Visible Luminescence and Surface Properties of Nanosized ZnO Colloids Prepared by Hydrolyzing Zinc Acetate

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Luminescence properties of nanosized zinc oxide (ZnO) colloids greatly depend on their surface properties. These surface properties in turn are largely determined by the method of preparation. The procedure for producing ZnO colloids consists of two major steps: (1) preparing the precursor by reacting zinc acetate with ethanol and (2) hydrolyzing the precursor to form the colloid by using lithium hydroxide. The sample colloids in this study were prepared by hydrolyzing zinc acetate precursors containing various concentrations of Zn^{2+} with different concentrations of lithium hydroxide. The luminescence properties were evaluated by the energy difference, ΔE, between the band gap and the emission energy which were obtained from the onset of the absorption spectrum and the peak wavelength of the emission spectrum, respectively. The surface properties of ZnO particles were studied using thermal gravimetric and infrared techniques. ZnO particles produced via these procedures are not pure but have acetate (CH_3COO^-) groups on their surface. These groups originate from the reagent, zinc acetate. These acetate groups consist of a mixture of unidentate, chelate, and bridging type structures. The amount and structure of the acetate groups depend on the concentrations of Zn^{2+} in the precursors and the amount of lithium hydroxide used to hydrolyze these precursors. The luminescence properties, ΔE, also changed with the concentrations of Zn^{2+} and lithium hydroxide. Our results, however, could be normalized to the concentration ratio of zinc acetate to lithium hydroxide, ZnAc/LiOH. The amount of acetate groups on the ZnO particles prepared at the same concentration ratio of ZnAc/LiOH were the same, and the IR spectra were also coincident with each other. Furthermore, the visible luminescence properties, ΔE, are also the same, for the ZnO colloids prepared at the same concentration ratio of ZnAc/LiOH, and increased with increasing ratios. These results suggest that the visible luminescence properties of ZnO particles depend on their surface properties which are in turn determined by the concentration ratio of ZnAc/LiOH.

Introduction

The photoelectrochemistry of nanosized semiconducting particles has been an area of active research.[1−6] The luminescence properties of nanosized luminescent semiconducting particles such as CdS, CdSe, and ZnO are substantially different from those of bulk crystalline materials.[1,2,7−11] The band gap energy increases as particles become smaller, and the hypsochromic shifts in optical absorption and luminescence spectra are noted. In addition, such small particles emit visible luminescence much stronger than bulk crystals due to the concentration of oscillator strength into just a few transitions.[10] These properties can be exploited for the proper design of varistors,[4,6] photoelectrodes,[5] or sensors.[12]

Several techniques for preparing nanosized luminescent semiconducting particles have been developed, including a novel method of synthesizing ZnO colloids composed of nanosized wurtzite crystals as reported by Spanhel et al.[8] and Bahnemann et al.[9] The preparation procedures used in both cases are

basically the same. The colloids prepared by these methods are extremely stable, and the intensity of visible luminescence is remarkably high as compared with that of UV luminescence, which is caused by the direct recombination of electron−hole pairs. These properties are considered to provide a major advantage in the ultimate development of a luminescent semiconducting sensor.

Both Spanhel[8] and Bahnemann[9] explained the mechanism of such high visible luminescence in terms of photogenerated electrons tunneling to preexisting, trapped holes. Since colloidal ZnO particles prepared by these methods are not likely pure crystals, organic molecules (derived from precursors used in the synthesis of the colloid) that are bound or adsorbed on ZnO crystallites might affect the visible luminescence. This hypothesis was not explored in the studies of Spanhel and Bahnemann. The structure and amount of such organic molecules might be altered by the preparation and the hydrolysis conditions of the precursors. In this work, we examine the effects of such preparation conditions on the visible luminescence properties of ZnO from the point of view that these

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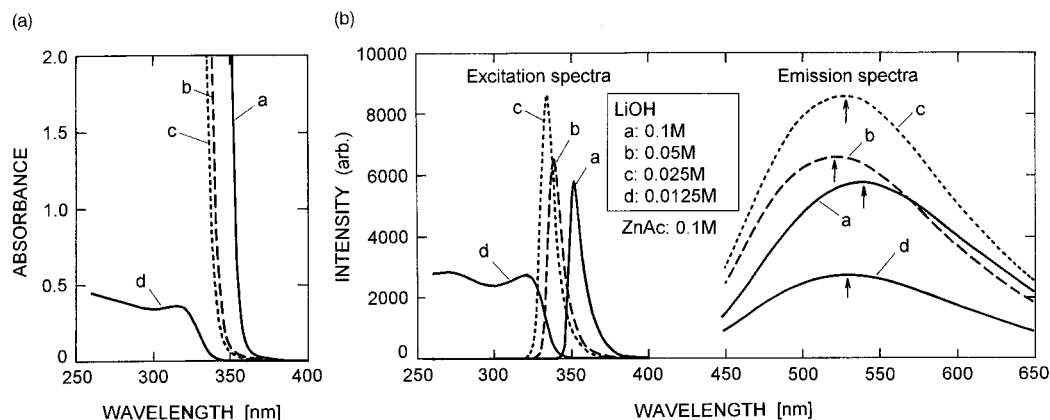
Figure 1. Absorption spectra (a) and luminescence spectra (b) of ZnO colloids prepared by hydrolyzing the precursors containing 0.1 M Zn^{2+} with various concentrations of lithium hydroxide.

preparation conditions will alter the surface chemistry and thereby change the luminescence properties of these colloids.

