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Microwave-assisted size control of CdS nanocrystallites

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The size and size-distribution of CdS nanocrystallites is controlled by the microwave-assisted reaction of cadmium acetate with thiourea in *N*,*N*-dimethylformamide (DMF). The absorption onset of the CdS nanocrystallites shifts to longer wavelength with increasing irradiation time, indicating particle size growth under prolonged irradiation. However, when the microwave irradiation of the solution is periodically interrupted and then repeated, keeping the solution at ambient temperature before each irradiation, the absorption onset remains at the same wavelength and only the optical density of the absorption band is increased, suggesting that the particle growth occurs only during the continuous irradiation and stops once the system is cooled down. Photoluminescence observed for the CdS nanocrystallites changes with the irradiation time and the repetition of the irradiation, suggesting a structural change of the nanocrystallite surface due to the consumption of excess Cd^{2+}.

Introduction

The control of the size and size-distribution of semiconductor nanocrystallites is of great importance from the viewpoint of applications such as photocatalysts and materials for optics and electronics.[1–3] Efforts have been made to develop methods to control size and size-distribution in the preparation of nanoparticles, *e.g.*, using stabilizers (terminators) such as thiols, selenols, phosphates, and phosphine oxides; regulating the reaction space by using matrices such as zeolites, glasses, polymers, reverse micelles, vesicles, LB films, multilayer films, xerogels, and silica.[4]

Microwave (MW) irradiation induces interaction of the dipole moment of polar molecules or molecular ionic aggregates with alternating electronic and magnetic fields, causing molecular-level heating which leads to homogeneous and quick thermal reactions. Thus, MW heating has recently begun to attract the attention of chemists as a new method not only for synthesizing organic compounds but also for preparing inorganic ones[5–8] such as nano-sized inorganic particles,[9–14] molecular sieve films,[15] and self-assembled monolayers.[16] Among the nano-sized inorganic materials reported so far, one can find nickel nanocrystallites,[17] platinum nanocrystallites,[9] iron oxides, Ni/NiO composite,[10] aluminium nitride,[11] iron oxide nanoparticles,[12,13] and alumina–ceria nano-sized composites.[14]

Although the formation mechanism of monodispersed nanoparticles under MW irradiation is not entirely understood, we can point out several factors important for precise control of the particle size and its distribution: the purity of the starting materials, effect of a reactor wall, temperature change, heating rate, homogeneity of the solution, and a stabilizing reagent. We demonstrate in this paper that MW heating in a periodical and intermittent mode (a kind of pulse irradiation) leads to a precise control of nano-sized CdS with a narrow size-distribution.

Experimental

Cadmium acetate ($Cd(OAc)_2{\cdot}2H_2O$, 99.9%) and thiourea (Research grade) were purchased from Wako Chemical Company.

A MW oven (Sanyo EM-650T, 2.45 GHz, max. power 650 W) was modified by Shikoku Keisoku Kogyo Co. so that the temperatures of samples inside the oven could be monitored *in situ* during irradiation. A thermo fiber sensor (Anritsu Meter Co., Ltd., 10117-*S) was inserted through a hole made in the ceiling of the oven. This hole was covered with a stainless steel sleeve to avoid MW leakage from the oven, which was monitored by a MW detector (Narda Corp., Model 8201) for safety. The temperatures were measured using a fiber optic thermometer (Anritsu Meter Co., Ltd., AMOTH FX8500).

An *N*,*N*-dimethylformamide (DMF) solution (10 ml) of $Cd(OAc)_2{\cdot}2H_2O$ (2.5×10^{-5} mol) and thiourea (2.5×10^{-5} mol) in a Pyrex glass vial was placed in a MW oven and irradiated with MW continuously or periodically, after cooling the irradiated solution down to ambient temperature before each irradiation. As examples of the temperature changes involved the solution temperature was found to be raised to 343 K after 15 s irradiation and to 403 K after 41 s irradiation.

A droplet of the resulting solution was placed on a carbon-coated copper mesh and dried *in vacuo* overnight at room temperature prior to analysis by transmission electron microscopy (TEM). An electron microscope (HITACHI H-9000) was employed for the measurements. Absorption and emission spectra were recorded with a UV-Vis absorption spectrometer

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(Hitachi U-3300) and a fluorescence spectrometer (Hitachi U-4500), respectively.

