Synthesis of ZnO sols by low-temperature heating of ethylene glycol solution and control of their photoluminescence with addition of glucose

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ZnO nanoparticles and their stable sols were prepared by heating an ethylene glycol solution of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.1 mol/L, 50 mL) with 2 mL of NH_3 aq at 328 K for 24 h. The obtained sol contained ZnO nanoparticles with average diameter of around 20 nm. The particle size decreased with increased the concentration of NH_3 . Furthermore, the ZnO nanoparticles dispersed in the sols showed a green photoluminescence peak around 550 nm. The heating procedure of the ethylene glycol solution at 328 K yielded stable sols of ZnO nanoparticles with photoluminescence characteristics. In order to control the photoluminescence characteristics of the ZnO nanoparticles, the ethylene glycol solution which contained zinc nitrate hydrate, glucose, and 1 mol/L of NH_3 aq was heated at 328 K for 24 h. The obtained ZnO nanoparticles dispersed in the sols showed a blue photoluminescence peak at around 420 nm. The glucose reacted with Zn^{2+} ions as a reduction agent. Accordingly, the simple one-pot synthesis process using the heating of the ethylene glycol solution containing zinc nitrate hydrate, NH_3 , and glucose achieved control of photoluminescence spectra and enabled the stable dispersion of ZnO nanoparticles.

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1. Introduction

Zinc oxide, an n-type oxide semiconductor, has been used for gas-sensing devices and varistors.^{1),2)} In recent years, applications for electrodes of dye-sensitized solar cells, transparent electrical conductive films, and ultraviolet (UV) emitters have also been investigated intensively.³⁾⁻⁵⁾ Furthermore, phosphor characteristics of ZnO have been studied to develop display devices.^{6),7)} For these applications, appropriate ZnO particles to obtain phosphor films and optical transparent thin films are necessary. It is important issue to control microstructure of these films. Therefore, the ZnO nanoparticles without aggregation are useful for formation of the films. The development of a novel and simple method of synthesizing ZnO nanoparticles with stable dispersion in solvents and high yield has become extremely important.^{8),9)} For preparing optical transparent ZnO films and complex materials with organic polymers, ZnO-stable sols are useful. Furthermore, ZnO nanoparticles in the sols can be used as biomarkers with their photoluminescence characteristics. These optical and electrical properties of ZnO particles depend greatly on the defect structure in the ZnO lattice. For example, oxygen vacancies in the ZnO lattice produce donor levels with electrons and luminescent centers.^{10),11)} Therefore, it is also important issue to develop a method of synthesizing ZnO nanoparticles and their stable sols with control of lattice defects.

In recent years, various ZnO nanoparticles preparation methods have been reported. The solution processes are suited to preparation of the nanoparticles and the sols because the particle size and morphology can be controlled by addition of ligands to zinc ions in the solution system. Chieng et al. prepared ZnO nanoparticles

by refluxing an ethylene glycol solution of zinc acetate hydrate at 433 K.¹²⁾ Vafaei et al. heated an ethanol solution of zinc acetate hydrate and triethanolamine at around 333 K to obtain ZnO nanoparticles.¹³⁾ Some researchers have synthesized ZnO nanoparticles using chemical methods in an alcohol base solution with capping agents to control particle growth processes.^{14),15)} Although these synthesis methods are useful to obtain ZnO nanoparticles, it has remained difficult to obtain their stable sols.

The authors have reported that stable sols of ZnO nanoparticles are obtainable by heating of $\text{Zn}(\text{OH})_2$ precipitate in ethylene glycol.^{16),17)} This simple synthesis process requires preparation of pure $\text{Zn}(\text{OH})_2$ precipitate without impurity ions. For that reason, it is necessary to develop simpler one-pot synthesis method to obtain stable sols of ZnO nanoparticles. In this study, low-temperature heating of an ethylene glycol solution of zinc salts and NH_3 aq in a closed vessel was examined to obtain the stable sols of ZnO nanoparticles. Ethylene glycol is a good solvent for zinc salts. It strongly coordinates to Zn^{2+} ions to control particle formation and to prevent nanoparticles aggregation. Furthermore, it is important to develop methods to control electrical and optical properties of ZnO nanoparticles. It is expected that action of a reducing agent to ZnO nanoparticles could form interstitial Zn atoms and change the electrical state. We focused on glucose as the reducing agent. In order to regulate photoluminescence characteristics of ZnO nanoparticles, the nanoparticle preparation was carried out by adding glucose to the ethylene glycol solution. The effect of glucose addition in the sols were examined.