Experimental Section

A. Preparation of Zinc Oxide Colloid. The preparation procedure followed in this work was essentially the same as that of Spanhel.[8] The procedure consists of two major steps: (1) preparation of precursor and (2) hydrolysis of the precursor to form the colloid. Zinc acetate ($ZnC_4H_6O_4\cdot2H_2O$ from Katayama Chemical) and ethanol (99.5% (v/v)) were used to prepare the precursor without further purification, and lithium hydroxide ($LiOH\cdot H_2O$ from Katayama Chemical) was used to hydrolyze the precursor, respectively.

A 0.5 L ethanolic solution containing a desired amount of zinc acetate (the concentration of which was changed from 0.0125 to 0.1 M) was placed into a 1 L round-bottom distillation flask fitted with a condenser and refluxed while stirring for 3 h at about 80 °C. The condensate was collected continuously. At the end of this procedure, 0.2 L of reaction product (precursor) and 0.3 L of condensate (which was discarded) were obtained. The reaction product was immediately diluted to the original volume of 0.5 L with ethanol and then cooled rapidly to room temperature. The precursor likely contains zinc compounds and the reaction byproducts such as acetic acid derivatives, although we did not determine their structures. In preparing the precursor, the time of reaction between zinc acetate and ethanol was an important factor used in obtaining a stable precursor. In the case of reaction times less than about 2 h, a precipitate was noticed in the diluted, cooled precursor. On the other hand, a turbid reaction product was produced for reaction times longer than 4 h. A transparent and stable precursor was only obtained after a 3 h reaction time.

A desired amount of lithium hydroxide powder (the concentration of which was also changed from 0.0125 to 0.1 M) was added to the diluted, cooled precursor. The mixture was then hydrolyzed in an ultrasonic bath (65 W, 40 kHz) to accelerate the reaction at room temperature. For the highest concentration of LiOH (0.1 M), more than 10 min were required to produce a clear solution. The effect of hydrolysis time on the luminescence properties was also examined using 0.1 M lithium hydroxide. No difference could be recognized until the hydrolysis time exceeded 10 min. From these results, hydrolysis time was fixed to 20 min. Finally, the ZnO colloidal solution was filtered though a glass fiber filter (GF/C, Whatman) to remove dust and any undissolved lithium hydroxide that might remain.

B. Spectroscopic Measurements. The excitation and emission spectra were measured using FP-777 Spectrofluorometer (Japan Spectroscopy) with a lamp source of 150 W xenon. Measurements were performed using a quartz cell having a path length of 10 mm. The intensity of emitted light was detected at a right angle to the incident light. An appropriate optical filter to avoid the second-order contribution was installed in the emission light path. The absorption spectra were also measured with this spectrofluorometer using a UV accessory (FP-1080), by which the light transmitted through a cell can be measured.

Infrared spectroscopic studies were conducted using a Report-100 infrared spectrometer (Japan Spectroscopy). Samples were prepared by drying ZnO colloids under a nitrogen stream at room temperature for more than a week and then heating them at 100 °C for 5 h to remove the solvent and the reaction byproducts such as acetic acid derivatives. Measurements were performed with pressed pellets, which were made using potassium bromide powder as a diluent.

C. Thermal Analysis Studies. Sample powders were prepared by drying ZnO colloids and heating them using the same procedures as mentioned above. Measurements were performed with a TGA-50 and TG-50 thermal analysis system (Shimadzu). A small amount of the sample powder (less than 10 mg) was heated from room temperature to 480 °C at the constant rate of 1 °C/min under an air flow of 20 mL/min. The change in the weight of the sample was measured continuously.

Results and Discussion

A. Absorption and Luminescence Spectra of ZnO Colloids. Both absorption and luminescence spectra largely depended on the concentrations of zinc acetate and lithium hydroxide used to prepare and hydrolyze the precursor, respectively. Figure 1 shows examples of absorption and luminescence spectra obtained from fresh ZnO colloids prepared by hydrolyzing the precursor containing 0.1 M Zn^{2+} with various concentrations of lithium hydroxide.

The wavelength of the onset of absorption (Figure 1a), which is obtained by extrapolating the steep part of the rising absorption curve, is lower than that of the macrocrystalline ZnO (about 372 nm [13]) for all ZnO colloids prepared in this work and shifts to the lower wavelength with decreasing concentration of lithium hydroxide. Spanhel reported that the size of ZnO particles prepared by hydrolyzing the precursor containing 0.1 M Zn^{2+} with 0.14 M lithium hydroxide was about 3.5 nm as determined from X-ray diffraction and transmission electron
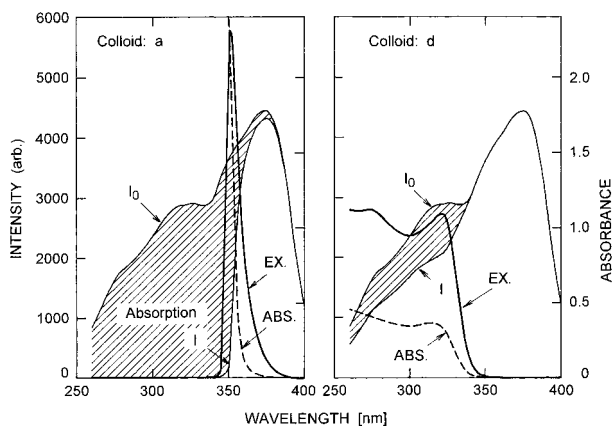
Figure 2. Relationship between absorption of incident light and excitation spectra. Colloids a and d were prepared by hydrolyzing the precursors containing 0.1 M Zn^{2+} with LiOH of 0.1 and 0.0125 M, respectively.

