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**Layer-by-Layer Accumulation of Cadmium Sulfide Core – Silica Shell  
Nanoparticles and Size-Selective Photoetching to Make Adjustable Void Space between  
Core and Shell**

Tsukasa Torimoto,<sup>†§</sup> Jocelyn Paz Reyes,<sup>†</sup> Shin-ya Murakami,<sup>§</sup> Bonamali Pal,<sup>§</sup>  
and Bunsho Ohtani<sup>·\*†</sup>

<sup>†</sup>*Catalysis Research Center, Hokkaido University, Sapporo 060-0811, Japan.*

<sup>§</sup>*“Light and Control”, PRESTO, Japan Science and Technology Corporation (JST), Japan*

Corresponding Author:

**Prof. Bunsho Ohtani**

Catalysis Research Center, Hokkaido University, Sapporo 060-0811, Japan

TEL: +81-11-706-3673

FAX: +81-11-706-4925

E-mail: ohtani@cat.hokudai.ac.jp

## **Abstract**

Layer-by-layer accumulation of monolayers of silica-coated cadmium sulfide (CdS) was achieved through repeated monolayer deposition-hydrolysis cycles using CdS particles (average diameter; 5 nm) modified with 3-mercaptopropyltrimethoxysilane (MPTS) and glass substrates. Absorption spectroscopic analyses of the resulting yellow films revealed that each layer had almost the same thickness, the estimated density of which corresponded to ca. 66 % of that for the close hexagonal packing of nanoparticles. Monochromatic light irradiation at 488, 458, or 436 nm onto the film immersed in oxygen-saturated aqueous methylviologen solution caused the decrease in the size of the CdS core depending on the irradiation wavelength, while atomic force microscopic analyses suggested that the size of silica shell of the immobilized nanoparticles was almost unchanged with irradiation; i.e., the immobilized silica-coated CdS nanoparticles had void spaces between the photoetched core and the silica shell and their size was regulated by choosing the wavelength of irradiation light. The size-selective photoetching could be successfully applied to the nanoparticulate films which were heat-treated at 473, 573, or 673 K to observe the blue-shift of absorption edge of CdS to the irradiation wavelength. The amount of CdS remaining in the film after the photoetching process depended on temperature of the heat treatment. The largest amount among as-prepared and heat-treated samples was obtained at 473 K and decreased with the elevating temperature. The growth of particles, i.e., the diminution of particle number, and/or the diminution of number of separated independent shells may account for the dependence.

## **Key words**

core-shell structure, nanoparticles, void space, layer-by-layer deposition, cadmium sulfide, photoetching

## 1. Introduction

Nanocomposites having well-defined nanometer-scale dimensions are an interesting and increasingly important class of materials and have been studied aiming at development of novel catalysts and optoelectronic devices. Among the nanocomposites, studies of surface coating of nanoparticles with different materials to produce core-shell structures have attracted attention [1-21], because physical and chemical properties of core materials can be modified or tailored by the shell components with negligible change in shape and size of the core particles. Also core-shell nanoparticles have been useful as precursors for the preparation of hollow structures by removing core materials through chemical etching or combustion [22-30], and partial removal of the core has enabled preparation of novel nanostructures inside the shell, such as the encapsulation of metal nanoparticles in hollow sphere and the void formation between the core and shell [31-37]. To utilize these nanoparticles in solid devices, such as optoelectronic devices and sensors, it is necessary to immobilize core-shell nanoparticles onto solid substrates. In recent years several techniques have been reported, which included the casting of the particles [10,38] and the layer-by-layer deposition using the charged particles and the ionic polymers [39-41].

