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Preparation of ZnS and CdS fine particles with different particle sizes by a spray-pyrolysis method

KIKUO OKUYAMA*, I. WULED LENGGORO, NORIKAZU TAGAMI
Department of Chemical Engineering, Hiroshima University, Kagamiyama, Higashi-Hiroshima 739, Japan
SHINKICHI TAMAKI, NOBORU TOHGE‡
Department of Industrial Engineering and ‡Department of Metallurgical Engineering, Kinki University, Kowakae, Higashi-Osaka 577, Japan

In the preparation of ZnS and CdS fine particles by an ultrasonic spray-pyrolysis method, the particle size was changed from submicrometre to micrometre size by changing the concentration of the metal nitrates in the starting aqueous solution containing $Zn(NO_3)_2$ or $Cd(NO_3)_2$ and $SC(NH_2)_2$. The effects of temperature profile in the reactor furnace on the properties of prepared particles were also investigated by varying the temperature profiles: constant and increasing temperature distributions. The volume mean diameter of the prepared particles was found to be approximately proportional to the one-third power of the concentration of the metal nitrates in the solution. The crystalline phase and fluorescence properties of ZnS and CdS particles did not depend on the particle size.

1. Introduction

The particle preparation process in which submicrometre-sized particles are dispersed in the gas phase is called aerosol synthesis. Aerosol synthesis can be divided into the gas-to-particle conversion process and droplet-to-particle conversion process [1, 2]. The preparation of fine particles using aerosol processes has become an important technique in making carbon black, oxide ceramic and magnetic materials. The spray-pyrolysis method is a representative droplet-to-particle conversion process, which has the following advantages: (i) the particles produced are spherical, (ii) the distribution of their diameters is uniform and controllable from micrometre to submicrometre, (iii) the purity of the products is high and (iv) the process is continuous. This technique has been applied to the preparation of a variety of particles. The authors have recently prepared several metal oxide particles such as high-T_c oxide superconductors in the Y–Ba–Cu–O and Bi–(Pb)–Ca–Sr–Cu–O systems, ZnO and ZnO–TiO_2 composites [3–6]. In general, aqueous solutions of metal salts are used as solutions to be sprayed, and the pyrolysed products are the particles of oxides.

On the other hand, thiourea forms complexes with a variety of metal salts in aqueous and alcoholic solutions. These thiourea complexes can be thermally decomposed to form metal sulphides and thus solutions containing thiourea complexes are used to prepare metal sulphide films by the spray deposition process (chemical aerosol deposition technology: CADT) and dip-coating process [7–11]. Thiourea complexes also have recently been applied to disperse sulphide particles of nanometre-size in silica glasses through the sol–gel process [12, 13]. In our previous papers [14, 15], we have confirmed the availability of spray-pyrolysis technique as a direct preparation process of fine powders of ZnS and CdS. In these studies, preparation conditions where ZnS and CdS particles were produced directly, were discussed without changing the concentration of the starting solution. In the spray-pyrolysis process, the particle size and morphology can be changed depending on the heating temperature, the rate of solvent evaporation, and the concentration of starting solutions.

In this study, the formation of fine particles of ZnS and CdS with different particle sizes was investigated by changing the concentration of the aqueous solutions of the corresponding thiourea complexes and the temperature profile in the reactor. The morphology and crystalline phase of metal sulphide particles were studied in terms of the preparation conditions and concentration of spraying solution, namely, the particle size distributions were controlled by changing the concentration of the spray solutions. The crystalline phases and fluorescence property of fine particles were examined as a function of particle size. The main goal was to demonstrate that the spray-pyrolysis method is an available and promising technique for the preparation of standard metal sulphide fine particles with different particle sizes.

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*Author for correspondence.

2. Experimental procedure

The system used for the preparation of ZnS and CdS fine particles is schematically shown in Fig. 1. This spray-pyrolysis system, which was similar to the system used in a previous study [15], consisted of an ultrasonic nebulizer, a reaction furnace and an electrostatic precipitator. The starting solution was atomized at a frequency of 1.75 MHz by an ultrasonic nebulizer (Omron Co., Model NE-U11B), which was cooled with running water and the level of the spray solution was kept constant, to ensure a constant rate of generation of droplets. The spray solution was prepared by dissolving the correct amounts of $Zn(NO_3)_2$ or $Cd(NO_3)_2$ and thiourea $SC(NH_2)_2$ into ultrapure water. The concentrations of $Zn(NO_3)_2$ and $Cd(NO_3)_2$ were changed from 0.001 to 0.1 $mol\,l^{-1}$ and from 0.01 to 0.3 $mol\,l^{-1}$, respectively, while the molar ratio of $Zn(NO_3)_2$ and $Cd(NO_3)_2$ to thiourea was kept at 1:2, respectively [13]. The tubular furnace, or laminar flow aerosol reactor, used in the present study was a high-quality ceramic tube of 15 mm inner diameter and about 1000 mm long. The reaction furnace consisted of five independently-controlled heating zones, each 200 mm in length, separated by about 5 mm low-density insulation zones. The temperature of each heating zone was controlled to within 2 °C with a temperature controller: T_1, T_2, T_3, T_4, and T_5 indicate the wall temperatures at the middle of the each heating zone. The setting of five zones enables provision of the desired temperature distribution.

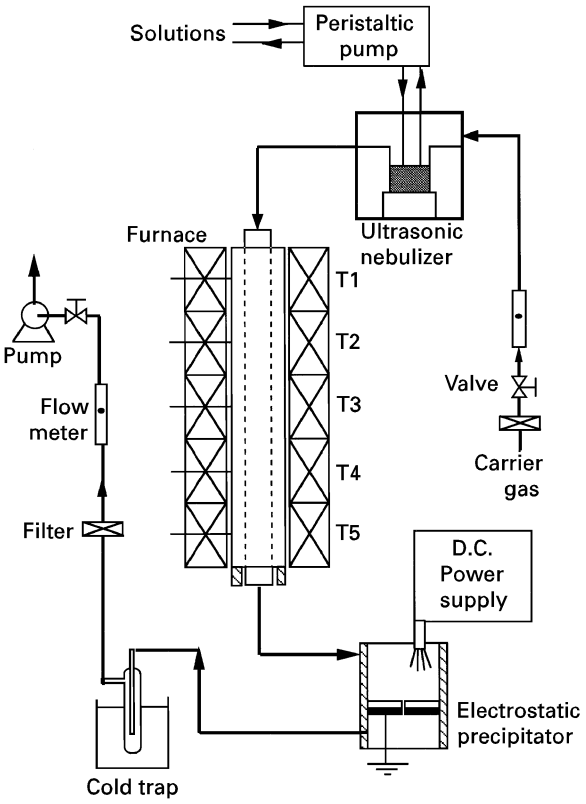


Figure 1 Schematic presentation of the ultrasonic spray-pyrolysis system used in the present study.