microscopy (TEM) measurements.[8] These small ZnO particles exhibited quantum-size effects.[2,8-11] The relationship between the particle size of quantum-size ZnO and the onset of absorption was examined by Haase et al.,[13] in detail. From their data, the particle size of ZnO prepared in this work is considered to be less than several nanometers, depending on the concentration of lithium hydroxide. Furthermore, the main factor of the shift of absorption onset to longer wavelength with increasing concentration of lithium hydroxide (the red shift) is considered due to the aggregation of ZnO particles which might increase with an increasing concentration of lithium hydroxide, because the absorption onset decreases by diluting the colloids as shown in the subsequent section.

The excitation spectra which were detected at the peak wavelength of the emission spectra are shown in Figure 1b. Essentially, the excitation spectra should be similar to those of absorption. The colloid solutions prepared in this work, however, have a sharp peak in the excitation spectrum except for colloid d, which was prepared by hydrolyzing the zinc acetate with a low concentration of lithium hydroxide, 0.0125 M. The onset of excitation shifts to lower wavelengths with decreasing concentrations of lithium hydroxide just as in the absorption spectra. Such peculiar excitation spectra are considered to be due to the fact that the concentration of ZnO particles in the colloidal suspensions prepared in this work is so high that the incident light cannot penetrate the quartz cell used to measure luminescence spectra. Figure 2 shows the relationship between the absorption of incident light and the

wavelength. The symbols I_0 and I in the figure denote the intensities of the incident light and the transmitted light, respectively. In the case of colloid a, which was prepared by hydrolyzing with 0.1 M lithium hydroxide, the incident light of lower wavelength is almost totally absorbed except for a part near the onset wavelength of absorption. This implies that incident light of lower wavelength is absorbed in a thin layer in the front part of the cell due to the high concentration of ZnO particles. Actually, a strong visible luminescence is also observed in the front part of the cell at these lower wavelengths. Except for a small portion of the spectrum near the onset of absorption, visible luminescence cannot be detected, and the excitation spectrum has a sharp peak around the onset wavelength only. In such cases, the luminescence intensity has no significant meaning. On the other hand, colloid d, in which the concentration of ZnO particles is low due to the smaller dose of lithium hydroxide, absorbs only a part of the incident light. In this case, all of the particles in the cell can be excited. Here, the excitation spectrum is similar to that of absorption.

The emission spectra (Figure 1b), which are generated at the peak wavelength or the top wavelength of the shoulder in the excitation spectra, show broad visible luminescence. The peak wavelength as shown by arrows is altered in a complicated manner by decreasing the concentration of lithium hydroxide. At the same time, the onset of absorption and excitation spectra shifts to lower wavelength. In other words, the blue shift of emission accompanying the reduction of particle size cannot be recognized. These results suggest that a change in the visible luminescence properties cannot be explained by only a change in particle size and that the surface properties of ZnO particles or the reaction byproducts included in the colloidal suspension also affect the luminescence properties as suggested in our previous paper.[12]

B. Evaluation of the Visible Luminescence Properties with Energy Differences between the Band Gap and Emission Energy. To quantitatively evaluate the visible luminescence properties of ZnO particles, the energy difference, ΔE, between the band gap, E_g, and the emission energy, E_{em}, which can be obtained from the onset wavelength of absorption, λ_{onset}, and the peak wavelength of emission spectrum, λ_{em}, respectively, is introduced. However, the ΔE obtained in such a way might include the effects of reaction byproducts such as acetic acid derivatives contained in the colloidal suspensions. In measuring ΔE, we attempted to reduce such effects by diluting these extraneous species with ethanol which is the main solvent.

Figure 3 shows an example of the changes of absorption and luminescence spectra of ZnO colloid by diluting with ethanol
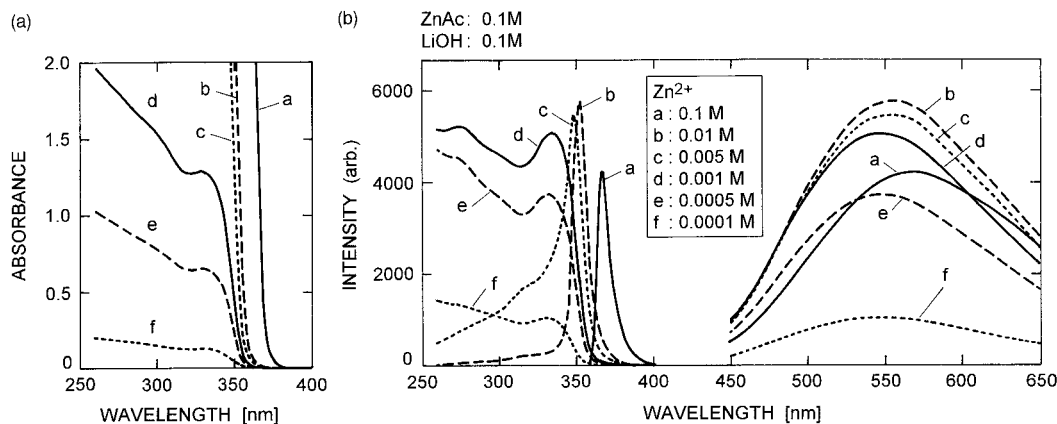

