

## Solventless Synthesis and Optical Properties of CdS Semiconductor Nanoparticles

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Solventless synthesis of CdS nanoparticles using 1-octadecanethiol and thiobenzoic acid as sulfur sources has been developed. When thiobenzoic acid was used as a nucleation agent, the size of CdS nanoparticles could be controlled in the range of  $4.3 \pm 0.5$  nm  $\sim$   $6.1 \pm 0.5$  nm. The absorption onset and emission peak are tunable in the 410 nm  $\sim$  500 nm range and in the 515 nm  $\sim$  580 nm range, respectively.

Key words: Semiconductor nanoparticle, CdS, Solventless synthesis, Thiobenzoic acid, Alkanethiol

### 1. INTRODUCTION

During the past decade, nanostructured semiconductor materials have been extensively studied due to their unique physicochemical and optical properties [1-14]. The formation of high-quality semiconductor nanoparticles, with well-controlled size and shape as well as well-confined surface passivation, can be achieved by controlling the thermodynamics and kinetics during the nucleation and growth of nanoparticles. Reliable methods which can reproducibly give a high yield of uniformly sized nanoparticles remain an active research goal in nanoparticle chemistry. The size dependent emission is the most attractive property of semiconductor nanoparticles. Cadmium sulfide (CdS) nanoparticles are one of the most attractive materials because of their size-dependent emission in a visible region. This size-dependent optical property can be applied to LEDs (light-emitting diodes), semiconductor lasers, biosensing devices, and so on. For this purpose, the size control of CdS semiconductor nanoparticles is quite important. To that end, the separation of the nucleation and growth stages is a prerequisite of producing high-quality nanoparticles.

Here, we report the novel solventless synthesis of CdS nanoparticles. The solventless synthesis of CdS nanoparticles is very simple and facile, because CdS nanoparticles can be produced from the mixture of cadmium precursor and sulfur precursor, where the sulfur precursor works as both a protective ligand and a sulfur source. Furthermore, we use thiobenzoic acid as a nucleation initiator in order to separate the nucleation and growth stages. To the best of our knowledge, this is the first report of synthesizing CdS nanoparticles by the solventless method.

### 1. EXPERIMENTAL

#### 1-1. Materials

Cadmium acetylacetonate hydrate ( $\text{Cd}(\text{acac})_2 \cdot x\text{H}_2\text{O}$ ) (99.9%, Aldrich), 1-octadecanethiol (97%, TCI), thiobenzoic acid (90%, Wako) chloroform (99%, Wako), acetone (99.5%, Kishida), and methanol (99.8%, Wako) were used as received.

#### 1-2. Synthesis of CdS Nanoparticles

A typical synthesis of CdS nanoparticles is as follows. 1-octadecanethiol (8.5 ml, 25 mmol) were loaded into a

50 mL three-neck flask and heated to 180-320 °C under a  $\text{N}_2$  flow. At a desired temperature,  $\text{Cd}(\text{acac})_2 \cdot x\text{H}_2\text{O}$  (80 mg, 0.25 mmol) was swiftly added into the reaction flask. During the reaction, aliquots of the reaction mixture were taken out to investigate the process of the nucleation and growth of CdS nanoparticles. In order to separate the nucleation and growth stages, thiobenzoic acid was used as a nucleation initiator. In that case, thiobenzoic acid was mixed with 1-octadecanethiol before reaction. Then, the reaction was carried out in a similar fashion.

#### 1-3. Characterization of CdS Nanoparticles

The size and shape of the resulting CdS nanoparticles were confirmed on JEOL JEM-100 transmission electron microscope (TEM) at 100 kV. TEM specimen were prepared by placing a drop of the CdS nanoparticles dispersed in chloroform on an amorphous carbon-coated copper grid and were allowed to be put into a dry desiccator. The UV-Vis and photoluminescence (PL) spectra were recorded on Hitachi U-3310 and Hitachi F-2500 (excitation wavelength: 300 nm), respectively. Samples were prepared by diluting the reaction mixture of CdS nanoparticles with chloroform. The X-ray diffraction (XRD) patterns were recorded on a MAC Science X-ray diffractometer (model-M18XHF-SRA,  $\text{CuK}\alpha$   $\lambda=1.540$  Å).