2. Experiments

2.1 Preparation of a stable sol of ZnO nanoparticles

The ZnO nanoparticles and their sols were prepared as follows: The zinc nitrate hexahydrate [$\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$] was dissolved in

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ethylene glycol. Then the total volume was adjusted to 50 mL. The concentrations of Zn^{2+} in the ethylene glycol solutions of zinc nitrate hydrate were 0.1 M. Two milliliters of NH_3 aq with concentration of 1 mol/L was added to 50 mL of ethylene glycol solution of zinc nitrate hydrate. The ethylene glycol solution was heated at 328 K for 24 h in a closed glass vessel. A stable sol without precipitate was finally obtained. To control the particle size of the obtained ZnO nanoparticles, the same synthetic process was also conducted using the NH_3 aq with other concentrations between 0.5 to 8 mol/L. Hereinafter, this concentration is designated as $[\text{NH}_3]$.

To ascertain the effects of reducing agents on the formation process of ZnO nanoparticles, glucose ($\text{C}_6\text{H}_{12}\text{O}_6$) was dissolved into the ethylene glycol solution of zinc nitrate hydrate. Then the total volume was also adjusted to 50 mL. The concentrations of Zn^{2+} and glucose were adjusted, respectively, to 0.1 and 0.01 mol/L. Then 2 mL of 1 mol/L NH_3 aq was added to the ethylene glycol solution, which was also heated at 328 K for 24 h in a closed glass vessel. The same synthetic process was also conducted using other concentrations of glucose. The concentrations were 0.001–0.1 mol/L. Hereinafter, this concentration of glucose is designated as $[\text{Glucose}]$. Furthermore, this synthesis procedure was conducted using mannitol ($\text{C}_6\text{H}_{14}\text{O}_6$) substituted for glucose. Hereinafter, this mannitol concentration is designated as $[\text{Mannitol}]$. All chemicals used in this preparation were of reagent grade (Wako Pure Chemical Industries Ltd.).

To separate the obtained nanoparticles in the sols, 50 mL of 0.1 mol/L NH_3 aq was added to the sols. The nanoparticles were aggregated and precipitated. The obtained precipitate was then separated by centrifugation at 3000 rpm for 5 min. To remove impurities such as ammonium ions and nitrate ions, the obtained precipitate was dispersed into 100 mL of ethanol and then separated again by centrifugation at 3000 rpm for 5 min. Then the precipitate was dried at 308 K for 24 h.

2.2 Characterization

The structure of the obtained powder was characterized by X-ray diffraction (XRD) (Cu $\text{K}\alpha$ 40 kV, 100 mA, MXP-18; Mac Science Ltd.). Particle shape was observed using field emission-scanning electron microscopy (FE-SEM: JEM-1200EX; JEOL Ltd.). The ultraviolet-visible (UV-VIS) transmittance and absorbance spectra of the obtained sol were measured using wavelengths of 300–800 nm (UV-2450; Shimadzu Corp.). In particular, the obtained sols had very strong optical absorption in UV wavelength region. In order to measure accurate optical absorbance, the sols were diluted by 50 times with ethylene glycol before the measurement. The photoluminescence (PL) spectra were measured using excitation light at 365 nm (λ_{ex}) (RF-5300PC; Shimadzu Corp.). The UV-VIS absorption spectra and photoluminescence spectra were measured using the obtained sol in a quartz glass cell.