Figure 3. Absorption spectra (a) and luminescence spectra (b) of ZnO colloids diluted with ethanol of the main solvent. The original colloid was prepared by hydrolyzing the precursor containing 0.1 M Zn^{2+} with 0.1 M LiOH.
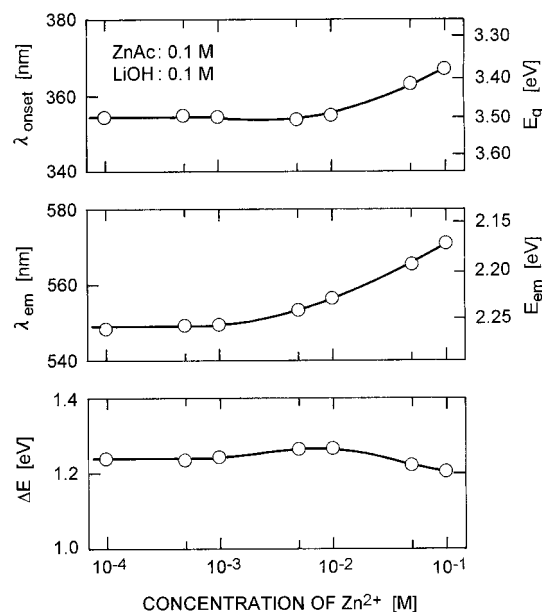
Figure 4. Changes in the onset of absorption, λ_{onset}, the peak wavelength of emission, λ_{em}, and the energy difference between band gap and emission energies, ΔE, by diluting the ZnO colloid with ethanol of the main solvent. These points were obtained from Figure 3.

from 10^{-1} M Zn^{2+} to 10^{-4} M Zn^{2+}. The colloid was prepared by hydrolyzing the precursor containing 0.1 M Zn^{2+} with 0.1 M LiOH. Even if the colloid was diluted to 10^{-4} M Zn^{2+}, the luminescence intensity was still significantly strong. With increasing dilution ratios, the onset of the absorption spectra shifts to lower wavelength with the first couple of dilutions finally becoming constant after 0.001 M (Figure 3a). The peak wavelength of the emission spectra also shifted to lower wavelength and then remained constant (Figure 3b). On the other hand, the excitation spectrum changed from a sharp peak to one similar to the absorption spectrum. This is simply due to dilution and to reduction of particle concentration as mentioned above. Furthermore, the absorbance of diluted colloid was almost proportional to the ZnO concentration. However, the intensity of emission or excitation spectra was not proportional to that even if the colloid was diluted sufficiently, although the intensity decreased by diluting. The effects of ZnO concentration on the intensity of emission spectra need to be investigated further.

In Figure 4 λ_{onset}, λ_{em}, and ΔE obtained from Figure 3 are plotted against the concentration of Zn^{2+} contained in the diluted colloids. Both λ_{onset} and λ_{em} decreased and then leveled off at a constant value with decreasing concentration of Zn^{2+} as mentioned above. According to such changes, ΔE also leveled off at a constant value under sufficient dilution. From these results, it can be said that the dilution of colloidal suspensions with ethanol enables one to evaluate ΔE without being affected by the reaction byproducts.

Figure 5 shows an example of changes in λ_{onset}, λ_{em}, and ΔE as a function of time. Both λ_{onset} and λ_{em} increase with time. These phenomena are considered due to the enlargement of particle size by particle growth and/or aggregation and the red shift of the emission wavelength accompanying such enlargement of particle size. The ΔE, however, did not change at all under the condition of sufficient dilution. These results suggest that the ΔE is independent of particle size.

