Synthesis of copper ion doped ZnS phosphor sols by peptization process of sulfide-citrate complex precipitates

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Optically transparent and stable sols of copper ion doped zinc sulfide (ZnS:Cu) nanoparticles were obtained by heating a mixture of ethylene glycol aqueous solution and sulfide precipitate at 348 K for 24 h. The sulfide precipitates containing zinc ions, copper ions and citrate ions were peptized in an aqueous solution of ethylene glycol having a 0.5 molar fraction of [Ethylene glycol]/([H2O]+[Ethylene glycol]). Photoluminescence characteristics and stability of the sols depended on the amount of citrate ions in the aqueous solution which was used for preparing sulfide precipitates. The citrate ions strongly affected the characteristics of the obtained sols with dispersion of the copper ion doped-ZnS nanoparticles. According to TG–DTA curves and N2 adsorption isotherms of the precipitated sulfides, the citrate ions in the aqueous solution containing zinc ions, copper ions coprecipitated in the sulfide precipitates formed by adding the sodium sulfide aq. The citrate ions played an important role for the peptization and the formation of stable sols.

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1. Introduction

Zinc sulfide (ZnS), a wide gap compound semiconductor material containing chalcogenides, is a more chemically stable and environmentally friendly material than other chalcogenides such as ZnSe and CdS.1,2,3 Because the band gap energy of ZnS nanoparticles depends on their particle size, control of the ZnS nanoparticle size enables control of their electrical and optical properties.4,5 Their luminescence characteristics can also be controlled by doping of cations in ZnS crystal lattice. Substitution of Mn2+ ions for Zn2+ ions in the ZnS lattice creates orange luminescence.6,7 Furthermore, substitution of Cu2+ ions for Zn2+ ion sites in ZnS produces green luminescence.8,9 Accordingly, methods of various kinds to control the ZnS phosphor characteristics have been investigated intensively to facilitate its various applications to flat-panel displays and electroluminescent devices. In recent years, the application of phosphor materials as a light source for light emitting devices (LEDs) has become important.8,9,10 Development of ZnS phosphor nanoparticles with dopant cations has become an important issue to prepare thin films for EL devices and composite materials with polymers for LEDs. Therefore, sols of the cation-doped ZnS nanoparticles without aggregation and precipitation are key materials for use in film and composite phosphor materials.

Copper ion doped zinc sulfide (ZnS:Cu) is a basic and important phosphor material. Various preparation methods of ZnS and ZnS:Cu nanoparticles have been reported.9,10,11,12 Manzoor et al. prepared ZnS:Cu nanoparticles by mixing the aqueous solution of zinc acetate and copper acetate with Na2S and Na2SO3 aqueous solution. PVP was used as a capping agent.11,12 Öztas et al. reported the preparation method of ZnS:Cu films using spray pyrolysis technique.13,14 Furthermore, ZnS nanoparticles were prepared by Wang et al. using a reverse micelle system as a nanostructure template.15

To obtain the ZnS:Cu nanoparticles and their stable sols in this study, peptization of complex compounds between metal sulfides and citrate ions was examined. Citrate ions coordinate to zinc ions and copper ions.16 That coordination affects the solubility of zinc sulfide and copper sulfide.17 The coordination of citrate ions to zinc and copper ions is expected to enable the formation of complex compounds between metal sulfide and citrate ions with homogeneous dispersion of the cations at the atomic level. Furthermore, it is expected that dissolution of the complex compounds causes peptization to form a sol with stable dispersion of ZnS:Cu nanoparticles. Using peptization processes of sulfide-citrate complex compounds, the formation process of ZnS:Cu nanoparticles and their stable sols were investigated in this study.