3. Results and discussion

3.1 Characterization of ZnO nanoparticles obtained by heating the ethylene glycol solution

Figure 1 presents XRD patterns of the particles obtained by heating ethylene glycol solutions of zinc nitrate hydrate with NH_3 aq at 328 K for 24 h. All peaks in the XRD patterns (a)–(e) in Fig. 1 can be assigned to wurtzite ZnO structure. Accordingly, the particles obtained using NH_3 aq of which the concentration range was 0.5–8 mol/L were single phases of ZnO. Crystallite sizes were calculated using Scherrer's equation at the peak of the (100) plane. As shown in the XRD patterns (a)–(e) in Fig. 1,

Fig. 1. XRD patterns of particles obtained by heating the ethylene glycol solution of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ with NH_3 aq at 328 K for 24 h. The $[\text{NH}_3]$ were (a) 0.5, (b) 1, (c) 2, (d) 4, and (e) 8 mol/L.

the crystallite sizes of the ZnO particles were, respectively, 30.3, 28.7, 24.8, 14.0, and 13.6 nm. The crystallite size decreased with the increase of the $[\text{NH}_3]$ value. Accordingly, the coordination of a NH_3 molecule to a Zn^{2+} ion inhibited the ZnO particle growth rate.

Figure 2 shows FE-SEM images of the ZnO particles obtained from the sols. As presented in Fig. 2(a), when the $[\text{NH}_3]$ was 0.5 mol/L, the obtained ZnO particles had the spherical aggregated morphology of the primary ZnO nanoparticles with average diameter of 32.1 nm. This aggregated morphology would be formed by heterogeneous nucleation on the formed ZnO nanoparticles. It is considered that the 0.5 mol/L of $[\text{NH}_3]$ was too low concentration for the homogeneous nucleation process of ZnO nanoparticles. However, when the $[\text{NH}_3]$ values were more than 1 mol/L, the spherical aggregated morphology was not observed. When the $[\text{NH}_3]$ values were 1, 2, and 4 mol/L as shown in Figs. 2(b)–2(d), the average particle diameters of the obtained ZnO particles were 25.2, 19.8, and 15.2 nm, respectively. The particle size decreased with increased $[\text{NH}_3]$. The coordination of NH_3 molecules to the Zn^{2+} ions forms stable complex molecules, which inhibited the formation reaction of the ZnO nanoparticles. This formation of the complex molecules affected the growth rate.¹⁸⁾

In order to examine the relationship between the obtained amount of ZnO nanoparticles and the $[\text{NH}_3]$, the UV-VIS absorbance spectra were measured as shown in **Fig. 3**. This spectra were measured by using the sols diluted by 50 times with ethylene glycol. The spectrum (a) in Fig. 3 describes optical absorbance spectra of the sol obtained with the condition of $[\text{NH}_3] = 0.5$ mol/L. An increase in optical absorbance was observed around 380 nm. This increase corresponded to the electronic transition from the valence band to the conduction band of ZnO. The optical absorption of the band-to-band transition of ZnO is proportional to the amount of ZnO dispersed in the sol. As shown in Fig. 3, the value of the optical absorbance of the band-to-band transition of ZnO increased with increase of $[\text{NH}_3]$. Therefore, the included amount of ZnO in the obtained sol increased with increase of $[\text{NH}_3]$ in the range from 0.5 to 4 mol/L.

To examine the dispersed state of the ZnO particles in the obtained sol, the UV-VIS transmittance spectra were measured as shown in **Fig. 4**. When $[\text{NH}_3]$ was 0.5 mol/L, the values of the optical transmittance were 73–0% when the wavelengths were 800–380 nm. In this case, the obtained solution was somewhat opaque. The observed optical absorbance resulted from light scattering. As shown in Fig. 2(a), when $[\text{NH}_3]$ was 0.5 mol/L, the secondary particles whose average diameter was 130 nm were dispersed in the sol. The particle size was larger than the particles in the sols obtained with $[\text{NH}_3] = 1$ –4 mol/L. Then, the light

Fig. 2. FE-SEM images of particles obtained by heating the ethylene glycol solution of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ with NH_3 aq at 328 K for 24 h. The $[\text{NH}_3]$ were (a) 0.5, (b) 1, (c) 2, and (d) 4 mol/L.