C. Effects of Preparation Conditions of ZnO Colloids on Their Visible Luminescence Properties. Figure 6 shows the change in λ_{onset}, λ_{em}, and ΔE by diluting ZnO colloid solutions
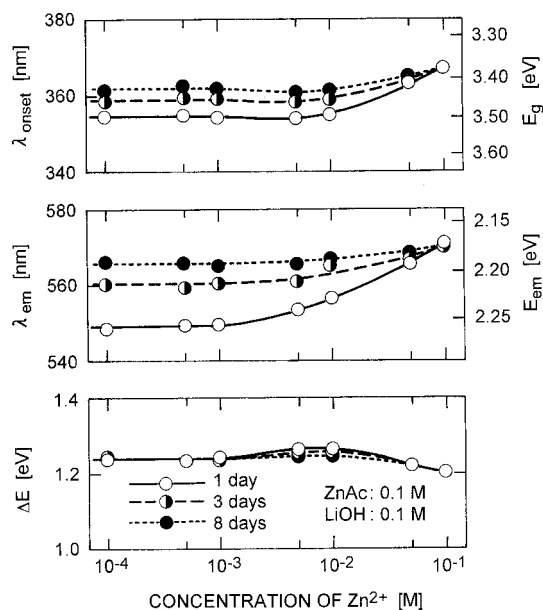
Figure 5. Changes of λ_{onset}, λ_{em}, and ΔE as a function of time. The ZnO colloid was prepared by hydrolyzing the precursor containing 0.1 M Zn^{2+} with 0.1 M LiOH.
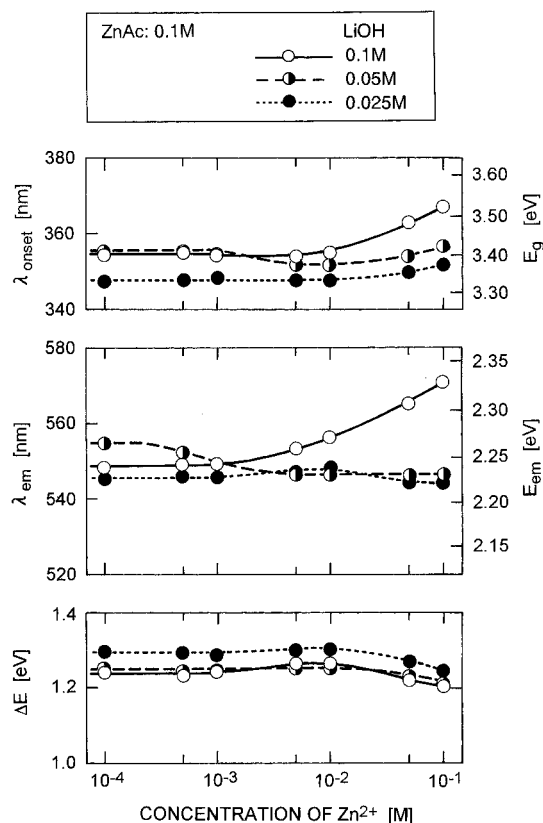

Figure 6. Effects of lithium concentration on λ_{onset}, λ_{em}, and ΔE. The ZnO colloids were prepared by hydrolyzing the precursor containing 0.1 M Zn^{2+} with various concentrations of LiOH and diluted with ethanol of the main solvent.

which were prepared by hydrolyzing the precursor containing 0.1 M Zn^{2+} using various concentrations of LiOH. The manner of change in both λ_{onset} and λ_{em} achieved by diluting the colloids differs with each colloid, and it is difficult to clearly identify the effect of the LiOH concentration. The ΔE in the region of sufficient dilution, however, was observed to increase with a decreasing concentration of LiOH. In the case of the colloidal
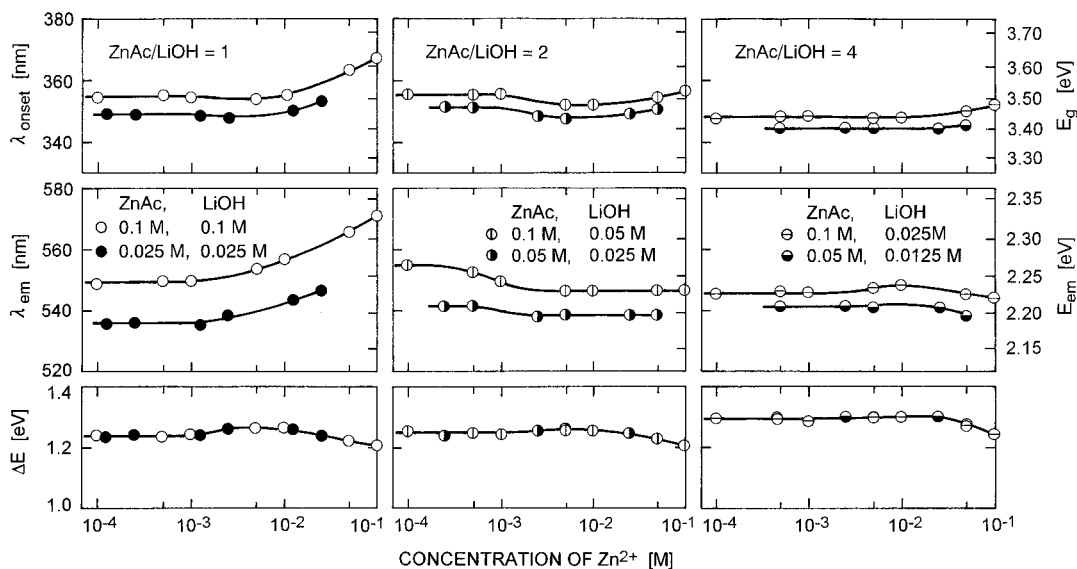
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Figure 7. Changes of λ_{onset}, λ_{em}, and ΔE by diluting ZnO colloids prepared with various concentration ratios of zinc acetate to lithium hydroxide, ZnAc/LiOH.

suspensions prepared by hydrolyzing precursors containing various concentrations of Zn^{2+} with a constant concentration of lithium hydroxide, ΔE decreased with decreasing concentrations of zinc acetate, although the results are not shown here.