In the present work, temperature profiles varied around 600 °C in ZnS preparation, and around 700 °C in the case of CdS preparation. Good crystallinity of ZnS and CdS particles can be formed at temperature profiles varying around 600 and 700 °C, respectively, as described in our previous papers [14, 15]. The present work also investigated the effects of the temperature distribution on the crystalline phases and morphology of the particles. Fig. 2 shows the temperature profiles in the reactor for two typical cases, (i) constant and (ii) increasing distributions.

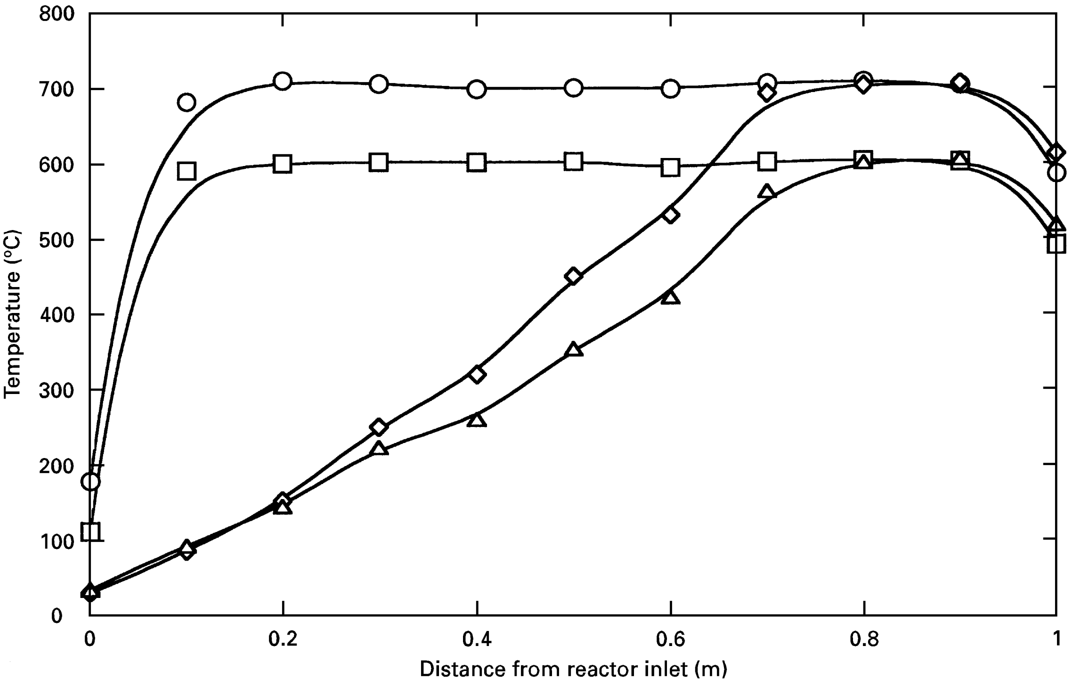


Figure 2 Measured temperature profiles in the reaction furnace for two typical cases: (i) constant and (ii) increasing temperature distributions. Key: –○– constant (CdS); –□– constant (ZnS); –◇– increasing (CdS); –△– increasing (ZnS).

The generated droplets were carried to the reaction furnace by N_2 gas, with a flow rate of 2.0 $l\,min^{-1}$, the corresponding residence time of a carrier gas in the furnace being estimated to be 5.3 s. The particles generated from the furnace exit were collected using an electrostatic precipitator, which was maintained at around 250 °C, to avoid the condensation of water on the particles [14].

The particles obtained were examined by X-ray diffraction (CuK_α, XRD, Rigaku-Denki Corp., model RINT 1000), scanning electron microscopy (SEM, Jeol Corp., model JSM-T100), respectively.

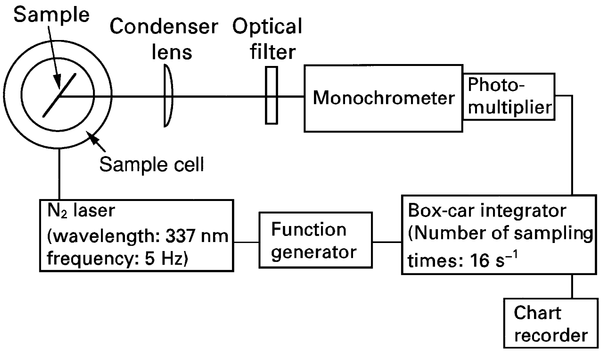


Figure 3 System for the measurement of fluorescence of the particles.

The fluorescence measurement system consisted of a N_2 laser (377 nm in wavelength) as the excitation light source, a sample cell, a monochrometer, a photo-multiplier, a box-car integrator and a function generator as the supplier of code to laser and box-car integrator (Fig. 3). An optical filter (UV36) was installed in a monochrometer to cut the excitation light reflecting from the sample cell. Each sample was spread on a non-fluorescent quartz plate with acetone, and after that, the samples were dried. All this equipment was placed inside a vessel under vacuum conditions, and cooled down to 80 ± 3 K by liquid nitrogen.

3. Results and discussion

3.1. ZnS particle preparation

Fig. 4 shows X-ray diffraction patterns of the ZnS particles obtained from different solution concentrations at a constant temperature distribution of 600 °C. The peaks assigned to the hexagonal phase of ZnS can be seen for all solution concentrations, but the peak height tends to decrease with decreasing solution concentration, showing a decrease in crystallite size.