We have reported size-selective photoetching technique as a means of preparation of monodisperse semiconductor nanoparticles in the size quantization regime. When the technique was applied to CdS, the particle size could be controlled within the range of 3.5 to 1.7 nm simply by selecting the wavelength of monochromatic irradiation light in the range of 488 to 365 nm [42-47]. Recently we have also applied this technique successfully to control core size in silica-coated CdS nanoparticles, i.e., a CdS core-silica shell structure. The resulting nanoparticles had a void space inside the silica shell and its size was adjusted by choosing the irradiation wavelength [48]. In this paper, we report a newly developed method of layer-by-layer accumulation of silica-coated CdS nanoparticles on glass substrates. It was revealed that the size of core, in

other words the size of void space, in the nanoparticle films could be controlled using the size-selective photoetching.

## 2. Experimental Section

### 2.1. Materials

Sodium di(2-ethylhexyl) sulfosuccinate (AOT), 1,1'-dimethyl-4,4'-bipyridinium dichloride ( $MV^{2+}$ ), and 3-mercaptopropyltrimethoxysilane (MPTS) were purchased from Tokyo Chemical Industry, and cadmium perchlorate was obtained from Kishida Reagents Chemicals. Other chemicals were supplied from Wako Pure Chemical Industries. Aqueous solutions were prepared with purified water prepared just before use by Yamato/Millipore WP501 Milli-Q system. Glass plates (Matsunami, S-1111, 3.8 cm  $\times$  1.3 cm  $\times$  0.1 cm) were treated overnight with a 1.0 mol dm<sup>-3</sup> NaOH aqueous solution and washed thoroughly with water before use.

### 2.2. Preparation of CdS nanoparticles

MPTS-modified CdS nanoparticles were prepared through the procedure reported previously [48]. To each of 200 cm<sup>3</sup> of heptane solutions containing 14 g AOT and 5.7 cm<sup>3</sup> of water was added each of 1.3 cm<sup>3</sup> portions of a 1.0 mol dm<sup>-3</sup> aqueous Cd(ClO<sub>4</sub>)<sub>2</sub> solution and a 1.0 mol dm<sup>-3</sup> aqueous Na<sub>2</sub>S solution. After being stirred for 1 h, they were mixed together, resulting in the formation of CdS nanoparticles in AOT reversed micelles. To make the particle surface cadmium-rich, an additional 0.26 cm<sup>3</sup> portion of a 1.0 mol dm<sup>-3</sup> aqueous Cd(ClO<sub>4</sub>)<sub>2</sub> solution was added to the solution. The solution was stirred for another 1 h and then the solvent was removed by vacuum evaporation. To a toluene solution (400 cm<sup>3</sup>) of the resulting yellow solid, a 5.0 cm<sup>3</sup> portion of 0.21 mol dm<sup>-3</sup> MPTS toluene solution was added to modify the CdS surface, and then the solution was stirred for several hours.

### 2.3. Layer-by-layer accumulation of core-shell nanoparticles

Regulated accumulation of silica-coated CdS (core-shell) nanoparticles was conducted by repeated cycles of procedure consisting of monolayer deposition of the MPTS-modified CdS particles and hydrolysis of remaining trimethoxysilyl groups to silica network (Scheme 1a), as follows. A glass plates was treated by a refluxing toluene solution of the MPTS-modified CdS nanoparticles for 2 h, rinsed with methanol several times, and then heated in water at 363 K for 0.5 h. This deposition-hydrolysis cycle was repeated up to, maximally, 17 times. Post-reaction curing was performed by heating for 1h in an electric furnace under vacuum.

#### *2.4. Size-selective photoetching of CdS core*

An argon-ion laser (Ion Laser Technology, Model 5500A) and a 400-W mercury arc lamp (Eiko-sha) were used as light sources. The former was used for the irradiation of monochromatic light at 488 and 458 nm. An emission line at 436 nm from the latter was extracted by the combination of various types of glass optical filters. The silica-coated CdS nanoparticle films on glass substrate were immersed in a 10 cm<sup>3</sup> oxygen-saturated aqueous solution of 50 μmol dm<sup>-3</sup> MV<sup>2+</sup> [47], and irradiated with the monochromatic light until their absorption spectra had become unchanged. The absorption spectra of the silica-coated CdS nanoparticle films on glass plates were measured using an Agilent 8453 spectrophotometer. Since both sides of a glass plate were covered with the nanoparticulate films, the absorption spectra originating from a CdS film on one side is shown in this study by halving the absorbance.