Results and discussion

Reaction conditions for MW irradiation

We selected *N*,*N*-dimethylformamide (DMF) as a solvent because DMF can disperse CdS nanocrystallites, giving a stable colloidal CdS solution. It has been already reported that this stabilization is ascribed to coordination of DMF molecules to cationic Cd atoms on the surface of the nanocrystallites.[18] We successfully prepared a colloidal dispersion of CdS nanocrystallites through the reaction of cadmium salt with sulfide anion (S^{2-}) under MW irradiation. Thiourea was selected as a source of S^{2-} because it is known to generate S^{2-} through the thermal decomposition, with the assistance of a base catalyst (see Scheme 1).[19–22]

The resulting dispersion or solution of CdS showed different behavior depending on the type of cadmium salts employed. Cadmium acetate and nitrate gave a yellowish clear solution, but its hydroxide and carbonate did not show any change in their appearance. When cadmium perchlorate was employed it gave a yellow precipitate, indicating severe aggregation. We selected cadmium acetate as an appropriate salt for examining the preparation method in this work because photoluminescence was only observed for the yellowish colloidal dispersion prepared from the acetate salt.[23]

CdS nanocrystallites prepared by MW heating

When the DMF solution containing $Cd(OAc)_2 \cdot 2H_2O$ and thiourea was irradiated by MW, the reaction mixture became clearer and its yellow color gradually deepened with further irradiation, indicating the formation of colloidal CdS in the system. The temperature of the solution was found to be raised up to 353 K after 18 s of irradiation. A TEM image of the solution after the 18 s irradiation revealed the formation of nanocrystallites of CdS (Fig. 1(a)). The electron diffraction pattern showed that the CdS nanocrystallites possessed a hexagonal crystal structure (Fig. 1(a)). The size distribution of CdS nanocrystallites was centered at 2.6 nm and ranged between 1.5 and 4 nm (Fig. 1(b)). No CdS nanocrystallites were observable for the sample solution irradiated for 15 s, suggesting the presence of a threshold for the release of S^{2-} from thiourea.

Water included in the Cd salt as water of crystallization and in DMF should lead to hydroxide anion formation in the presence of DMF. The MW-assisted hydrolysis of thiourea catalyzed by hydroxide leads to release of S^{2-} in the system (see Scheme 1). Furthermore, DMF molecules will interact weakly with the surface of the fresh CdS nanocrystallites by coordination to exposed Cd cations, resulting in stabilization of the nanocrystallites without coagulation.[18]

For comparison of the MW heating method with conventional heating methods, the same starting solution was heated up to 353 K in a hot oil bath and maintained at that temperature for 30 s. The color of the solution changed to yellow but precipitation was visually detected. This clear contrast between MW heating and conventional heating demonstrates that MW irradiation induces the controlled and homogeneous release of S^{2-}, resulting in homogeneous nucleation and crystal growth without competitive and random particle growth.

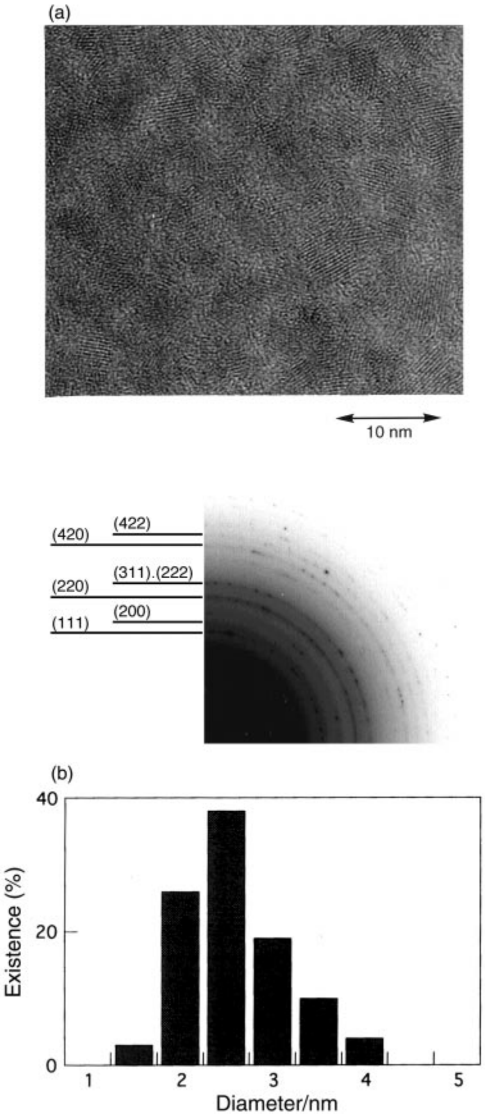
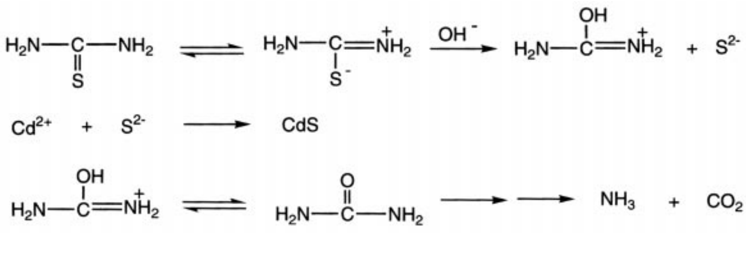