To help the clarification of the effects of changing zinc acetate and lithium hydroxide concentrations on λ_{onset}, λ_{em}, and ΔE, we have plotted our results in terms of the concentration ratio of zinc acetate to lithium hydroxide, ZnAc/LiOH. These results are shown in Figure 7. As can be seen in the figure, if the ZnAc/LiOH ratios were the same, the patterns of change in λ_{onset} and λ_{em} by diluting the colloids were similar to each other, and changes in ΔE were almost the same. Furthermore, ΔE in the region of sufficient dilution was observed to increase with increasing ratios of ZnAc/LiOH. From these results, it can be said that the visible luminescence properties of ZnO ethanolic colloids largely depend on the concentration ratio of zinc acetate and lithium hydroxide used to prepare ZnO particles.

D. Thermal Analysis of ZnO Particles. Figure 8 shows the results of thermal gravimetric studies for the sample powders obtained by drying ZnO colloids under the conditions mentioned above. The colloids were prepared by using various concentrations of ZnAc and LiOH. The sample weight, which is shown by normalizing against the final weight, was observed to decrease sharply between about 200 and 350 °C, depending on the samples, and then to level off at a constant value. The weight loss is considered due to the degradation of acetate groups bound on the surface of ZnO particles as discussed in our previous paper or in the subsequent section on infrared spectroscopy.

The weight loss decreased with increasing concentrations of LiOH (Figure 8a) but increased with increasing concentration of ZnAc (Figure 8b). On the other hand, the temperature at which the weight decreased markedly, decreased with an increasing concentration of ZnAc (Figure 8a) and increased with an increasing concentration of LiOH (Figure 8b). From these results, it can be expected that both the weight loss and the degradation temperature also depend on the concentration ratio of zinc acetate to lithium hydroxide, ZnAc/LiOH. Actually, the changes of weight with temperature for the samples prepared with the same ZnAc/LiOH ratio are almost the same (e.g., ZnAc/LiOH = 1 or 2 in Figure 8a,b), and the weight loss increased with increasing ratios, while the degradation temperature
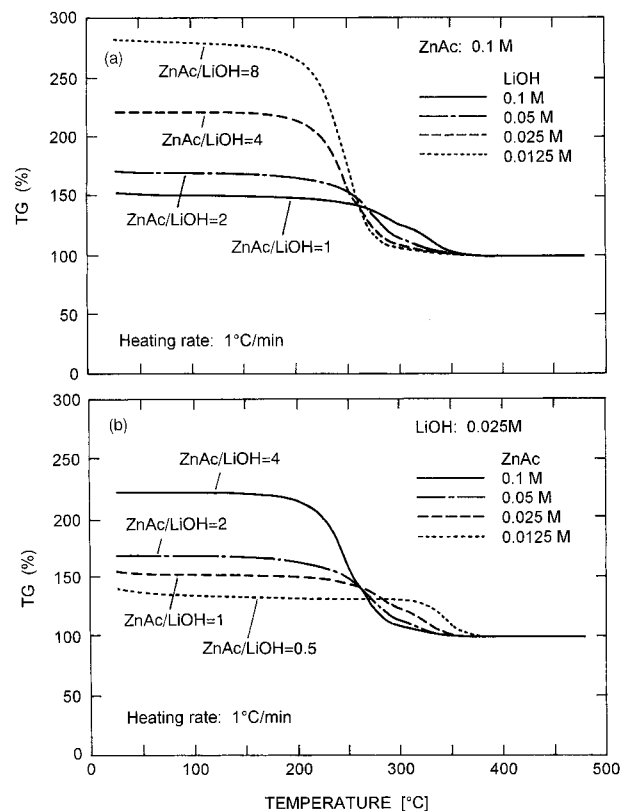

Figure 8. Results of thermogravimetry analysis for ZnO particles. The sample weight is shown by normalizing against the final weight: (a) samples prepared by hydrolyzing the precursor containing 0.1 M Zn^{2+} with various concentrations of lithium hydroxide; (b) samples prepared by hydrolyzing containing various concentrations of Zn^{2+} with 0.025 M lithium hydroxide, respectively.

decreased. From these results, it appears that the amount of acetate groups on ZnO particles also depends on the concentration ratio of ZnAc/LiOH.