#### *2.5. Characterization of core-shell nanoparticle films*

The surface of the film was observed by an atomic force microscopy (AFM) (Digital Instruments, Nanoscope IIIa) in a tapping mode using Nanosensors NCH cantilevers. The size of silica-coated CdS nanoparticles was obtained by measuring the lateral dimension of the particle images (more than 60 particles).

### 3. Results and discussion

#### 3.1. Layer-by-layer deposition of nanoparticle films

Absorption spectrum of MPTS-modified CdS nanoparticles in toluene was shown in Fig. 1a, which had the exciton peak around 445 nm and the absorption onset at 530 – 550 nm. Since the energy gap of bulk CdS was reported to be 2.4 eV [49] (corresponding to the absorption onset of ca. 520 nm), the large part of CdS nanoparticles possessed the energy gap similar to that of bulk material. As reported in the previous paper [48], CdS nanoparticles prepared by almost the same procedure had a wide size distribution ranging from 3 to 7 nm, and the average diameter was 5.0 nm with the standard deviation of 0.79 nm.

Before the addition of MPTS to the CdS particles in AOT reversed micelle, their surface was cadmium-rich. It has been presumed that thiol group in MPTS (R-SH) reacts with these surface cadmium sites to make R-S-Cd(CdS) linkage, i.e., outmost surface of the particles is covered with trimethoxysilyl groups, which have high reactivity toward surface hydroxyl group on the glass substrate to give Si(glass)-O-Si(MPTS) bond, as shown in Scheme 1a. Since no chemical reaction which binds between these particles are expected under the dehydrated conditions as employed in the first deposition step, attachment of MPTS-modified CdS particles should be limited to coverage of, at most, a monoparticle layer; no three dimensional growth of the film may occur. The remaining trimethoxysilyl groups on anchored CdS nanoparticles are hydrolyzed in hot water to form silica shell-CdS core structure, as was proved by FT-IR spectroscopy in our previous paper [48]. Using produced surface hydroxyl groups on the shell, another monolayer of MPTS-modified CdS particles were attached followed by the hydrolysis. This layer-by-layer accumulation of silica-coated CdS was repeated up to 17 times.

Figure 1b shows the absorption spectra of the silica-coated CdS nanoparticle films deposited on glass plate. Although there was upward shift of spectra in the whole wavelength range due to the light scattering of the films, the exciton peak of CdS nanoparticles could be detected at around 445 nm in the spectra that agreed with that of MPTS-modified CdS nanoparticles in solution and its intensity was enhanced with increasing number of accumulation cycles. On the assumption that the absorbance shift due to the light scattering of the films is independent of wavelength, the absorbance ( $\Delta A$ ) owing to CdS was roughly estimated from the absorbance difference between the absorption onset (550 nm) and the exciton peak (445 nm). Figure 2 shows  $\Delta A$  as a function of the number of accumulation cycles. Number of samples for each number of accumulation was 8 – 11 samples and their average and standard deviation (error bar) were plotted. Relatively large error in  $\Delta A$  measurement is due to different light scattering at the peak wavelength. However, it is clear that there is a tendency of increasing  $\Delta A$  with the repeated number of accumulation and a linear line can be drawn as shown in Fig. 2. From the slope of the linear relation, the number of the particle immobilized per one cycle is estimated to be  $2.1 \times 10^{12}$  particles  $\text{cm}^{-2}$  using the absorption coefficient of  $536 \text{ mol}(\text{CdS})^{-1} \text{ dm}^3 \text{ cm}^{-1}$  at exciton peak and the average diameter of CdS nanoparticles (5.0 nm). This value was 66 % as large as that expected from the monoparticle layer of CdS nanoparticles ( $3.2 \times 10^{12}$  particles  $\text{cm}^{-2}$ ), which was obtained by assuming two-dimensional hexagonal closed packing of silica-coated CdS nanoparticles consisting of the core of 5.0-nm diameter and the MPTS overlayer of 0.5-nm thickness. One of the possible reason for the loose packing is heterogeneity of size of MPTS-modified CdS nanoparticles; the diameter of CdS core ranges from 3 to 7 nm [48].