Fig. 1 (a) Transmission electron micrograph of CdS nanocrystallites prepared by MW irradiation and the electron diffraction pattern. (b) Size distribution of CdS nanocrystallites, as determined by TEM.

Special techniques such as sonic sprays[24,25] or electrostatic sprays[26] have been employed to obtain small particles of CdS through a similar reaction using thiourea as the sulfide source. When compared to their methods, the MW method shows a clear contrast in that CdS nanocrystallites of 2–3 nm are instantly prepared with a narrow size distribution. We previously reported that cooling of the solutions down to 253 K is a prerequisite for the preparation of CdS nanocrystallites with sizes below 2 nm by the reactions of



Scheme 1

$Cd(OAc)_2{\cdot}2H_2O$ with H_2S or Na_2S in DMF.[27,28] With MW heating, however, CdS nanocrystallites with sizes around 2 nm are readily preparable at ambient temperature, demonstrating how advantageous MW heating is for the homogeneous nucleation.

In general, the synthesis of nanoparticles from their precursors in solutions consists of two main processes: nucleation and particle growth. In addition, termination of the particle growth is also important. Each step can be controlled by changing the preparation conditions such as: starting materials, solvent, additives such as stabilizers, and reaction time and temperature. When the synthesis is carried out under conventional heating, the temperature distribution of the solution will be inhomogeneous because the reaction system is heated by thermal conduction through a container wall, convection, and agitation. The above two processes, nucleation and particle growth, should depend on the local temperature distribution of the solution, and then the inhomegeneity in the temperature distribution should cause a broad distribution in the particle size. We would emphasize in this paper that MW heating should lead to homogeneous, *i.e.*, molecular-level, heating of the polar solution system, achieving automatic control of the above two processes which is indispensable for the selective preparation of nanoparticles.[17]

Pinning the nanocrystallite growth

For the solution after 18 s irradiation, the absorption onset was observed at 422 nm, in agreement with that estimated by the dependence of the bandgap energy on the particle size observed by TEM (2.6 nm, Fig. 2).[28–30] The absorption spectra of the colloidal solution prepared by MW irradiation moved to longer wavelength in their onsets when the irradiation time was prolonged (Fig. 2). By increasing the irradiation time up to 27 s, the sample was heated up to 373 K and gave an absorption onset at 445 nm. This shift in the absorption onsets indicated size-growth of the CdS nanocrystallites induced by the continued irradiation. The growth of the particle size could be estimated to be 0.2–0.4 nm from the shift of the absorption onset observed for the two samples.[28] The integrated absorption intensities also increased with increasing irradiation time, showing that the concentration of CdS nanocrystallites was also increased with increasing nanocrystallite size.

The irradiation of the colloidal CdS solution was periodically interrupted several times, keeping the irradiation time constant. After each irradiation the solution was cooled down to ambient temperature. Under such periodical MW heating the absorption onset was pinned at the same wavelength and only the optical density of the absorption band of the CdS solutions was increased (Fig. 3). By periodic and intermittent irradiation of the solution for 18, 21, or 27 s, the absorption onsets were pinned at 430, 440, or 460 nm, respectively. These results showed that the periodic and intermittent MW irradiation increased the number of CdS nanocrystallites but not the particle size, leading to the size-controlled production of CdS nanocrystallites.