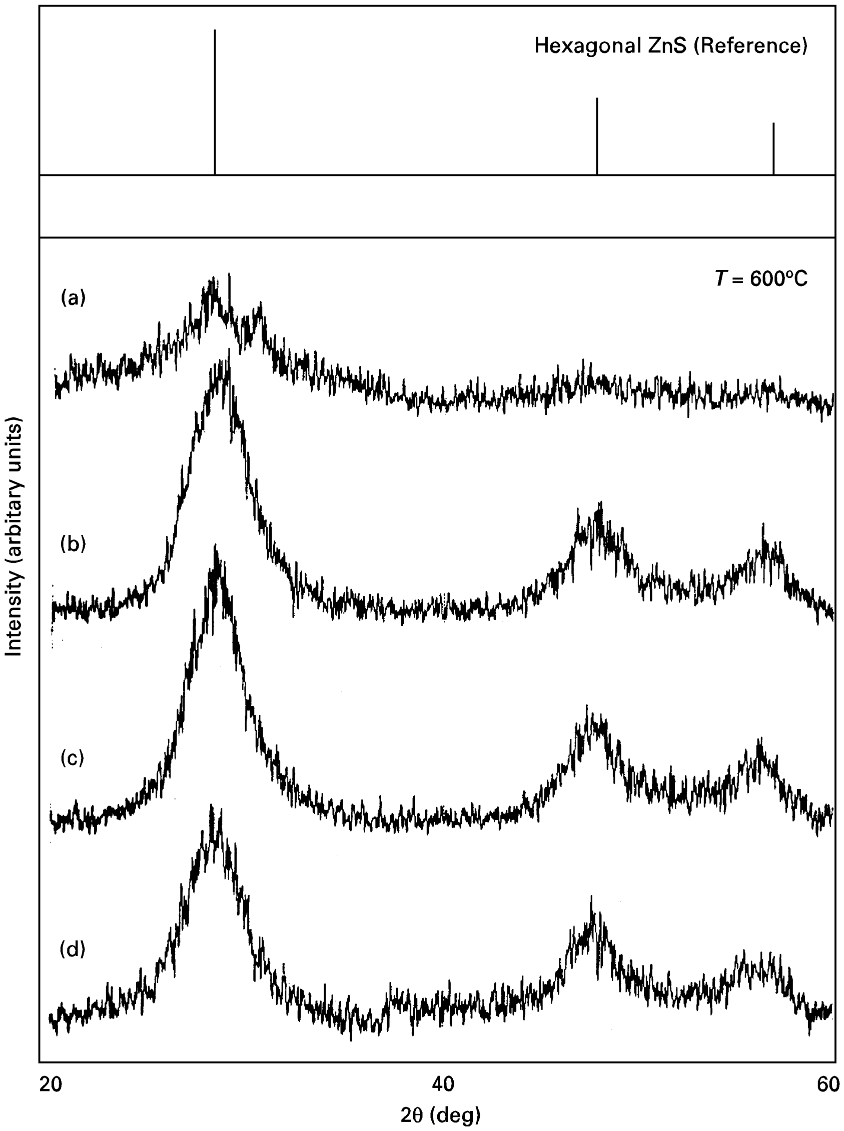


Figure 4 X-ray diffraction patterns of ZnS particles prepared at different starting-solution concentrations (C_S); (a) 0.001 mol l^{-1}, (b) 0.05 mol l^{-1}, (c) 0.1 mol l^{-1} and (d) 0.5 mol l^{-1}.

In the pattern of particles generated at the metal nitrate concentrations of 0.05 and 0.1 $\mathrm{mol\,l^{-1}}$, their peaks show that ZnS particles of good crystallinity are formed.

Fig. 5 shows SEM photographs of ZnS particles prepared under the same conditions as those in Fig. 4. As observed in the previous paper [14], the surface of the particle is found to be rather smooth. As the concentration increases, it can be observed that the particle sizes also increase. At the lowest concentration of 0.001 $\mathrm{mol\,l^{-1}}$, the prepared particles necked together, but at higher concentrations, particles seem to be separately formed. This shows that the particle size can be controlled by changing the concentration of the starting solution.

Fig. 6 shows the fluorescence spectral of the ZnS particles obtained by changing the solution concentration, 0.01, 0.05, and 0.5 $\mathrm{mol\,l^{-1}}$. For all the particles, a rather broad emission peak is observable at around 475 nm. This emission can be ascribed to the electronic transition involving defect or impurity centres but not to the band transition, because the excitation energy (N_2 laser) used here was insufficient for the excitation of fundamental adsorption of ZnS. There are no changes of fluorescence spectra in these concentration ranges. Thus, particle size did not affect the fluorescence spectra in this range.

3.2. CdS particle preparation

Fig. 7 shows XRD patterns of particles prepared at 700 °C from different starting solutions: 0.01, 0.05, 0.1 and 0.3 $\mathrm{mol\,l^{-1}}$. As with ZnS particles, the peaks assigned to the cubic phase of CdS can be seen for all