Fig. 3. The UV-VIS absorbance spectra of the sols of ZnO nanoparticles diluted by 50 times with ethylene glycol. The sols were obtained by heating the ethylene glycol solution of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ with NH_3 aq at 328 K for 24 h. The $[\text{NH}_3]$ was: (a) 0.5, (b) 1, (c) 2, (d) 3, and (e) 4 mol/L.

Fig. 4. UV-VIS transmittance spectra of the sols of ZnO nanoparticles obtained by heating the ethylene glycol solution of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ with NH_3 aq at 328 K for 24 h. The $[\text{NH}_3]$ was (a) 0.5, (b) 1, (c) 2, (d) 4, and (e) 8 mol/L.

scattering of the sol obtained with $[\text{NH}_3] = 0.5$ mol/L was also larger than the other sols. Spectrum (b) in Fig. 4 describes the UV-VIS transmittance spectrum of the sol obtained with the condition of $[\text{NH}_3] = 1$ mol/L. When the wavelength was 800–400 nm, the optical transmittance was greater than 95%, meaning that the obtained sol was almost entirely transparent. Furthermore, a steep decrease in optical transmittance was observed around 380 nm. This decrease corresponded to the band-to-band transition of ZnO. When the $[\text{NH}_3]$ values were 2 and 4 mol/L, as shown in spectra (c) and (d) in Fig. 4, the optical transmittance in the wavelengths of 400 and 800 nm was more than 93 and 84%, respectively. Therefore, the obtained sols had highly homogeneous dispersion of ZnO nanoparticles and optical trans-

parency. Furthermore, the transmittance spectra of these sols shown in spectra (c) and (d) in Fig. 4 exhibited a steep decrease of the transmittance around 380 nm, which corresponded to the band-to-band transition of ZnO. For $[\text{NH}_3] = 8$ mol/L, the values of the optical transmittance were 29–0% for wavelengths of 800–450 nm. In this case also, the obtained solution was opaque. For these wavelengths, the gradual decrease of the transmittance corresponded to the light scattering of the aggregated particles in the sol. When $[\text{NH}_3]$ was 8 mol/L, it is considered that the included amount of ZnO particles in the sol is larger than that in the sol of $[\text{NH}_3] = 4$ mol/L. Increase of the amount of the ZnO particles in the sol caused the aggregation of the particles. Accordingly, heating the ethylene glycol solution of zinc nitrate

Fig. 5. (Color online) Photoluminescence spectra of the sols of ZnO nanoparticles obtained by heating the ethylene glycol solution of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ with NH_3 aq at 328 K for 24 h. The $[\text{NH}_3]$ was (a) 0.5, (b) 1, (c) 2, and (d) 4 mol/L. The photograph in this figure shows the obtained sols with irradiation of black light (365 nm).

hydrate with NH_3 at concentrations of 1 to 4 mol/L produced a homogeneous stable sol of ZnO nanoparticles.

Figure 5 shows photoluminescence (PL) spectra of the obtained sols of ZnO nanoparticles. The excitation wavelength (λ_{ex}) was 365 nm. The PL spectrum (a) in Fig. 5 presents the PL spectrum of the sol obtained with the condition of $[\text{NH}_3] = 0.5$ mol/L. The PL spectrum of the obtained sol had no peak at wavelengths of 400–680 nm. In contrast, when the $[\text{NH}_3]$ was larger than 1 mol/L, the PL peak around 550 nm appeared. This green PL emission of ZnO can be attributed to donor–acceptor pair recombination involving point defects in the ZnO lattice. The PL peak intensity increased when $[\text{NH}_3]$ was increased from 1 to 2 mol/L as shown in spectra (b) and (c) in Fig. 5. However, the PL peak intensity decreased when $[\text{NH}_3]$ increased from 2 to 4 mol/L, as shown in spectra (c) and (d) in Fig. 5. Although the amount of ZnO nanoparticles in the sol increased with an increase of $[\text{NH}_3]$, the PL intensity decreased. It is considered that concentration extinction phenomenon affected the change of the PL intensity. Although the preparation method was a simple heating process, stable sols of ZnO nanoparticles with the PL emission around 550 nm were obtained. The heating process at 328 K suited the formation of lattice defects to induce PL emission.