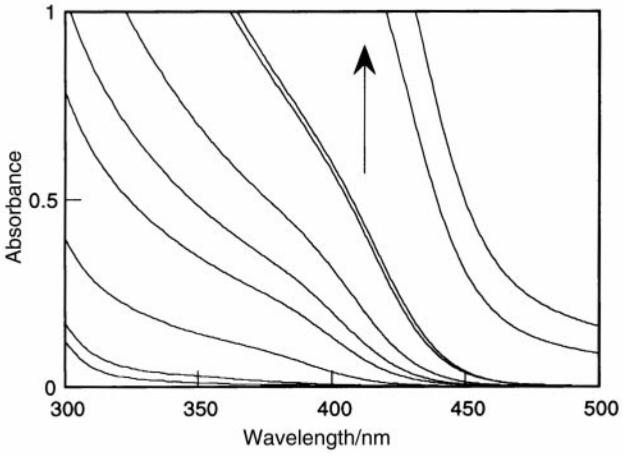


Fig. 2 Absorption spectra of the colloidal CdS solutions prepared by MW irradiation. The irradiation times and the temperatures of the samples after irradiation were as follows: 0 s, 15 s (343 K), 18 s (353 K), 21 s (360 K), 24 s (368 K), 27 s (373 K), 30 s (378 K), 33 s (383 K), 36 s (388 K), 39 s (393 K).

Photoluminescence of CdS nanocrystallites prepared under MW heating

Photoluminescence of CdS nanocrystallites can give us much information on their size and surface structures.[31–34] Fig. 4 shows the emission spectra of the CdS colloidal solutions used for the measurements of the absorption spectra in Fig. 2. The emission intensity was increased with increasing irradiation time up to 18 s and decreased by further irradiation. The emission was almost quenched for the samples irradiated for longer than 36 s. The emission peak first observed after 15 s irradiation shifted to longer wavelength on further irradiation. The emission spectra were also examined for the colloidal CdS solutions prepared by the periodic and intermittent irradiation (Fig. 5). The emission was observed at longer wavelength for the solution prepared by longer irradiation. When the irradiation was repeated, an appreciable shift to longer wavelength was observed for the emission peak. By further

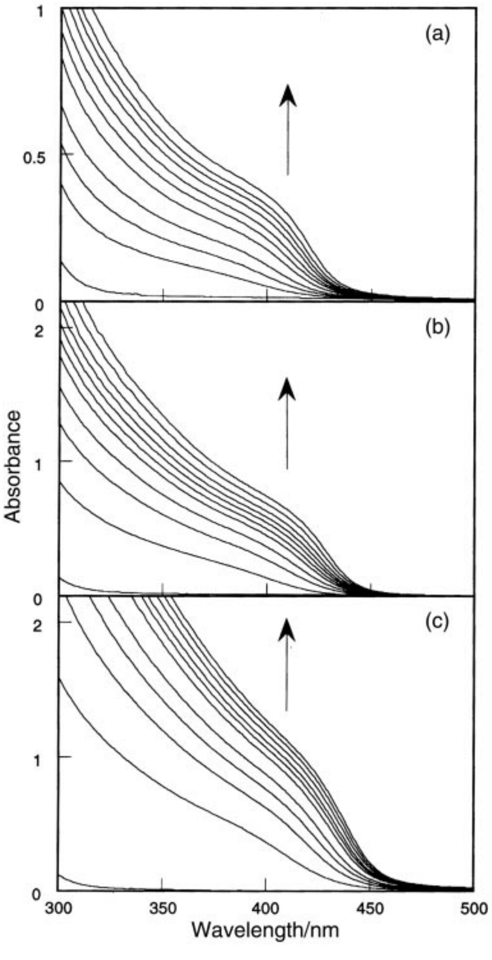


Fig. 3 Absorption spectra of the colloidal CdS solutions prepared by intermittent MW irradiation. The solutions were intermittently irradiated for a constant time: 18 (a), 21 (b), and 27 s (c), respectively. The solutions were cooled to room temperature after each irradiation.

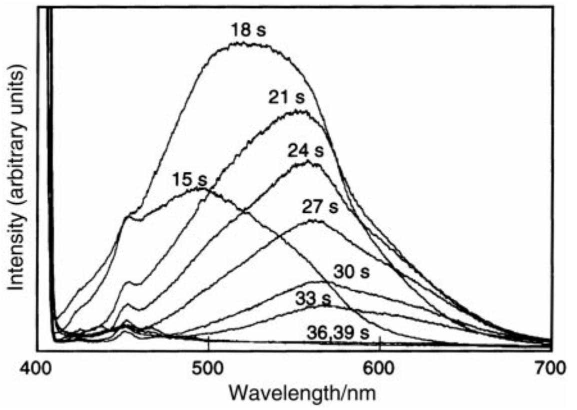


Fig. 4 Emission spectra of the colloidal CdS solutions prepared by MW irradiation. The solution was excited at 400 nm. The irradiation times were 15, 18, 21, 24, 27, 30, 33, 36, and 39 s. The peak at 450 nm is due to Raman scattering of DMF.

repetition of the irradiation, the emission intensity decreased and the extent of the peak shift was diminished.