### 2. RESULTS AND DISCUSSION

First 1-octadecanethiol was used as both a sulfur source and a protective ligand. Faster nanoparticle formation was observed at higher temperature and both absorption and emission peaks were gradually red-shifted with elapsing the reaction time, indicating the nanoparticle growth. However, only the polydisperse CdS nanoparticles were obtained due to the relatively low reactivity and strong ligation of 1-octadecanethiol, leading coexistence of nucleation and growth stages. Furthermore, the particle sintering was observed in the temperature above 280 °C, so the following experiments were carried out below 280 °C.

Figure 1 shows the TEM images of CdS nanoparticles synthesized at 240 °C. The large CdS nanoparticles were obtained with elapsing the reaction time from 3 to 300 min, where polydisperse particles were observed in all

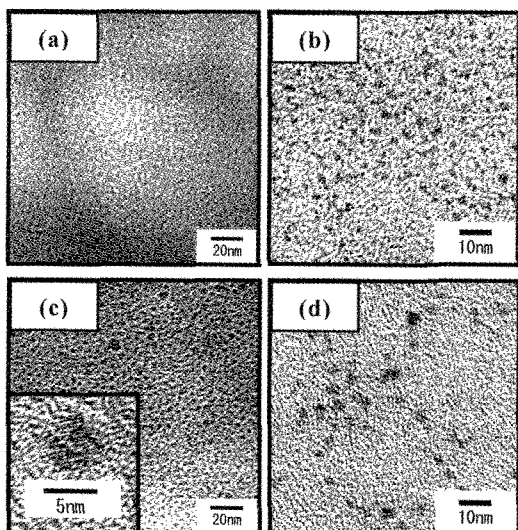


Fig. 1 TEM images of CdS nanoparticles synthesized at 240 °C for (a) 3, (b) 20, (c) 120 and (d) 300 min. Inset in (c) shows representative HR-TEM image of CdS nanoparticle.

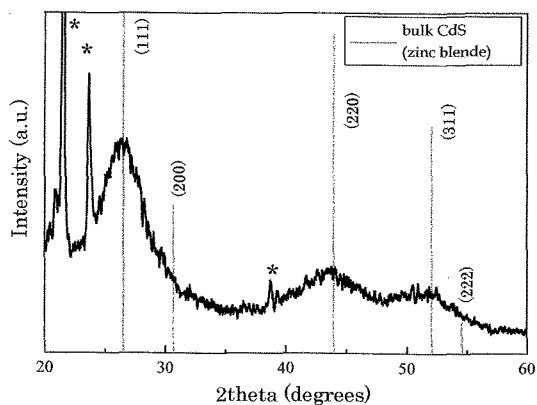


Fig. 2 XRD patterns of the CdS nanoparticles synthesized at 240 °C for 20 min. The peaks indicated by “\*” were caused by the impurities.

cases. The particle size for Fig. 1c is about 5 nm, and the HR-TEM image shown in the inset of Fig. 1c shows distinct lattice fringe, indicating each CdS nanoparticle is a single crystal. Figure 2 presents the XRD patterns of CdS nanoparticles synthesized at 240 °C for 20 min, which indicates that the obtained nanoparticles have a zinc blende structure. The full widths at half-maximum (fwhm) of representative crystal planes decreased with the reaction time, suggesting the particle growth. Figure 3 shows the PL and UV-Vis spectra of CdS nanoparticles synthesized at 240 °C. The absorption edges and emission peaks were gradually red-shifted with increasing the reaction time, also indicating the particle growth. Although the emission is derived from the surface defects, the emission peaks are controllably changed in the range of 490 to 575 nm.