2. Experiments

2.1 Preparation of ZnS:Cu nanoparticles and their sols

ZnS:Cu nanoparticles were prepared as follows. The zinc nitrate hexahydrate [Zn(NO3)2·6H2O], copper chloride dihydrate (CuCl2·2H2O), and trisodium citrate trihydrate (Na3C6H5O7·3H2O) were dissolved in deionized water, and the total volume was adjusted to 100 mL. The concentrations of Zn2+ ions in the aqueous solutions ([Zn]) were 0.1 mol/L. The concentration of sodium citrate hydrate ([Citrate]) was 0.2 mol/L. Copper chloride was also dissolved for copper ion doping in the ZnS lattice. The concentration of Cu2+ in the aqueous solution is hereinafter referred as [Cu]. The molar ratios of [Cu]/[Zn] in the aqueous solutions were 0–0.01. Hereinafter, the molar ratio of [Cu]/[Zn] in the aqueous solution is designated as X_{Cu,Zn}. The 50 mL of Na2S·10H2O aqueous solution (0.1 mol/L) was added to the 100 mL of the aqueous solution of zinc nitrate hydrate and copper chloride hydrate. The white sulfide precipitate was obtained. The added molar amount of sulfide ions was half of that of Zn ions in the aqueous solution. When the molar amount of sulfide ions is excess against that of Zn ions, adsorbed sulfide ions on the precipitates inhibit their peptization process. In order to avoid the...
inhabitation of the peptization, the molar amount of the sulfide ions added to the aqueous solution with Zn$^{2+}$ and Cu$^{2+}$ ions was adjusted to half molar amount of the Zn$^{2+}$ and Cu$^{2+}$ ions. The obtained precipitate was then separated by centrifugation at 3000 rpm for 5 min. To remove impurities such as nitrate ions and chloride ions, the obtained precipitate was dispersed into 100 mL of ethanol and was then separated again by centrifugation at 3000 rpm for 5 min. This dispersion of the precipitate into ethanol and was then separated again by centrifugation at 3000 rpm for 5 min. The obtained sulfide precipitate was then dispersed in 100 mL of a mixed solution of ethylene glycol (EG) and H$_2$O. The molar fraction of [Ethylene glycol]/[(H$_2$O)+[Ethylene glycol]] was 0.5. Hereafter, the molar fraction of the solvents for a peptization is designated as X$_{EG}$. The solution of the dispersed sulfide precipitate in the ethylene glycol aqueous solution was heated at 348 K for 24 h in a closed glass vessel. A stable sol without precipitate was finally obtained. This synthesis procedure was also conducted using the value of X$_{EG}$ from 0 to 1 and the value of [Citrate]/[Zn] from 0 to 3. All chemicals used in this preparation were of reagent grade (Wako Pure Chemical Industries Ltd.). The solubility products of ZnS and CuS are 1.51 x 10$^{-24}$ and 7.94 x 10$^{-36}$ mol$^2$/L$^2$, respectively, at 298 K. Accordingly, the formation of sulfide precipitate adding sulfide ions into the aqueous solutions occurs quantitatively with the added amount of sulfide ions.

To separate the obtained nanoparticles in the sols, 100 mL of 0.1 mol/L NH$_3$ aqueous solution 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 ions such as ammonium ions, the obtained precipitate was dispersed into 100 mL of ethanol and was then separated again by centrifugation at 3000 rpm for 5 min. The precipitate was dried at 308 K for 24 h.

2.2 Analysis of [Cu]/[Zn] molar ratio in sulfide precipitates

The amount of copper ions included in the obtained sulfide precipitates was examined as follows. The 1.0 g of the sulfide precipitates was fired at 973 K for 1 h in air to change the sulfide to oxide powders. The obtained oxide powders were weighted and dissolved in 3.5 mL of 12 mol/L HCl aq. The 4.5 mL of 15 mol/L NH$_3$ aq was added to the HCl solution described above and [Cu(NH$_3$)$_2$]$^{2+}$ was formed in the solution. Then deionized water was added to the solution with the complex. Its total volume was adjusted to 50 mL with a mess flask. The optical absorbance at 580 nm, which is the characteristic absorption peak position of the [Cu(NH$_3$)$_2$]$^{2+}$ complex, was measured to estimate the Cu$^{2+}$ ion concentration in the solution. The molar amount of the Cu$^{2+}$ ions in a unit weight of the sulfide precipitate powder was calculated from the results. The amounts of Zn$^{2+}$ ions were also calculated based on the assumption that the obtained oxide powder was almost ZnO. The [Cu]/[Zn] molar ratio in the obtained sulfide precipitate is designated as X$_{PCu}$.