Judging from the fact that no shift was observed in the absorption spectra of the solutions, no growth in the particle size should occur during the intermittent irradiation. Therefore the decrease in the emission intensity and the shift of the emission peak should be attributed not to size growth but to changes in the surface structures which should be related to the emission such as surface defects. The photoluminescence observed in the present work can be attributed to a sulfur vacancy.[31,35,36] When the excess Cd^{2+} was added to CdS nanocrystallites, the broad red emission was induced and enhanced with increasing added Cd^{2+}.[36] This emission was attributed to the formation of a sulfur vacancy on the surface of the nanocrystallites.[35,36] In the MW-assisted preparation of CdS, the surface compositions of Cd and S should be changed during the MW irradiation: the surfaces of the nanocrystallites are mainly covered with Cd^{2+} in the early stages of the irradiation, resulting in the formation of sulfur vacancies. In other words, the sulfur vacancy giving photoluminescence is predominantly formed in the early stages and the excess Cd^{2+} is decreased in the latter stages because of its consumption for the production of more CdS nanocrystallites. This change in the number of sulfur vacancies would cause changes in the photoluminescence observed during the MW irradiation.

Conclusions

MW heating at the molecular level enables one to control the size and size-distribution of metal sulfide nanoparticles. Precise size-control of CdS nanocrystallites has been achieved by applying MW irradiation and manipulating the irradiation conditions without using any of the chemical matrices or special instrumentation required when conventional heating is employed. The cooperative role of DMF as a surface-stabilizing molecule should be important in the size-controlled growth of nanocrystallites. Especially the periodic and intermittent irradiation mode is important for the controlled release of S^{2-} and the suppression of size growth until Cd^{2+} is consumed. MW heating will provide a new methodology for the controlled preparation of nanomaterials.

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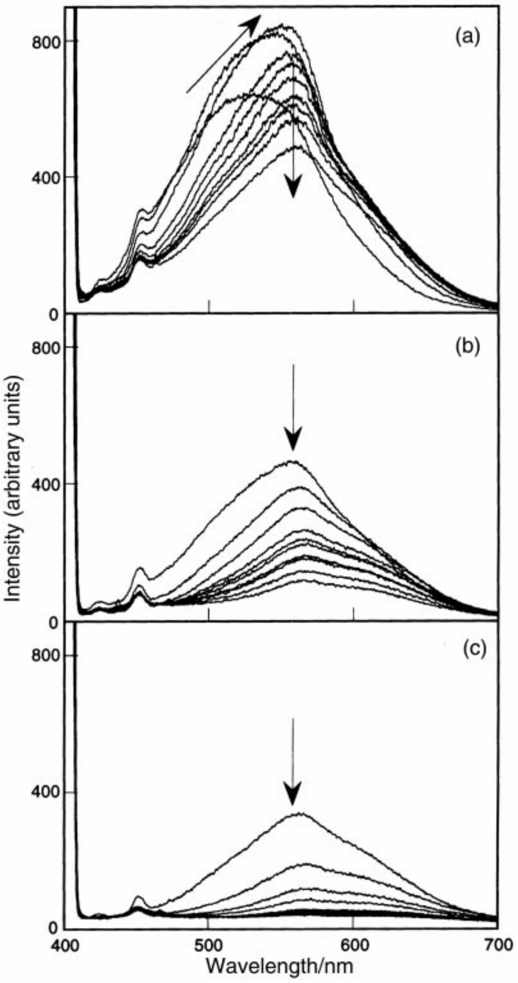

Fig. 5 Emission spectra of the colloidal CdS solutions prepared by intermittent MW irradiation. The solutions were intermittently irradiated for a constant time: 18 (a), 21 (b), and 27 s (c), respectively. The solution was cooled to room temperature after each irradiation. The peaks at 420 and 450 nm are due to Raman scattering of DMF.

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