Then, in order to clearly separate the nucleation and growth stages, thiobenzoic acid was used as a nucleation

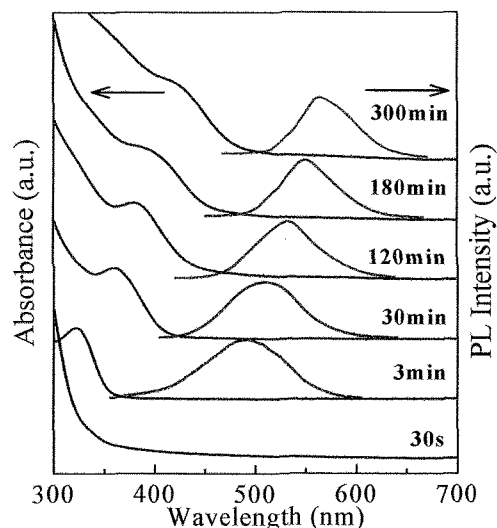


Fig. 3 UV-Vis and PL spectral changes of a chloroform solution of the CdS nanoparticles synthesized at 240 °C.

initiator because of its relatively high reactivity. Since a sulfur atom of thiobenzoic acid is directly bound to a carbonyl group, thiobenzoic acid has a potential to easily release sulfur anionically. Figure 4 shows a TEM image of CdS nanoparticles synthesized in the presence of 1-equiv. of thiobenzoic acid to cadmium ion as a nucleation initiator. The larger and monodisperse CdS nanoparticles were obtained in this system, indicating that the nucleation and growth stages were clearly separated. The obtained CdS nanoparticles are spherical and have the diameter of  $6.1 \pm 0.5$  nm in the reaction time of 120 min. Figure 5 presents the UV-Vis and PL spectral changes of a chloroform solution containing CdS nanoparticles synthesized in the presence of thiobenzoic acid at 240 °C. The sharp absorption proves the monodispersity of particles. The absorption onset are dependent on the particle size, meaning that the absorption peak is tunable in the 410 nm ~ 500 nm range by changing the reaction time. As shown in Fig. 5, the emission peak is red-shifted as the particle size increases, the peak values being 515 (30 s), 520 (1 min), 550 (30 min), 575 (60 min) and 580 nm (120 min), respectively.

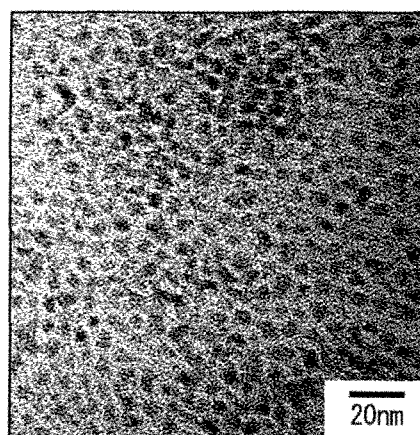


Fig. 4 TEM image of the CdS nanoparticles synthesized in the presence of 1-equiv. of thiobenzoic acid at 240 °C for 120 min ( $6.1 \pm 0.5$  nm)

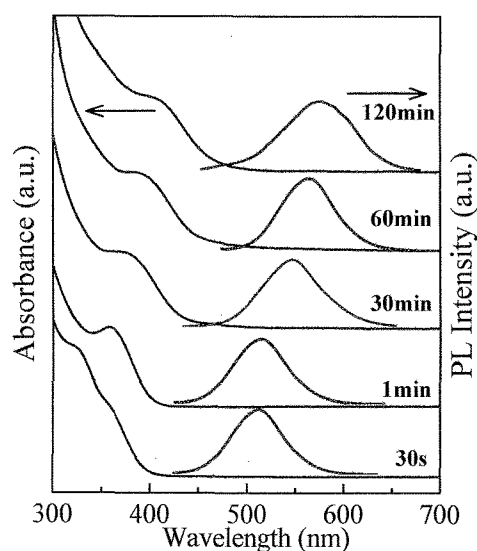


Fig. 5 UV-Vis and PL spectral changes of a chloroform solution containing the CdS nanoparticles synthesized in the presence of 1-equiv. of thiobenzoic acid at 240 °C.

The broad emissions are also attributed to a recombination of trapped electrons / holes at surface defects.