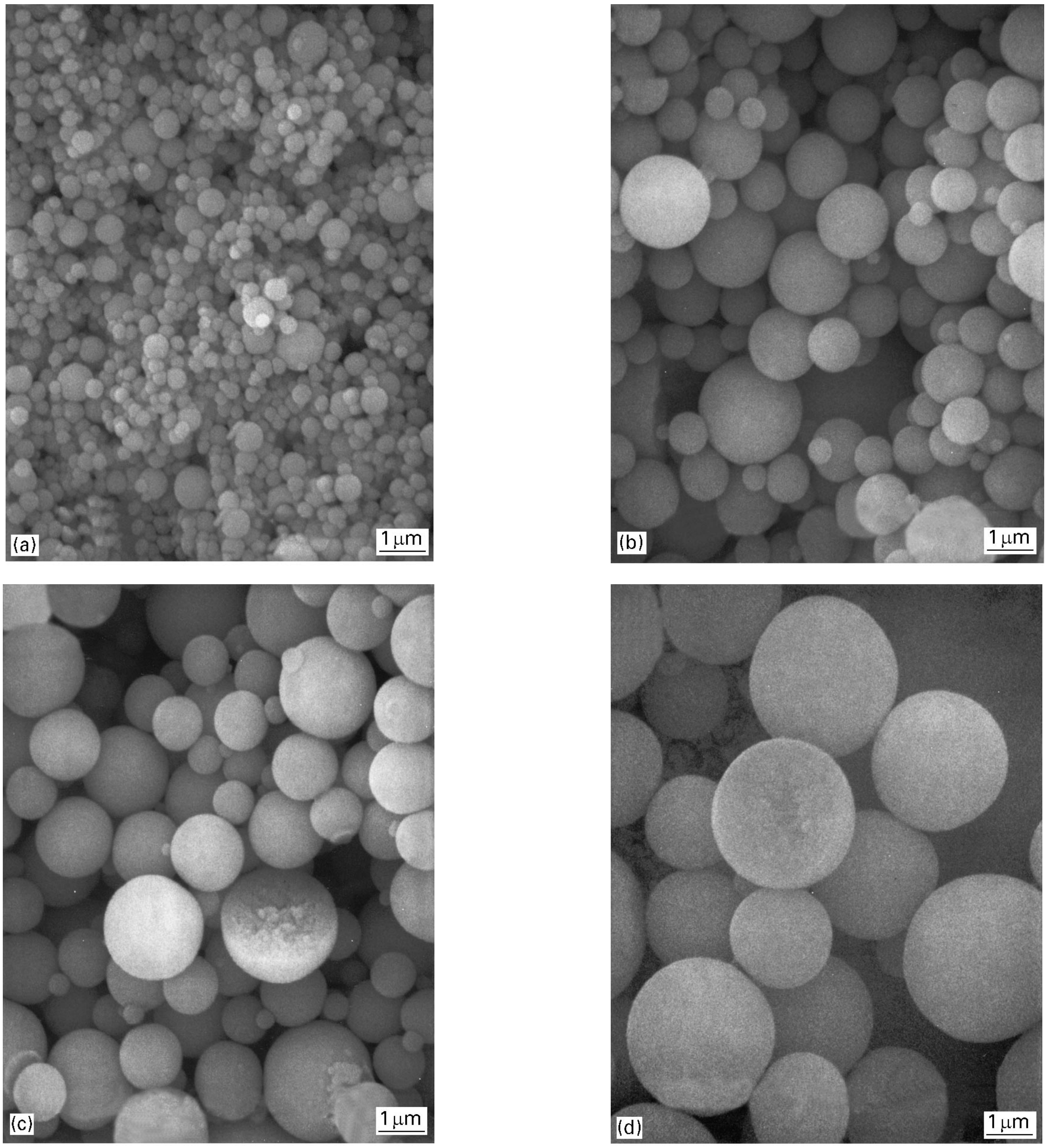


Figure 5 SEM photographs of ZnS particles prepared at different starting-solution concentrations (C_S); (a) 0.001 $\mathrm{mol\,l^{-1}}$, (b) 0.05 $\mathrm{mol\,l^{-1}}$, (c) 0.1 $\mathrm{mol\,l^{-1}}$ and (d) 0.5 $\mathrm{mol\,l^{-1}}$.

Figure 7 X-ray diffraction patterns of CdS particles prepared at different starting-solution concentrations (C_S); (a) 0.01 $\mathrm{mol\,l^{-1}}$, (b) 0.05 $\mathrm{mol\,l^{-1}}$, (c) 0.1 $\mathrm{mol\,l^{-1}}$ and (d) 0.3 $\mathrm{mol\,l^{-1}}$.

solution concentrations, but the peak height tends to decrease with decreasing solution concentration showing a decrease in crystallite size. Fig. 8 shows SEM photographs of CdS particles prepared at different concentrations. CdS particles have rough surfaces due to the growth of crystallites in the particles, whereas the surface of ZnS was smooth. The rough surface originated from primary particles which aggregated together. It shows that both aggregation and primary particle sizes become larger with increasing solution concentrations.

Fig. 9 shows the fluorescence spectra of CdS particles obtained by changing the solution concentration, 0.01, 0.05, and 0.5 mol l^{-1}. These particles show a sharp emission peak at around 500 nm, which is very close to the band gap of CdS. As ZnS particles, there are no changes of fluorescence spectra in these concentration ranges, indicating that CdS particle size did not affect the fluorescence spectra.