3.2 Effects of glucose on photoluminescence characteristics of ZnO nanoparticles

The PL characteristics of ZnO nanoparticles depend on the amount of point defects in the ZnO lattice, as described in a previous section. Introducing these lattice defects can affect the PL spectra of the obtained ZnO nanoparticles. In this study, glucose was used as a reducing agent for ZnO nanoparticles to introduce a new electron energy level which corresponds to lattice defects. **Figure 6** shows PL spectra of the sols of ZnO nanoparticles obtained by heating the ethylene glycol solution of zinc nitrate hydrate and glucose with 2 mL of NH_3 aq, of which the concentration was 1 mol/L. The excitation wavelength (λ_{ex}) was 365 nm. When the $[\text{Glucose}]$ was 0 and 0.005 mol/L, the PL peak around 550 nm appeared as shown in spectra (a) and (b) in Fig. 6. Furthermore, when the $[\text{Glucose}]$ was 0.01 mol/L, as presented in spectrum (c) in Fig. 6, the strong PL peak around 422 nm appeared. For the case in which the $[\text{Glucose}]$ value increased from 0.01 to 0.1 mol/L as shown in spectra (c)–(f) in Fig. 6, the peak position of this blue PL emission shifted to longer wavelength from 422 to 462 nm. Recently, some researchers have reported blue luminescence of ZnO. The detailed mechanism of the blue PL emission remains unclear,

Fig. 6. Photoluminescence spectra of the sols of ZnO nanoparticles obtained by heating the ethylene glycol solution of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and glucose with NH_3 aq at 328 K for 24 h. The $[\text{NH}_3]$ was 1 mol/L. The $[\text{Glucose}]$ was (a) 0, (b) 0.005, (c) 0.01, (d) 0.02, (e) 0.05, and (f) 0.1 mol/L.

Fig. 7. Photoluminescence spectra of the sols of ZnO nanoparticles obtained by heating the ethylene glycol solution of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and mannitol with NH_3 aq at 328 K for 24 h. The $[\text{NH}_3]$ was 1 mol/L. The $[\text{Mannitol}]$ was (a) 0, (b) 0.005, (c) 0.01, and (d) 0.1 mol/L.

but the energy interval from the level of the interstitial Zn (Zn_i) to the valence band is consistent with the energy of the blue PL emission around 422 nm (2.95 eV) when $[\text{Glucose}]$ was 0.01 mol/L.¹⁹⁾ Accordingly, we infer that the formation of the interstitial Zn sites occurred by the reduction reaction of Zn^{2+} with glucose molecules under the basic condition of NH_3 aq in the ethylene glycol solution.

To clarify the effect of glucose as a reduction agent, the effect of the addition of sugar alcohol molecules in the ethylene glycol solution was investigated. Mannitol ($\text{C}_6\text{H}_{14}\text{O}_6$) is a sugar alcohol molecule that is obtainable by reduction of sugar molecules [mannose ($\text{C}_6\text{H}_{12}\text{O}_6$)] with H_2 . The mannitol does not act as a reduction agent. Therefore, the ZnO sol was prepared by heating the ethylene glycol solution of zinc nitrate hydrate and mannitol with NH_3 aq, of which the concentration was 1 mol/L, at 328 K for 24 h. **Figure 7** presents PL spectra of the sols obtained using mannitol. Spectrum (a) in Fig. 7 shows the PL spectrum of the ZnO sol obtained without adding mannitol ($[\text{Mannitol}] = 0$ mol/L), which was identical to that of spectrum (b) in Fig. 5. When the $[\text{Mannitol}]$ were 0.005 and 0.01 mol/L, as shown in spectra (b) and (c) in Fig. 7, broad PL emission peaks around 550 nm, which was the same wavelength of the peak in spectrum (a) in Fig. 7 were observed. Furthermore, in the case in which $[\text{Mannitol}]$ was 0.1 mol/L, the intensity of the PL peak around 550 nm greatly decreased, as shown in spectrum (d) in Fig. 7. It is considered that adsorption and coordination of mannitol molecules on the obtained ZnO nanoparticle surface