When excess 4-equiv. of thiobenzoic acid was used, smaller CdS nanoparticles were formed. The obtained CdS nanoparticles have the diameters of  $4.3 \pm 0.5$  nm  $\sim$   $5.0 \pm 0.7$  nm in the reaction time from 30 s to 120 min (Fig. 6). The size of CdS nanoparticles also increases with the reaction time. Excess thiobenzoic acid may provide larger amount of sulfur anion, resulting in accelerating the first nucleation step to form the small CdS nanoparticles. Figure 7 presents the UV-Vis and PL spectral changes of a chloroform solution containing the CdS nanoparticles synthesized in the presence of 4-equiv. of thiobenzoic acid. The absorption edges are tunable in the 450 nm  $\sim$  500 nm range by changing the reaction time. As shown in Fig. 7, the emission peak is also red-shifted as the particle size increases, the peak values being controlled in the range of 545 (30 s)  $\sim$  575 nm (120 min).

#### 4. CONCLUSIONS

We have succeeded in developing a novel solventless synthesis of CdS semiconductor nanoparticles. The zinc blende CdS nanoparticles were formed by heating the mixture of  $\text{Cd}(\text{acac})_2 \cdot x\text{H}_2\text{O}$  and 1-octadecanethiol at 180  $\sim$  320 °C, although the obtained nanoparticles were polydisperse and non-spherical. By adding thiobenzoic acid to the reaction mixture, the CdS nanoparticles became larger and spherical. Thiobenzoic acid surely worked as a nucleation initiator to separate the nucleation and growth stages. When the reaction was carried out in the presence of thiobenzoic acid at 240 °C, the size of CdS nanoparticles could be controlled in the range of  $4.3 \pm 0.5$  nm  $\sim$   $6.1 \pm 0.5$  nm. The absorption onset and emission peaks are tunable in the 410 nm  $\sim$  500 nm range and in the 515 nm  $\sim$  580 nm range, respectively. A broad emission in the 500  $\sim$  600 nm

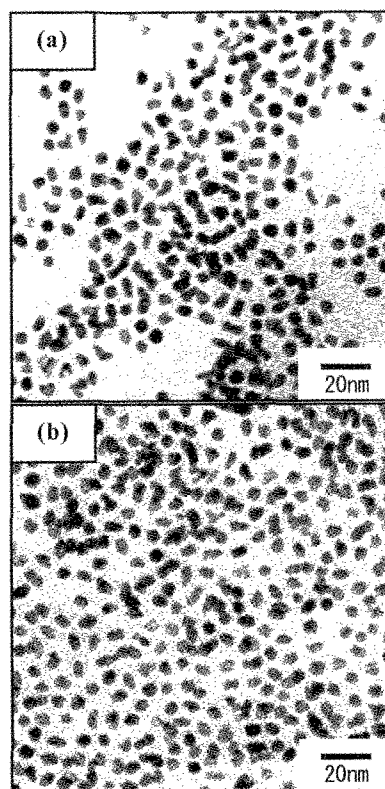


Fig. 6 TEM images of the CdS nanoparticles synthesized in the presence of 4-equiv. of thiobenzoic acid at 240 °C for (a) 30 s ( $4.3 \pm 0.5$  nm) and (b) 120 min ( $5.0 \pm 0.7$  nm)

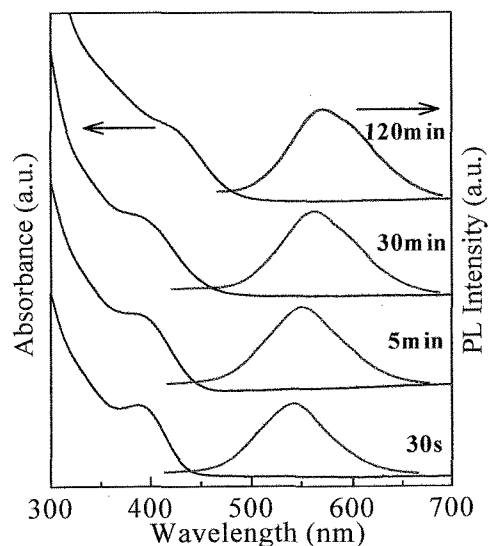


Fig. 7 UV-Vis and PL spectral changes of a chloroform solution of the CdS nanoparticles synthesized in the presence of 4-equiv. of thiobenzoic acid at 240 °C.

region is attributed to a recombination of trapped electrons / holes at surface defects. This surface-trapped luminescence is expected to possess little self-reabsorption and can provide proper features for certain optical devices such as LEDs.

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