2.3 Characterization

The structure of the obtained particles was characterized using X-ray diffraction (XRD) (Cu K$\alpha$ 40 kV, 15 mA, Mini Flex; Rigaku Corp.) with a Ni filter. The particle shape was observed using transmission electron microscopy (TEM: H-67650; Hitachi High-Technologies Corp.). The ultraviolet-visible (UV–VIS) spectra of the sols and the solutions were measured using quartz cell (UV/2000; Shimadzu Corp.) with wavelengths of 300–800 nm. The photoluminescence (PL) spectra of the obtained sols were measured using excitation light at 365 nm ($\lambda_{ex}$) (RF-5300PC; Shimadzu Corp.). The N$_2$ adsorption isotherms of the obtained powders were measured at 77 K using the volumetric method (BELSORP-max; BEL Japan Inc.) after pretreatment at 383 K in 1 mPa for 1 h. The TG–DTA curves were measured (Thermo plus EVO II, Rigaku Corp.).

3. Results and discussion

3.1 Dispersion behavior of sulfide–citrate complex precipitates in ethylene glycol aqueous solution and photoluminescence characteristics of the obtained sols

Figure 1 portrays the photoluminescence (PL) spectra of the solution obtained by peptization of sulfide precipitate in H$_2$O ($X_{EG}=0$) at 348 K for 24 h. The [Cu]/[Zn] molar ratio in the aqueous solution ($X_{S,Cu}$) before the precipitation was 0.001. As shown in Figs. 1(a) and 1(b), when the molar ratios of [Citrate]/[Zn] were 0 and 0.005, the PL peak did not appear. However, when the molar ratios of [Citrate]/[Zn] were from 0.05 to 0.5, as shown in the Figs. 1(c)–1(e), the PL peak intensity around 500 nm increased with the increase of the molar ratios. This PL peak corresponds to the electron transition from the energy level of the copper ions in the ZnS lattice. Furthermore, in the case in which the [Citrate]/[Zn] molar ratios were 1.0 and 2.0, as shown in the Figs. 1(f) and 1(g), the PL peak intensity was almost saturated.

Figure 2 shows the relation between $X_{S,Cu}$, which is the [Cu]/[Zn] molar ratio in the aqueous solution and $X_{PCu}$, which is the [Cu]/[Zn] molar ratio in the obtained sulfide precipitate. The values of $X_{PCu}/X_{S,Cu}$ were 5 in [Citrate]/[Zn] = 0 and 2.
in \([\text{Citrate}]/[\text{Zn}]\) at 2 was as presented in Fig. 2. Therefore, the whole amount of \(\text{Zn}^{2+}\) ions in the solution did not precipitate with the condition of the \([\text{Citrate}]/[\text{Zn}]\) = 0. When \([\text{Citrate}]/[\text{Zn}]\) was 2, the entire of the \(\text{Cu}^{2+}\) ions and half amount of the \(\text{Zn}^{2+}\) ions included in the solutions were precipitated simultaneously because the solubility product of \(\text{ZnS}\) is much larger than that of \(\text{CuS}\) and the molar amount of \(\text{S}^{2-}\) ions added to the aqueous solution was half molar amount of the transition metal cations (\(\text{Zn}^{2+}\) and \(\text{Cu}^{2+}\)). Accordingly, the presence of citrate in the aqueous solution of zinc nitrate and copper chloride affected the degree of the homogeneous dispersion of cations in the obtained sulfide precipitates. This was also related to PL characteristics of the solution obtained by peptization of the precipitates.

To examine formation of stable sols by peptization, UV–VIS transmittance spectra were measured as shown in Fig. 3. The precipitation condition of \(\text{XS,Cu}\) = 0.001 and \([\text{Citrate}]/[\text{Zn}]\) = 2 was used for good PL intensity of the obtained sols as discussed in the Fig. 1. When a molar fraction of \(\text{XEG}\) equal to 0 (\(\text{H}_2\text{O}\)) in the solution used for the peptization of the sulfide precipitate, the optical transmittance spectrum of the obtained sols was almost 0 for wavelengths of 300–800 nm, as depicted in Fig. 3(a). This result means that the obtained solution included the aggregated particles to cause the scattering of light. Pure \(\text{H}_2\text{O}\) did not suit for the peptization of the sulfide precipitate. When the \(\text{XEG}\) value of the solution used for the peptization increased from 0.3 to 0.5, the optical transmittance above 400 nm increased from 1–83%, as shown in Figs. 3(b)–3(d). The optical transparency higher than 80% means that light scattering caused by the aggregated particles in the sols is at quite a low level. Stable sols were formed with increased \(\text{XEG}\) in the solution. Furthermore, when the \(\text{XEG}\) value increased from 0.5 to 0.8, the optical transmittance at 400 nm decreased from 83 to 0%, as shown in Figs. 3(d)–3(f). Accordingly, \(\text{XEG} = 0.5\) best suited for clear stable sol formation.