### 3.2. Photoetching of CdS core

Figure 3 shows absorption spectra of the silica-coated CdS layers after irradiation of monochromatic light in water under aerated conditions. The absorption spectra of the resulting nanoparticles were blue-shifted and the exciton peak appeared more clearly along with decrease in wavelength of irradiation light. It is well-known that CdS particles are photocorroded to become smaller by irradiation under aerated conditions in the presence of appropriate electron relay, such as  $MV^{2+}$  [42]. The absorption onset of each spectrum seemed to agree with the wavelength of irradiation light, suggesting that the photocorrosion of CdS nanoparticles proceeded until the nanoparticles could not absorb the light during the course of the photocorrosion to make the absorption onset shift to shorter wavelength due to an increase in the energy gap along with a decrease in the particle size, *i.e.*, the size quantization effect. The exciton peak appeared at 440, 430, and 400 nm with monochromatic light irradiation at wavelength of 488, 458, and 436 nm, from which diameter of photoetched CdS nanoparticles was estimated to 3.3, 3.0, and 2.4 nm, respectively, by applying the experimentally obtained data to a theoretical relation between energy gap and particle diameter of CdS [50]. Thus size-selective photoetching of silica-coated CdS nanoparticle films can be successfully performed and the size of the resulting CdS nanoparticles is adjustable by varying the wavelength of the monochromatic light, as already reported in our previous paper [48]. The silica shell surrounding a photoetched CdS nanoparticle might prevent coalescence between nanoparticles.

Figure 4 shows an AFM image of the silica-coated CdS nanoparticle films after photoetching with irradiation at 458 nm. It was found that the silica-coated CdS nanoparticles were packed densely in the film and roughness of the film surface was large ( $>50$  nm). The average diameter of the photoetched particles was determined to 15 nm with the standard deviation of 5.3 nm by measuring the lateral dimension of the particle images. When the surface of the film was measured before irradiation, similar morphology was observed and the average diameter of

original particles was 16 nm with the standard deviation of 7.4 nm, which was almost the same as those obtained after size-selective photoetching. Considering that the uppermost layer, i.e., the silica shell of nanoparticles reflected the AFM image, these results implied that the monochromatic light irradiation did not induce shrinking of the shell structure even when the size of CdS core decreased with irradiation, resulting in the formation of a void space between the photoetched CdS core and the silica shell (Scheme 1b). Similar behavior has been observed in TEM measurement for suspended silica-coated CdS nanoparticles, where the size of silica shell was almost equal to that of CdS nanoparticles before irradiation, regardless of the irradiation wavelength [48]. Although the diameter of the nanoparticles observed by AFM was much larger than that observed in the TEM measurement, ca. 5.0 nm, it is well-known that in AFM images lateral size is often overestimated because of radius of the curvature of the point of AFM tips [51,52].

### *3.3. Effect of pre-irradiation curing*

In order to increase the stability of the silica-coated CdS nanoparticle films, they were cured at various temperature before photoetching. Figure 5 shows the influence of curing temperature on the absorption spectra before and after the size-selective photoetching. Before photoetching, the absorption spectrum of the film heat-treated at 473 K was almost same as that of the film without curing, but the heat treatment higher than 573 K caused appreciable red shift of absorption spectra, indicating the increase in the size of deposited CdS nanoparticles. In the as-prepared nanoparticle films, network of Si-O-Si linkage is formed to surround the CdS particles and separates them. This silica network is connected to the CdS core particles through alkyl (C3) chain stems. When a part of the network surrounding one CdS particle is considered as a chamber, number of chambers in the whole film is equal to that