Weight loss, however, was observed from about 200 °C for high ZnAc/LiOH ratios (e.g., ZnAc:LiOH = 0.1 M:0.0125 M in Figure 8a), but only from 300 °C for low ratios (e.g., ZnAc: LiOH = 0.0125 M:0.025 M in Figure 8b). These temperatures are almost coincident with those for ZnAc and LiAc, respectively. Furthermore, the weight loss of samples prepared with
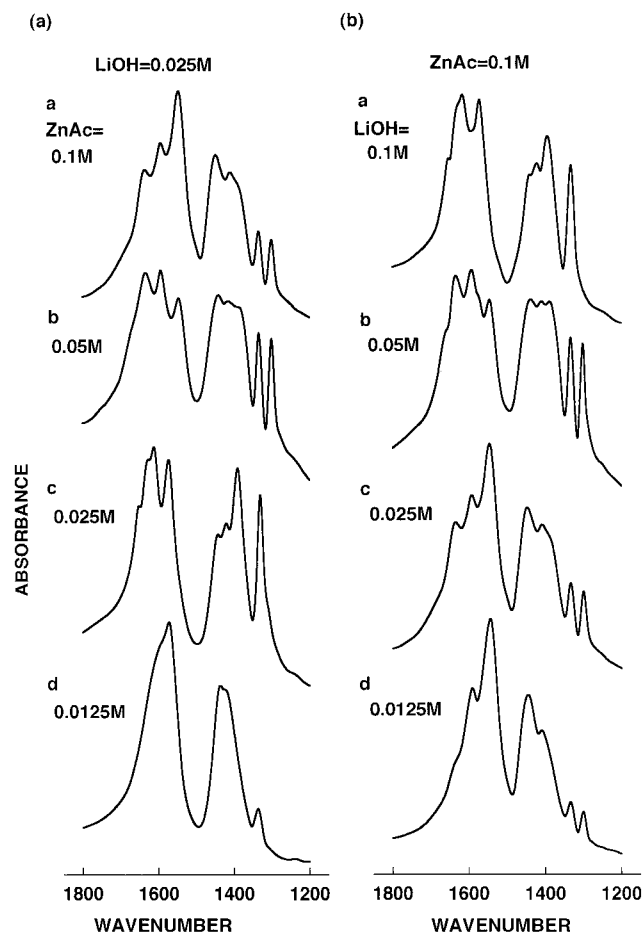
(a)   (b)

LiOH=0.025M   ZnAc=0.1M

Figure 9. Infrared spectra of ZnO particles: (a) samples prepared by hydrolyzing the precursor containing various concentrations of Zn^{2+} with 0.025 M LiOH; (b) samples prepared by hydrolyzing the precursors containing 0.1 M Zn^{2+} with various concentrations of LiOH.
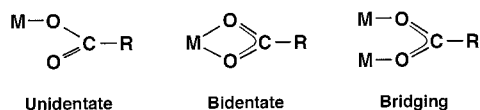

Figure 10. Types of bonding structures for acetate and metal.

high ratios seems to be too large. These facts suggest that the ZnO colloid prepared with high ratios of ZnAc/LiOH contain unreacted ZnAc and that LiOH reacts to form LiAc. These suggestions will be confirmed by infrared spectroscopy in the following section.

E. Infrared Spectroscopic Studies of ZnO Particles. Figure 9 shows the IR spectra of sample powders which were identical to those used above in the thermal analysis section. Each spectrum has two large absorption bands and some peaks in such bands. Two large bands are almost coincident with those observed typically for acetate group complexed with a metal such as zinc and correspond to C=O stretching (the left band) and C–O stretching (the right band), respectively. Some peaks in the two large bands, whose wavenumber and absorbance largely depend on the sample, are considered to be due to a variety of forms of acetate complexes present on the surface of ZnO particles, as discussed in our previous paper.[12] In general, three bonding structures are well-known for the acetate group complexed with a metal such as zinc.[14,15] These are the unidentate, bidentate (chelate), and bridging types, as shown in Figure 10. Table 1 shows the C=O and C–O stretching frequencies of these complexes.[14] Although it is difficult to resolve each of the peaks in the spectra shown in Figure 9, these

TABLE 1: Peak Wavenumber of Compounds with Zinc and Acetate Groups[14]

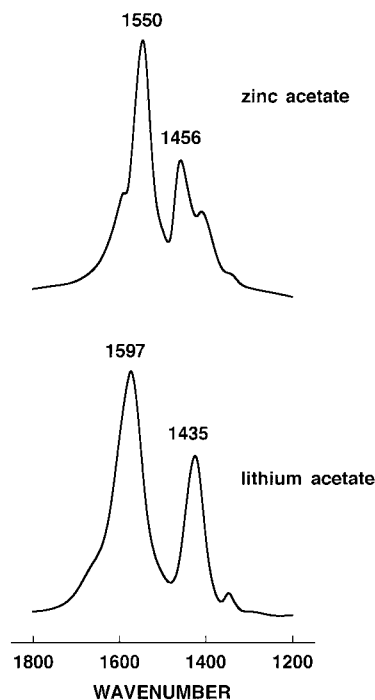|	$\nu_{C=O}$	ν_{C-O}	$\Delta\nu$
unidentate	1577	1425	152
bidentate	1550	1456	94
bridging	1600	1441	159

Figure 11. Infrared spectra of zinc acetate and lithium acetate.

results suggest that the structures of acetate complexes on the surface of ZnO particles depend on the concentrations of ZnAc and LiOH used to prepare the colloids. Although most of the samples have some peaks in the two large bands as mentioned above, the spectra of two samples prepared with low concentrations of LiOH (the spectrum of d in Figure 9a) and ZnAc (the spectrum of d in Figure 9b) are relatively simple as compared with others and are almost the same as those of ZnAc (bidentate[14]) and LiAc (bridging[14]) shown in Figure 11, which were measured in this work with KBr pellets and have the same peak wavenumbers as those shown in the literature.[14] These facts suggest that large amounts of unreacted ZnAc remain under such high ratios and that LiOH reacts to form LiAc, as mentioned in the previous section.