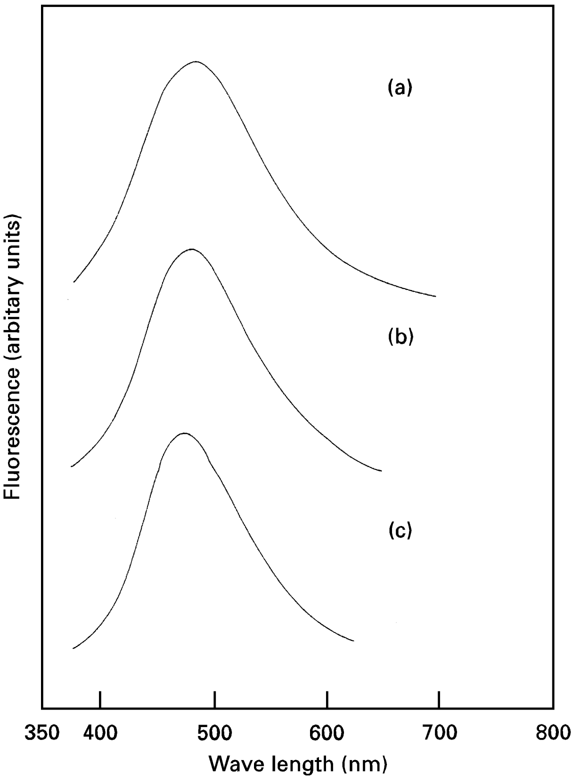
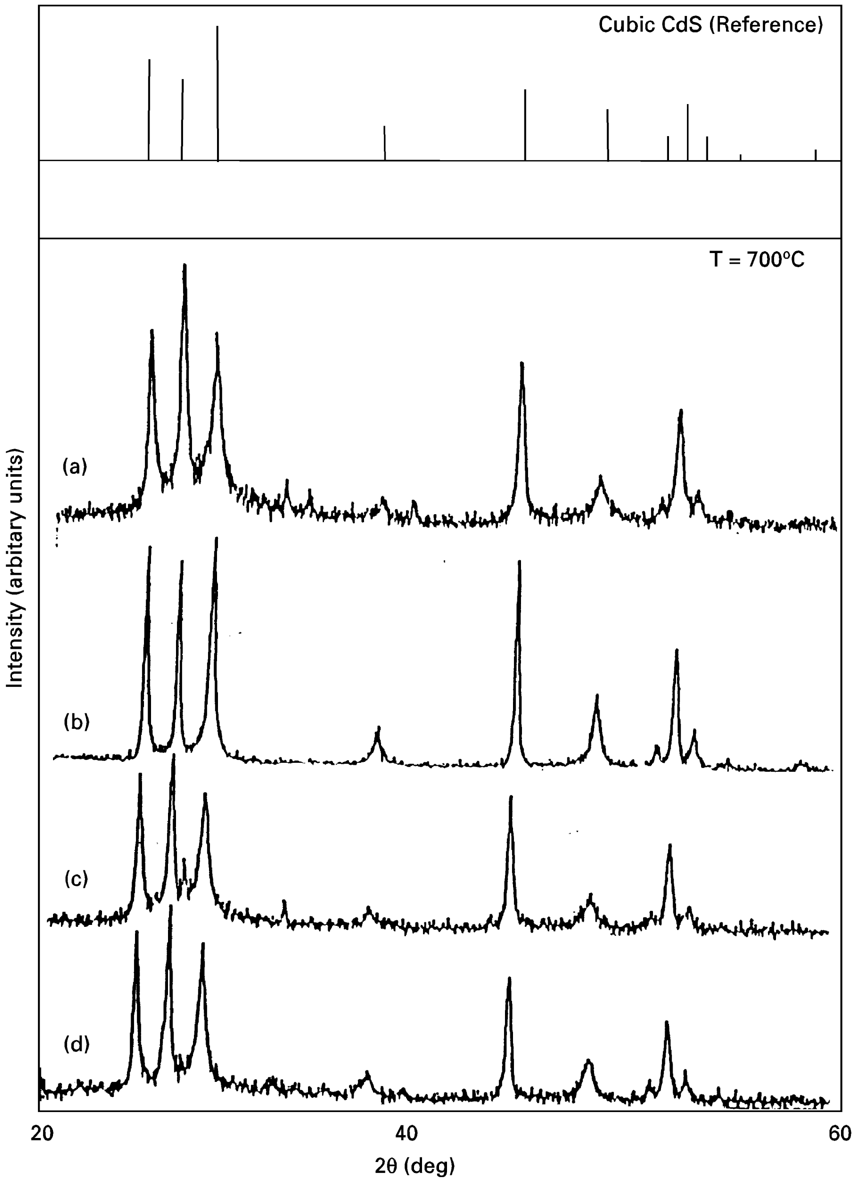


Figure 6 The relation between the fluorescence spectra of ZnS particles and the starting-solution concentrations (C_S); (a) 0.01 mol l^{-1}, (b) 0.05 mol l^{-1}, and (c) 0.5 mol l^{-1}.



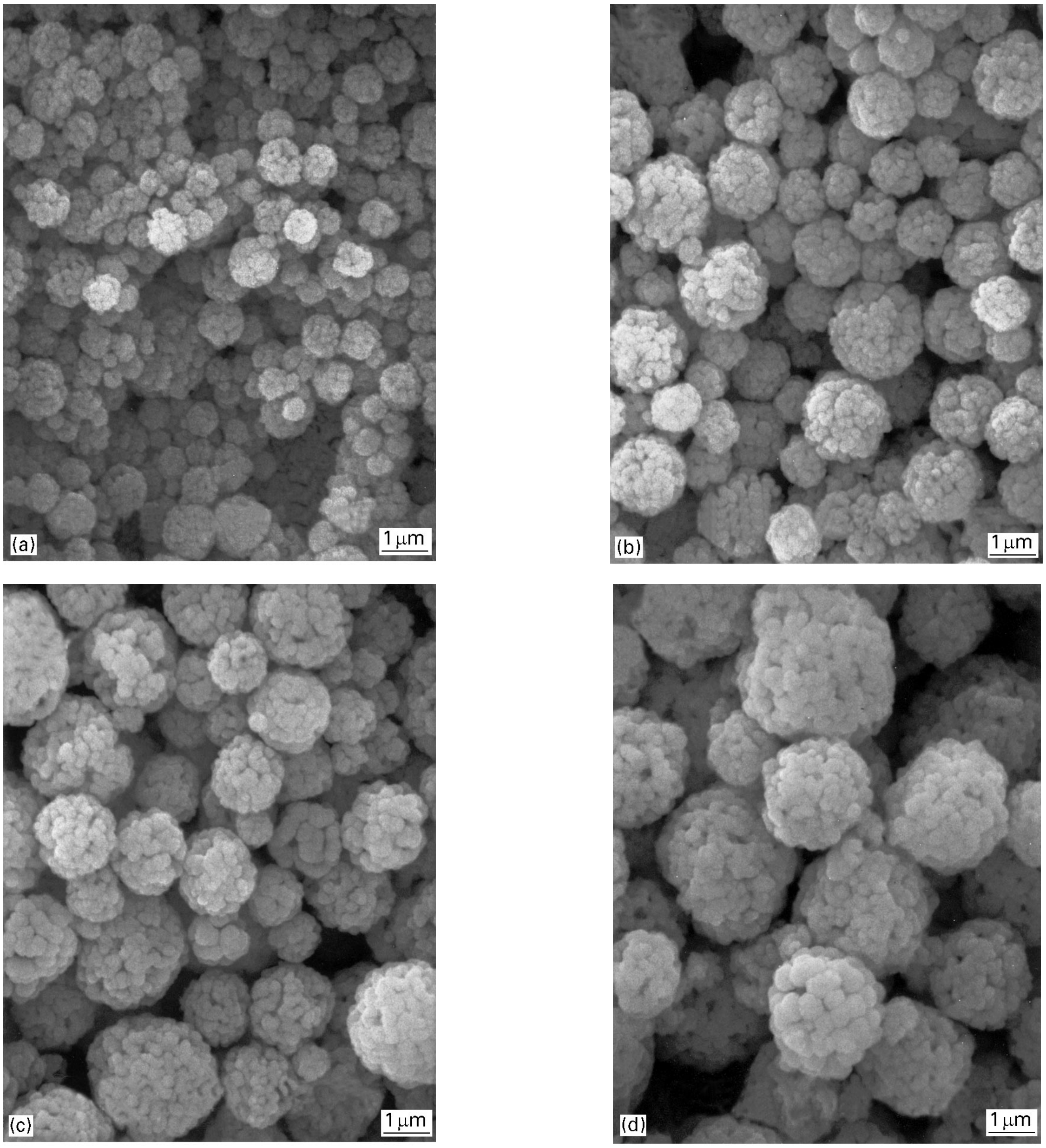


Figure 8 SEM photographs of CdS particles prepared at different starting-solution concentrations (C_S); (a) 0.01 $\mathrm{mol\,l^{-1}}$, (b) 0.05 $\mathrm{mol\,l^{-1}}$, (c) 0.1 $\mathrm{mol\,l^{-1}}$ and (d) 0.3 $\mathrm{mol\,l^{-1}}$.