of particles before curing. Heat treatment, especially that at the temperature higher than 573 K, might induce decomposition of the stems and appreciable shrinkage of the silica network to result in the formation of windows through the chambers. Growth of CdS particles by the curing, as indicated by their spectral red shift, is attributable to coalescence of CdS in the neighboring chambers with the connecting window between them, the size of which is larger than that of the particles(s). The higher the temperature of curing, the larger the size of window, i.e., the larger the average size of CdS particles might be formed after curing. Thermal acceleration of particle coalescence also accounts for the growth at the higher temperature. This view was supported by the AFM measurement of the nanoparticle film heat-treated at 673 K, where the average size and the standard distribution of silica-coated CdS nanoparticles was determined to 19 and 8.5 nm which were larger than those obtained before heat-treatment, 16 and 7.4 nm, respectively.

Size-selective photoetching were successfully performed regardless of the curing temperature as also shown in Fig. 5. The absorption spectra were blue-shifted and the absorption onset of each spectrum almost coincided with the irradiation wavelength. Furthermore the monochromatic light irradiation at 488, 458, and 436 nm gave exciton peaks at almost same wavelength with or without curing (and regardless of curing temperature), except for the film cured at 673 K. It is noticeable that the absorbance, i.e., the amount of CdS after photoetching decreased with elevating curing temperature. Plots of  $\Delta A$  as a function of the curing temperature are shown in Fig. 6, where the data of the as-prepared film were plotted at the refluxing temperature, 383 K. At present we have no interpretation for the increased  $\Delta A$  before irradiation at 473 K other than that R-S-Cd moiety in the stem of the as-prepared film is converted to CdS via R-S-bond scission with negligible increase in particle size. The facts that absorbance changes were not observed during the process of MPTS modification but sulfur atoms originally included in MPTS molecules are expected to remain on CdS particles after

curing support this speculation. At the higher temperature,  $\Delta A$  before irradiation decreased along with the red shift of absorption spectra, i.e., growth of CdS particles, by the curing, probably due to the decrease of the molar absorption coefficient of CdS unit with an increase in the diameter of CdS nanoparticles up to ca. 6 nm [53].

During the course of irradiation, CdS particles in the chamber independent or connecting through windows the size of which are smaller than that of the particle undergo photoetching until their size become small to be able to pass through the window, resulting that the photoetched CdS nanoparticles easily coalesced with each other to give the bigger particles which were subjected to further photocorrosion. This implies that the photocorrosion goes on unless the total number of remaining particles becomes small not enough to coalesce. Similar values of  $\Delta A$  for original and 488-nm photoetched samples at the curing temperature between 473-573 K suggests that the average size of windows formed at this temperature range is smaller than the size of original particles or that of nanoparticles photoetched at 488 nm irradiation. On the other hand, this window size might be large enough to coalesce for the particles photoetched at 458 or 436 nm irradiation, resulting in the marked decrease in  $\Delta A$ . The behavior of  $\Delta A$  for the films cured at 673 K can be explained similarly. On the basis of these results, it is presumed that the silica shell in the core-shell nanoparticles is stabilized by the alkyl chain stems anchored to the CdS core surface, but shrinks, because of the removal of stems, by the curing to lead to the formation of windows connecting the chambers and allowing the coalescence of photoetched particles.

## **Conclusion**

We have successfully immobilized the silica-coated CdS core-shell nanoparticles on glass substrates through the newly developed layer-by-layer accumulation technique. Spectroscopic analyses revealed the packing density of nanoparticles a little loosened compared with that