Citrate ions in the aqueous solution with the transition metal cations play important roles for the PL intensity of the obtained sols. All XRD peaks in Figs. 5(a)–5(f) can be assigned to \(\text{ZnS}\).

Figure 5 shows XRD patterns of the particles in the obtained sols. All XRD peaks in Figs. 5(a)–5(f) can be assigned to \(\text{ZnS}\). The crystallite size was estimated by using the Scherrer’s equation for the half width of the XRD peaks of \(\text{ZnS}\) (111). When \([\text{Citrate}]/[\text{Zn}]\) was 2 and \(\text{XS,Cu} = 0\) and \(\text{XEG} = 0.001\), the crystallite sizes were 5.16, 5.22, 5.34, 4.86 nm, respectively. The crystallite size slightly decreased in case that the \(\text{XS,Cu}\) was increased from 0 to 0.001. The \(\text{Cu}^{2+}\) ion doping affected the \(\text{ZnS}\) particle.
growth rate. Furthermore, as shown in Figs. 5(c) and 5(f), when $X_{SCu}$ were 0.001 and [Citrate]/[Zn] were 1 and 0, the crystallite sizes were 5.16 and 6.73 nm, respectively. When the added amount of citrate ions in the solution decreased, the crystallite size of the obtained ZnS nanoparticles increased. This result indicated that the citrate ions inhibited the ZnS nanoparticle growth process.

Figure 6 presents PL spectra of the obtained sols of ZnS:Cu. The preparation condition of the sols was XEG = 0.5 and [Citrate]/[Zn] = 2, which was the most appropriate condition for preparing clear stable sols. For $X_{SCu} = 0$, the PL peak appeared at 450 nm [Fig. 6(a)]. However, for $X_{SCu} = 0.002$, the PL peak appeared at 490 nm [Fig. 6(b)]. This result can be explained by copper ion doping. Furthermore, when the doped amount of copper ion increased from $X_{SCu} = 0.002$ to $X_{SCu} = 0.006$, the PL peak wavelength did not shift. Moreover, the intensity decreased because of the concentration extinction. Accordingly, when the sulfide precipitate of Cu$^{2+}$ and Zn$^{2+}$ ions with the citrate ions was peptized in the ethylene glycol aq of XEG = 0.5 at 348 K for 24 h, the stable sols of the ZnS:Cu phosphor particles were obtained for $X_{SCu} = 0$ to $X_{SCu} = 0.006$.

3.2 Effects of citrate ions on ZnS:Cu stable sol formation process

To examine the role of the citrate ions for dispersion of the sulfide precipitate, TG–DTA curves were measured as indicated in Fig. 7. Figure 7(a) shows the TG–DTA curve of the sulfide precipitate obtained from the aqueous solution of $X_{SCu} = 0$ with [Citrate]/[Zn] = 0. The exothermic peak with the decrease of weight appeared around 880 K. This peak corresponded to the oxidation of ZnS. However, when the aqueous solution with [Citrate]/[Zn] = 2 was used for the preparation of the zinc sulfide precipitate, the TG–DTA curve in Fig. 7(b) shows two exothermic peaks. The exothermic peak of the DTA curve around 580 K with the weight loss can be assigned to oxidation of organic compound, i.e. the citrate ions. The exothermic peak of the DTA curve around 880 K can be assigned to the oxidation of ZnS, as in the discussion on Fig. 7(a). The weight loss around 880 K in Fig. 7(b) is too small as compared with the Fig. 7(a). Partial oxidation of ZnS precipitate occurred around 580 K, at which the weight loss occurred with the exothermic process and the weight loss around 880 K was quite small. Accordingly, the sulfide precipitate obtained from the aqueous solution of the metal salts and citrate ion included the citrate ions, which affects the peptization process of the precipitates. A citrate ion is one of chelate ions so that citrate ions can coordinate to zinc ions strongly. When zinc nitrate and sodium citrate were dissolved in H$_2$O and the concentrations of [Zn] and [Citrate] were 0.1 and 0.2 M, the precipitate of zinc citrate did not occur. Furthermore, the zinc citrate precipitate did not coexist in the precipitate.