3.3. The effects of the temperature distribution on the characteristics of the particles

In the increasing temperature distribution, the temperatures were set so that the particles were subjected to gradual evaporation and subsequent nucleation in the liquid-to-particle conversion process.

In the present work, the effects of the temperature distribution on the crystalline phases and morphology of the particles were expected. We prepared ZnS and CdS particles under the temperature profiles of the reactor furnace for the two typical cases described in Fig. 2, respectively. The X-ray diffraction patterns and SEM photographs of the particles obtained for the two cases of reactor temperature distributions are shown in Figs. 10 and 11.

The X-ray diffraction patterns and SEM photographs of the particles obtained at increasing reactor temperature distributions showed trends similar to the characteristics of particles prepared at constant reactor temperature. But the SEM photographs of the CdS particles (Fig. 11b) showed a morphological change. Comparing with the particles obtained at increasing temperature, at constant reactor temperature distributions sintered-like primary particles of CdS were observed. More studies are needed to investigate the effects of temperature distribution of the reactor furnace, since only the crystalline phases and morphology of the particles were examined in this work.

3.4. Relation between particle size and concentration of metal nitrate

The relation between the droplet size and the solid particle size was discussed by Zhang and Messing [16] and by Pluym *et al.* [17].

Now, assuming that one droplet changed into one dense spherical particle inside the reaction furnace, the final volume mean diameter of the solid fine particles, d_p, can be given by the following equation, derived from the mass balance of the system.

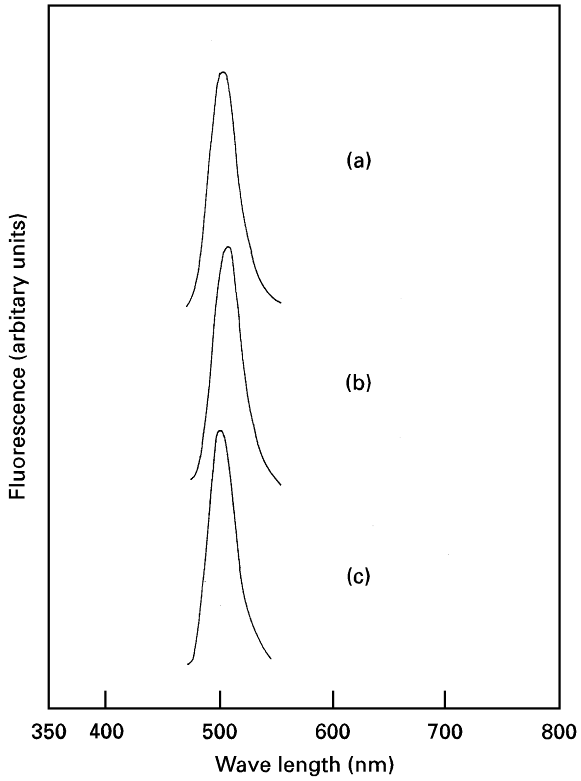


Figure 9 The relation between the fluorescence spectra of CdS particle and the starting-solution concentrations (C_S); (a) 0.01 mol l^{-1}, (b) 0.05 mol l^{-1}, and (c) 0.5 mol l^{-1}.

$$d_p = \left(\frac{M}{\rho_p}\frac{D_p^3}{1000}C_S\right)^{1/3} \tag{1}$$

where C_S is the concentration of the solution in mol l^{-1}, M is the molecular weight, ρ_p is the theoretical density of ZnS and CdS, and D_p is the volume mean diameter of the solution droplets. For ZnS, ρ_p is known to be 4.09 g cm^{-3} and M is 97.46 and for CdS, ρ_p is reported to be 4.80 g cm^{-3} and M is 144.47. Accordingly, Equation 1 can be written as

$$\text{ZnS: } d_p = 0.288\, D_p C_S^{1/3} \tag{2}$$

$$\text{CdS: } d_p = 0.311\, D_p C_S^{1/3} \tag{3}$$

Fig. 12 shows the changes in the volume mean diameter d_p, of ZnS and CdS particles formed with the concentration of the starting aqueous solution, C_S. Fig. 13 shows a volume mean diameter distribution of atomized water droplets using an ultrasonic nebulizer; this was measured by a light-scattering particle-size analyser (Malvern Instruments Corp., Mastersize DPF). Δn is the number concentration in the size range, and N is the total particle number concentration. The average volume mean diameter of water droplets was 4.56 µm. The droplet size distribution did not change for the concentration range of metal nitrate in the solution used in this experiment. The solid lines in Fig. 12 are Equation 1.

ZnS particle size agrees quite well with the theoretical results. CdS particle size was shown to be bigger