of hexagonal close packing of particles of uniform size. This was attributed to heterogeneity of the actual particle size to interfere the close packing. In the next step of the study, we will try to accumulate the nanoparticles of monodispersed size prepared, e.g. using the size-selective photoetching. Size-selective photoetching of the nanoparticle films led to the decrease in the size of CdS core depending on the wavelength of irradiation light, as expected, while the shell structures of the immobilized nanoparticles were almost unchanged, indicating that void spaces are prepared between the photoetched core and the silica shell and their size can be regulated by choosing the irradiation wavelength. The nanospace of regulated size in the photoetched particulate films containing semiconducting materials of uniform size (i.e., of uniform chemical and physical properties) can be a new type of material, e.g., nanoflask array for semiconductor photocatalytic reactions. It is revealed, being opposites to our expectation, that curing of the film induced the shrinkage of the silica network of the shell to decrease the amount of remaining photoetched CdS core. In order to avoid this, it is necessary, for example, to fill the gap among the core-shell particles or to thicken the silica shell layer. Work in this direction is currently in progress.

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## Figure Captions

**Scheme 1** (a) Preparation of silica-coated CdS nanoparticle film by a layer-by-layer deposition. Immobilization of MPTS-modified CdS nanoparticles (1, 3) and hydrolysis of trimethoxysilyl groups (2). (b) Regulation of a void space inside the shell structure by the size-selective photoetching technique.

**Figure 1** (a) Absorption spectra of MPTS-modified CdS nanoparticle dissolved in toluene. (b) Changes in the absorption spectra of silica-coated CdS nanoparticle films with the number of the accumulation cycles. The number of accumulation cycles was indicated in the figure.

**Figure 2** The absorbance difference ( $\Delta A$ ) between exciton peak and absorption onset of silica-coated CdS nanoparticle films as a function of the number of accumulation cycles.

**Figure 3** Absorption spectra of silica-coated CdS nanoparticle film prepared by irradiation with various wavelengths: original film (1) and films prepared by irradiation at (2) 488, (3) 458, and (4) 436 nm. The number of accumulation cycles was 17. The arrows show the position of exciton peaks.

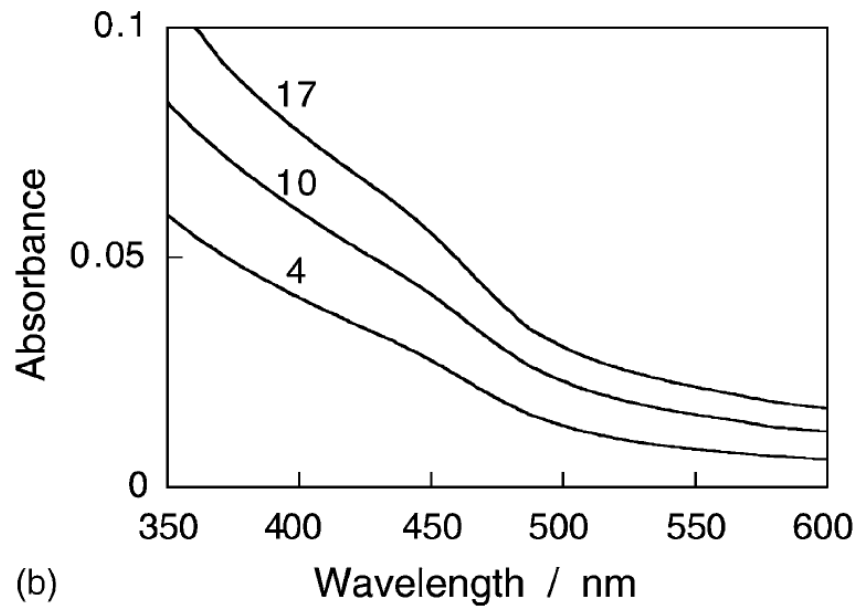
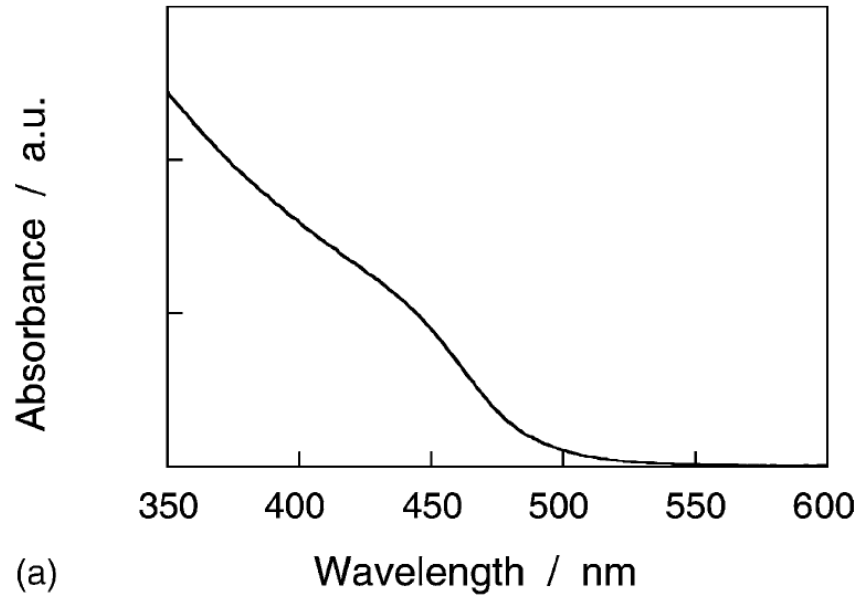
**Figure 4** An AFM image of a silica-coated CdS nanoparticle film after irradiation at 458 nm. The number of accumulation cycles was 17.