However, by comparing these spectra with each other, we have found that the IR spectra are almost the same under the same concentration ratio of ZnAc/LiOH, as shown in Figure 12. This fact implies that the structures of acetate complexes on the surface of ZnO particles are also determined by the concentration ratio, ZnAc/LiOH. From the results of thermal gravimetric and these IR studies, it would seem that the surface properties of ZnO particles are determined by the concentration ratio, ZnAc/LiOH. Upon comparing these results with the ΔE and the visible luminescence properties discussed using such a concentration ratio in section C above, it can be concluded that the visible luminescence properties of ZnO colloids strongly depend on the surface properties of ZnO particles, i.e., the type of acetate complex and the amount adsorbed on ZnO particles. In our previous paper,[12] it has been shown that the luminescence intensity is related to the amount of unidentate complexes present at the surface of ZnO particles and that the unidentate type of complex would appear to be more capable of trapping
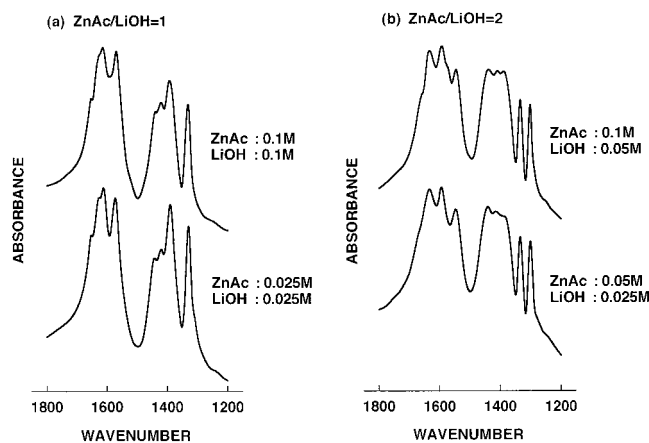
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Figure 12. Comparison of infrared spectra of ZnO particles prepared with the same concentration ratio of zinc acetate and lithium hydroxide: (a) ZnAc/LiOH = 1; (b) ZnAc/LiOH = 2.

photogenerated holes to enhance the luminescence intensity as compared with other types of complexes. The results obtained by this work were also supported by such previous results. Furthermore, the results in this work suggest that the trap depth depends on the type of complex, although further investigation is warranted.

F. Colloid Stability. The stability of ZnO colloids was also observed to depend on the concentration ratio, ZnAc/LiOH, used to prepare and hydrolyze the precursor. The colloid prepared with the high ratio, for example ZnAc:LiOH = 0.1 M:0.025 M, was quite stable and maintained transparency in a refrigerator for more than a month. Moreover, both the luminescence intensity and the peak wavelength of the emission spectrum hardly changed except for the first 1 or 2 days following its preparation. On the other hand, in the case of colloids prepared with a low ratio, for example ZnAc:LiOH = 0.025 M:0.025

M, a precipitate was observed within 2 days, despite the low particle concentration of ZnO.

Upon comparing these results with the surface properties of ZnO particles mentioned above, we find that colloidal stability depends on the amount of acetate groups bound on the surface of ZnO particles. The stability of colloids having fewer acetate groups on the surface is observed to be poor. From these results, it can be said that the acetate groups act to stabilize the colloids. Bahnemann et al.[9] found similar results as well. It can be concluded that the acetate groups on the particle surface affects both the stability and the visible luminescence properties of these colloids.

References and Notes

(1) Hoffman, A. J.; Yee, H.; Mills, G.; Hoffmann, M. R. *J. Phys. Chem.* **1992,** *96*, 5540−5546.

(2) Kamat, P. V.; Patrick, B. *J. Phys. Chem.* **1992,** *96*, 6829−6834.

(3) Zhang, Y.; Raman, N.; Bailey, J. K.; Brinker, C. J.; Crooks, R. M. *J. Phys. Chem.* **1992,** *96*, 9098−9100.

(4) Olsson, E.; Dunlop, G.; Osterlund, R. *J. Am. Ceram. Soc.* **1993,** *76* (1), 65−71.

(5) Rao, T. N.; Bahadur, L. *J. Electrochem. Soc.* **1997,** *144* (1), 179−185.

(6) Wang, H.; Chiang, Y.-M. *J. Am. Ceram. Soc.* **1998,** *81* (1), 89−96.

(7) Henglein, A. *Chem. Rev.* **1989**, *89*, 1861−1873.

(8) Spanhel, L.; Anderson, M. A. *J Am. Chem. Soc.* **1991**, *113*, 2826−2833.

(9) Bahnemann, D. W.; Karmann, C.; Hoffmann, M. R. *J. Phys. Chem.* **1987**, *91*, 3789−3798.

(10) Alivisatos, A. P. *J. Phys. Chem.* **1996**, *100*, 13226−13239.

(11) Srikant, V.; Clarke, D. R. *J. Appl. Phys.* **1997**, *81* (9), 6357−6364.

(12) Sakohara, S.; Tickanen, L. D.; Anderson, M. A. *J. Phys. Chem.* **1992**, *96*, 11086−11091.

(13) Haase, M.; Weller, H.; Henglein, A. *J. Phys. Chem.* **1988**, *92*, 482−487.

(14) Deacon, G. B.; Phillips, R. *J. Coord Chem. Rev.* **1980**, *33*, 227−250.

(15) Nakamoto, K. *Inftared and Raman Spectroscopy of Inorganic and Coordination Compounds;* John Wiley and Sons: New York, 1986*;* pp 231−233.