mol/L, (e) Z–Sol–0.05 mol/L, and (f) Z–Sol–0.1 mol/L.



Fig. 9. Raman spectra of Z–Par. The particles used for the Raman spectra measurements were: (a) Z–Par–0 mol/L, (b) Z–Par–0.01 mol/L, and (c) Z–Par–0.1 mol/L.

around 580 cm<sup>-1</sup>, and a band around 1050 cm<sup>-1</sup>. The peak at 437 cm<sup>-1</sup> can be assigned to the lattice vibrational mode E2(high) of ZnO.<sup>20),21)</sup> The peak around 580 cm<sup>-1</sup> can be assigned to the lattice vibrational mode E1(low) of ZnO.<sup>22),23)</sup> The band around 1050 cm<sup>-1</sup> can be attributed to overtone and/or combination bands.<sup>23)</sup> When the concentrations of zinc nitrate hydrate in the ethylene glycol solution increased from 0 mol/L to 0.1 mol/L, the Raman peak position E1(low) was slightly shifted from 581 cm<sup>-1</sup> to 569 cm<sup>-1</sup>. Windisch, Jr. et al. and Wei et al. have reported that the peak intensity and the position of the E1(low) mode depends on the number of lattice vacancies in ZnO lattice.<sup>23),24)</sup> It can therefore be inferred that the shift of the Raman peak position of E1(low) involves some contribution of the lattice defects in the obtained ZnO nanoparticles. A steep increase in the Raman band around 1050 cm<sup>-1</sup> was also observed with an increase in the concentrations of zinc nitrate hydrate from 0.01 mol/L to 0.1 mol/ L. Windisch, Jr. et al. have also reported that the intensity of the Raman bands depends on the change in symmetry caused by defects.<sup>23)</sup> Then, the change in the intensity of the band around 1050 cm<sup>-1</sup> also involves some contribution of the lattice defects in the obtained ZnO nanoparticles.

# 4. Conclusion

ZnO nanoparticles and their stable sols were prepared by heating Zn(OH)<sub>2</sub> precipitates in an ethylene glycol solution of zinc nitrate hydrate at 308 K. The formation of ZnO nanoparticles from Zn(OH)<sub>2</sub> occurred within 1 h at 308 K in the 0.05 mol/L ethylene glycol solution of zinc nitrate hydrate. The obtained sol was homogeneous, with no aggregation of the ZnO nanoparticles being observed. The absorption edge of the obtained sol depended on the heating time at 308 K. Furthermore, the intensity of photoluminescence of the obtained ZnO nanoparticles increased with increases in the concentrations of zinc nitrate hydrate in the ethylene glycol solution. The zinc nitrate hydrate in the ethylene glycol solution greatly affected the formation process of the ZnO nanoparticles and their photoluminescent characteristics. Accordingly, the ZnO nanoparticles with photoluminescence characteristics can be obtained by a simple and low-temperature synthesis process near room temperature.

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