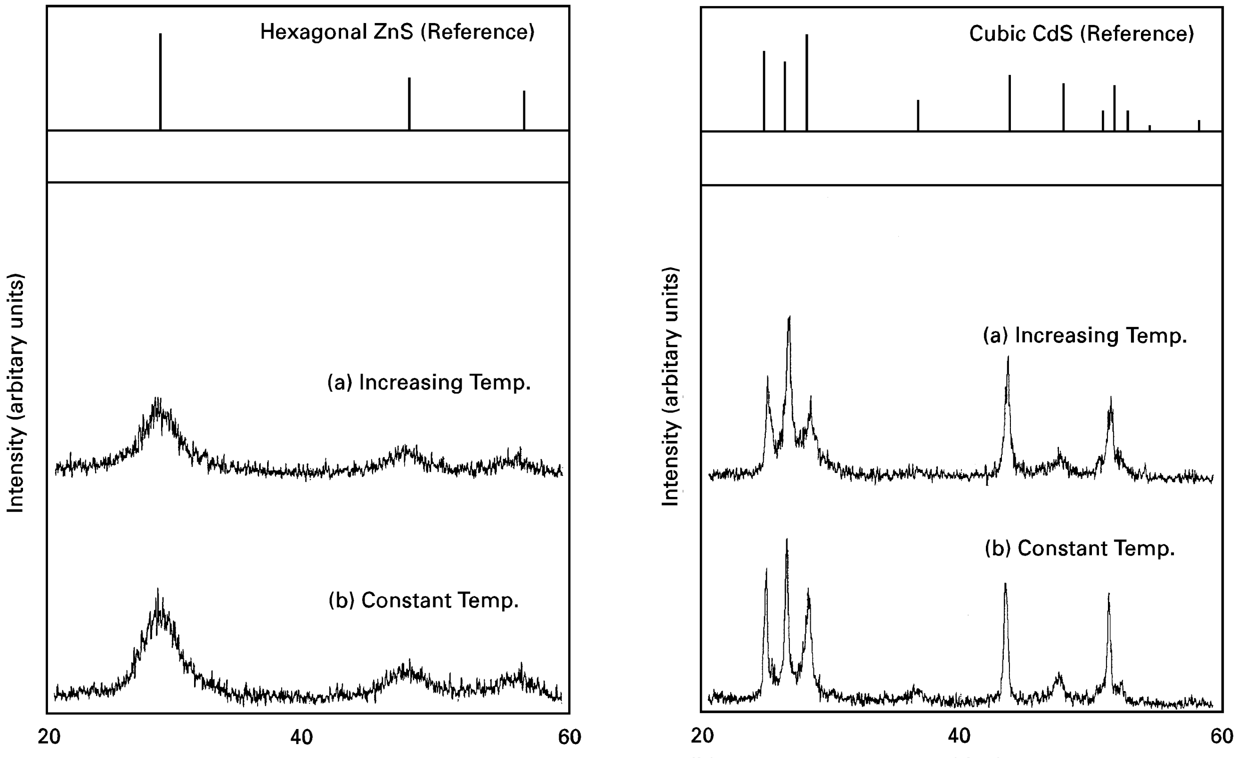
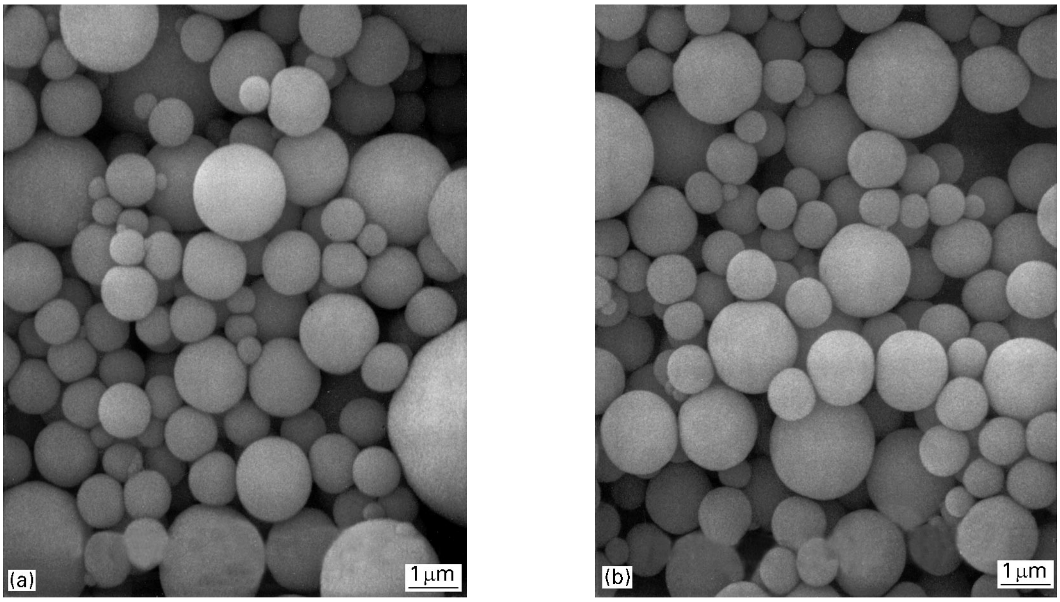
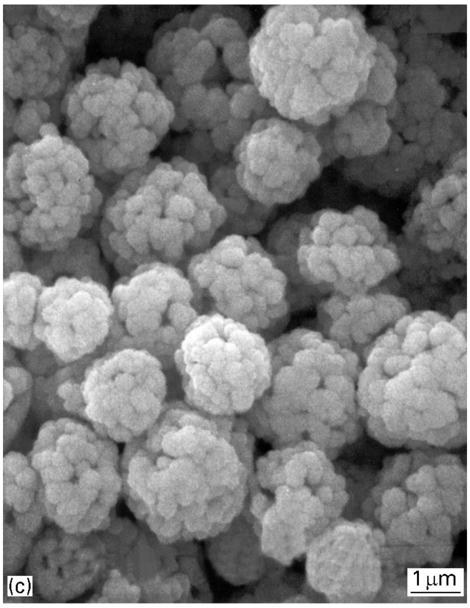


Figure 10 X-ray diffraction patterns of ZnS and CdS particles prepared at constant and increasing temperature distribution.





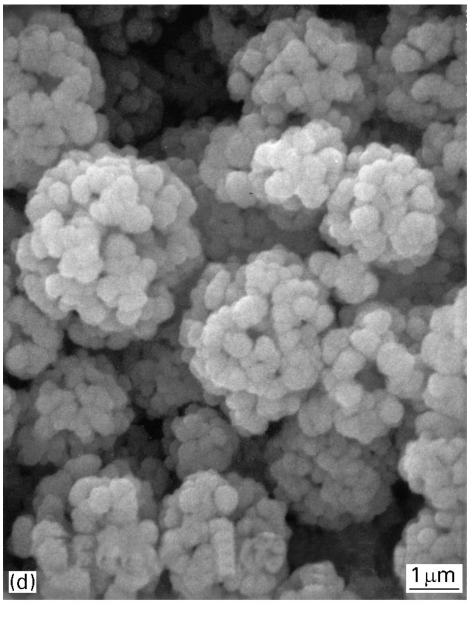


Figure 11 SEM photographs of ZnS and CdS particles prepared at constant and increasing temperature distribution: (a) ZnS ($C_S = 0.05\ \mathrm{mol\,l^{-1}}$), constant temperature; (b) ZnS ($C_S = 0.05\ \mathrm{mol\,l^{-1}}$), increasing temperature; (c) CdS ($C_S = 0.05\ \mathrm{mol\,l^{-1}}$), constant temperature; (d) CdS ($C_S = 0.05\ \mathrm{mol\,l^{-1}}$), increasing temperature.