To examine the aggregated state of the sulfide particles in the precipitates, N$_2$ adsorption isotherms of the sulfides at 77 K were measured as presented in Fig. 8. When the molar ratio of [Citrate]/[Zn] = 2, as shown by the squares, the N$_2$ adsorbed amount was quite low compared to the isotherm of the precipitate of [Citrate]/[Zn] = 0 shown with the circles. The Brunauer–Emmett–Teller (BET) specific surface area ($S_{BET}$) of the sulfide precipitate with the [Citrate]/[Zn] = 0 was 176 m$^2$/g. However, when [Citrate]/[Zn] was 2, the $S_{BET}$ was 7.0 m$^2$/g. For the case in which the citrate ions coexisted, the aqueous solution and the obtained sulfide precipitate, the $S_{BET}$ value decreased greatly. This result shows that the ZnS particles in the precipitate were aggregated strongly in the case of [Citrate]/[Zn] = 2. The coordinated citrate ions on the ZnS particle surface caused the aggregation and the interparticle pores decreased. Dissolution process of the citrate complex of zinc ions among the sulfide particles accelerated the peptization and dispersion of the sulfide nanoparticles in the precipitate.

The TEM images of the ZnS precipitate with the citrate ions obtained with the condition of the [Citrate]/[Zn] = 2 are shown in Fig. 9(a). The average particle diameter was 11.1 nm. The particles in the sol prepared by peptization of the ZnS precipitate with the aqueous solution ($X_{EG} = 0.5$) at 348 K for 24 h were
the desorption isotherms. The symbols represent the adsorption isotherms. The closed symbols represent citrate ions in the aqueous solution of ethylene glycol. Accordingly, dissolving the decreased after peptization. The citrate dissolved readily into the aqueous solution used for obtaining the sulfide precipitate. The PL intensity increased concomitantly with the increase of the molar ratio of [Citrate]/[Zn] in the aqueous solution formed during the peptization process enabled the formation of the stable sols.

4. Conclusion

Transparent and stable sols with dispersion of copper ion doped zinc sulfide (ZnS:Cu) nanoparticles were obtained by heating a mixture of ethylene glycol aq and sulfide precipitate at 348 K for 24 h. The sulfide precipitate obtained from the aqueous solution of zinc nitrate, copper chloride, and sodium citrate was well peptized into the ethylene glycol aq whose X_{EG} value was 0.5. Furthermore, the PL characteristics and the stability of the sols depended on the amount of citrate ions in the aqueous solution of zinc nitrate and copper chloride used for obtaining the sulfide precipitate. The PL intensity increased concomitantly with the increase of the molar ratio of [Citrate]/[Zn] in the aqueous solution used for obtaining the sulfide precipitate. Furthermore, when [Citrate]/[Zn] was 2, the peptization occurred. Then clear and stable sols of ZnS:Cu were obtained. The citrate ions strongly affected the characteristics of the obtained sols with dispersion of the ZnS:Cu particles. According to the TG–DTA curves and the N2 adsorption measurements of the sulfide precipitates, the citrate ions in the aqueous solutions were coprecipitated into the sulfide precipitates formed by adding the sodium sulfide aqueous solution. Dissociation of the citrate into the ethylene glycol aq during the peptization process enabled the formation of the stable sols.

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![Graph](image-url) Fig. 8. N2 adsorption isotherms of the sulfide precipitates. The [Citrate]/[Zn] molar ratios were ○, ● and □, 2. The open symbols represent the adsorption isotherms. The closed symbols represent the desorption isotherms.

![TEM images](image-url) Fig. 9. TEM images of the sulfide precipitates and particles in the obtained sol. The [Citrate]/[Zn] molar ratio was 2. (a) TEM image of the sulfide precipitate. (b) TEM image of the particles in the sol obtained by peptization.