Fig. 8. UV-VIS transmittance spectra of sols obtained by heating the ethylene glycol solution of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ with NH_3 aq at 328 K. The $[\text{NH}_3]$ was 1 mol/L. Heating times were (a) 0, (b) 0.5, (c) 1, (d) 2, (e) 4, (f) 8, and (g) 24 h.

affected the PL intensity. The interaction between ZnO surface and mannitol formed some energy levels between ZnO band gap so that frequency of electronic transition with radiation decreased. Accordingly, the blue PL emission did not appear when mannitol, which can not act as a reduction agent, was added to the ethylene glycol solution of zinc nitrate hydrate substituted for glucose. These results indicate that mannitol did not produce defects corresponding to the blue PL emission. Mannitol molecules have a similar coordination property to that of glucose molecules. The fundamental difference between glucose and mannitol is their reduction activity. Therefore, the reduction of Zn^{2+} ions by glucose molecules plays an important role in the appearance of blue PL emission.

3.3 ZnO nanoparticles formation processes in the ethylene glycol solution

Figure 8 shows the change of the UV-VIS transmittance spectra of the sols obtained by heating the ethylene glycol solution of zinc nitrate hydrate with 2 mL of NH_3 aq (1 mol/L) at 328 K for various heating times. Figure 8(a) shows the UV-VIS transmittance spectrum of the ethylene glycol solution before heating. This spectrum has two low-transmittance wavelength regions around 300 and 250 nm. The strong optical absorption around 300 nm corresponds to the charge transfer absorption.²⁰⁾ Furthermore, the strong absorption around 250 nm corresponds to the absorption of NO_3^- ions. Figure 8(b) depicts transmittance spectrum of the ethylene glycol solution heated for 0.5 h. The spectrum also has two low-transmittance wavelength regions around 300 and 250 nm, which respectively correspond to the charge transfer absorption and NO_3^- ions. In this spectrum of Fig. 8(b), small shoulder absorption around 360 nm appeared, which corresponds to the electronic transition in the band gap of ZnO. This result indicates that the formation of a small amount of ZnO nanoparticles in the ethylene glycol solution occurred by heating at 328 K for 0.5 h. When the heating time was 1 h, the transmittance of the obtained solution became 0% in the shorter wavelength range from 345 nm, as portrayed in Fig. 8(c). This strong absorption corresponds to the band-to-band transition of ZnO. Accordingly, the ZnO nanoparticles were present in the solution heated at 328 K for only 1 h. Furthermore, the absorption edge of the spectra shown in Figs. 8(d)–8(g) shifted to the longer wavelength from 350 to 367 nm when the heating time was changed from 2 to 24 h. This shift of the absorption edge was related to the change of the size and amount of ZnO nanoparticles in the obtained sols. Accordingly, heating of the ethylene glycol solution of zinc nitrate hydrate with NH_3 aq at 328 K for 1 h is sufficient to obtain a stable sol of ZnO nanoparticles.

Fig. 9. Photoluminescence spectra of the sol of ZnO nanoparticles. The sol was obtained as follows. An ethylene glycol solution of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ with NH_3 aq (1 mol/L) was heated at 328 K for (a) 0, (b) 0.5, (c) 0.75, (d) 1, and (e) 3 h. Subsequently, glucose (0.01 mol/L) was dissolved in the solution, which was heated at 328 K for 24 h.