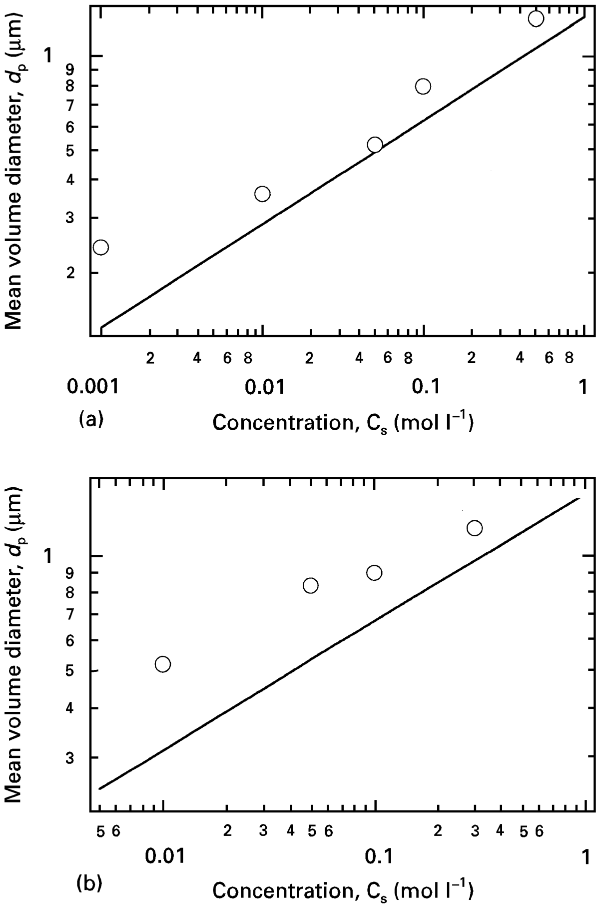


Figure 12 The relations between the mean volume diameter of (a) ZnS and (b) CdS particle and the starting-solution concentrations (C_S). Key: –calculation; ○ experimental.

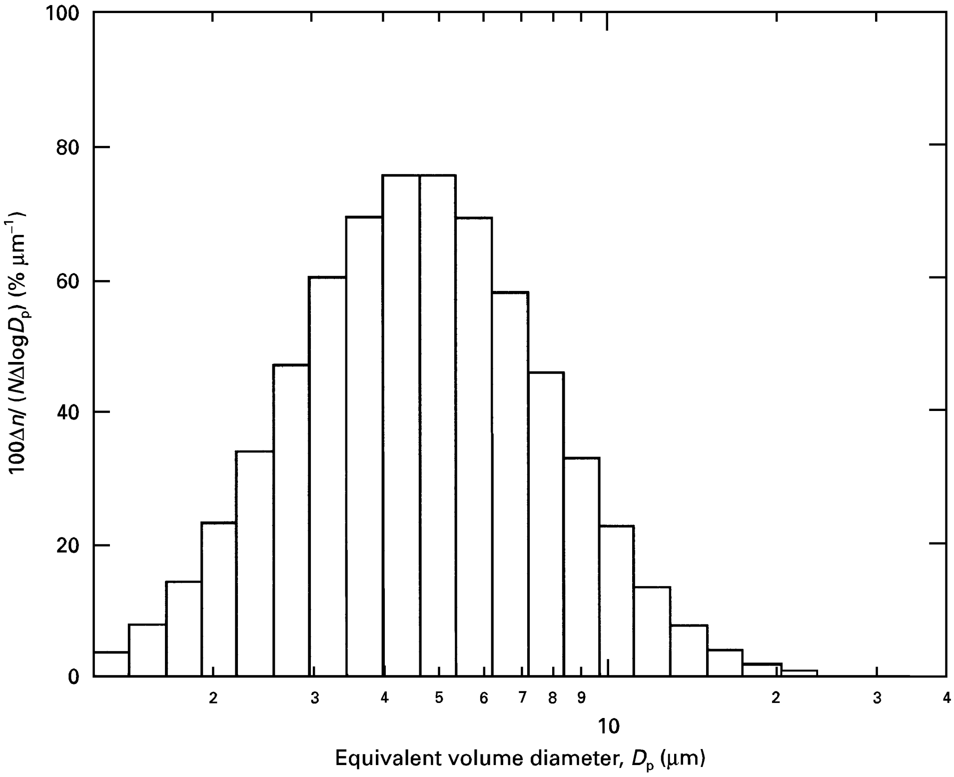


Figure 13 Volume mean diameter distribution of droplets using an ultrasonic nebulizer.

than the theoretical particle size. This is due to the existence of primary particles that construct the aggregated particles of CdS. From the tendency of Fig. 12 that particle size obtained by the experiment differs from the theoretical one, especially at low concentration of start solution, we also consider that inside the reactor, the evaporation rate of low concentration droplets is larger than that for droplets of high concentration, and therefore low concentration particles tend to aggregate.

4. Conclusion

Fine particles of ZnS and CdS with different sizes were prepared by an ultrasonic spray-pyrolysis technique using various concentrations of the starting solutions. It was observed that both ZnS and CdS particles were spherical, but CdS was formed from aggregations of particles constructed from the primary particles which gave a rough surface, whereas the surface of ZnS particle was smooth. As the concentrations increase, it can be found that both ZnS and CdS particle sizes also increase. The effects of the temperature distribution on the crystalline phases and morphology of the particles obtained were investigated and a morphological change was shown in the case of CdS particles. This study also indicated that changing the concentrations of the starting solutions did not affect the fluorescence spectra of the particles.

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