To examine interaction among Zn^{2+} ions, ZnO nanoparticles, and glucose in the ethylene glycol solution, effects of the timing for addition of glucose into the ethylene glycol solution of zinc nitrate hydrate on the PL spectra of the obtained sols were examined. The glucose was dissolved into the ethylene glycol solution of zinc nitrate hydrate with the NH_3 aq (1 mol/L) after heating at 328 K for various durations from 0 to 24 h. Thereafter, the ethylene glycol solution of zinc nitrate hydrate, glucose, and NH_3 aq was heated again at 328 K for 24 h. Figure 9 shows the PL spectra of the obtained sols. The molar ratio of ZnO nanoparticles and Zn^{2+} ions in the ethylene glycol solution can be regulated by the heating time before dissolving glucose. Then, the investigation of the relation between the heating time before dissolving glucose and the PL spectra of the finally obtained sols will enable clarification of which of Zn^{2+} ions or ZnO nanoparticles reacts with glucose. Figure 9(a) presents PL spectra for the heating of the ethylene glycol solution without glucose of 0 h. This PL spectrum is identical to that shown in Fig. 6(c). When the heating time without adding glucose was 0.5 h, the intensity of the blue PL emission peak around 420 nm decreased. A shoulder peak around 550 nm appeared as presented in Fig. 9(b). Furthermore, when the heating time without adding glucose increased from 0.5 to 0.75 h, the intensity of the blue PL emission peak around 420 nm decreased and the PL peak intensity at around 550 nm increased, as presented in Fig. 9(c). When the heating times without adding glucose were 1 and 3 h, the blue PL emission peak disappeared, as shown in Figs. 9(d) and 9(e). The PL peak around 550 nm corresponded to the electronic transition in the ZnO nanoparticles. This appearance of the green PL emission around 550 nm corresponded to formation of the ZnO nanoparticles as presented in Fig. 8. Accordingly, the PL peak around 550 nm can be assigned the ZnO nanoparticles in the sols. Therefore, the PL emission of ZnO nanoparticles was unaffected by reduction reaction of glucose. However, a decrease of the peak intensity of the blue PL emission around 420 nm occurred when the heating time without adding glucose increased from 0 to 3 h. The increase of the heating time decreased the amount of Zn^{2+} ions in the sol because the ZnO nanoparticle formation occurred. Accordingly, the reduction reaction of Zn^{2+} ions in the ethylene glycol solution by glucose molecules played an important role in the appearance of the blue PL peak. This reduction process formed electron energy level which corresponded to the interstitial Zn atom lattice defects. Therefore, when the ethylene glycol solution of zinc nitrate hydrate and glucose with NH_3 aq was heated, the reduction reaction of Zn^{2+}

ion with glucose molecules occurred and the formed Zn atoms were incorporated in the formed ZnO lattice to create interstitial Zn sites, which corresponds to the blue PL emission. Furthermore, the PL intensity around 550 nm decreased when the heating time without adding glucose increased from 1 to 3 h as shown in spectra (c) and (d) in Fig. 9. When the heating time increased, the unreacted Zn^{2+} ions in the sol decreased. The amount of glucose which was not used for reducing Zn^{2+} ions in spectrum (d) was more than those in spectrum (c). Therefore, the unreacted glucose molecules interacted with ZnO nanoparticle surface and the PL intensity decreased as discussed in Fig. 7.

4. Conclusion

ZnO nanoparticles and the sols with their stable dispersion were prepared by heating an ethylene glycol solution of zinc nitrate hydrate with NH_3 aq at 328 K for 24 h. The obtained sol contained ZnO nanoparticles with average diameter of around 20 nm. The particle size depended on the NH_3 concentration. Furthermore, the ZnO nanoparticles dispersed in the sols showed a green PL peak at around 550 nm. The heating procedure of the ethylene glycol solution at 328 K yielded stable sols of ZnO nanoparticles with PL characteristics. To control the PL spectra of the obtained ZnO nanoparticles, the reduction reaction of the ZnO nanoparticles in the ethylene glycol solution with glucose molecules was examined and the PL peak shifted successively to shorter wavelengths. According to an investigation of the interaction among Zn^{2+} ions, ZnO nanoparticles, and glucose molecules in the ethylene glycol solution, the interaction between glucose and Zn^{2+} ions was important for formation of point defects in the ZnO lattice, which causes the blue PL emission around 420 nm. Accordingly, the simple one-pot synthesis process using the heating of the ethylene glycol solution containing zinc nitrate hydrate, NH_3 , and glucose achieved control of PL spectra and enabled the stable dispersion of ZnO nanoparticles.

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