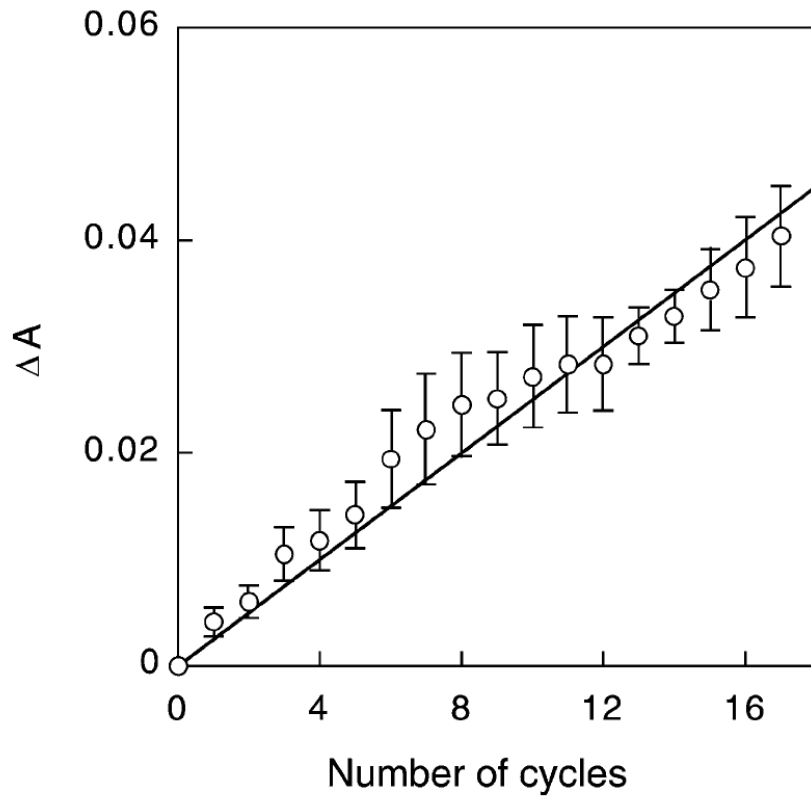
**Figure 5** Changes in the absorption spectra of silica-coated CdS nanoparticle films heat-treated at 473 (a), 573 (b), and 673 K(c) before (1) and after irradiation at (2) 488, (3) 458, and (4) 436 nm. The number of accumulation cycles was 17. The arrows show the position of exciton peaks and vertical dotted lines indicate the position of the exciton peak of the as-prepared films.

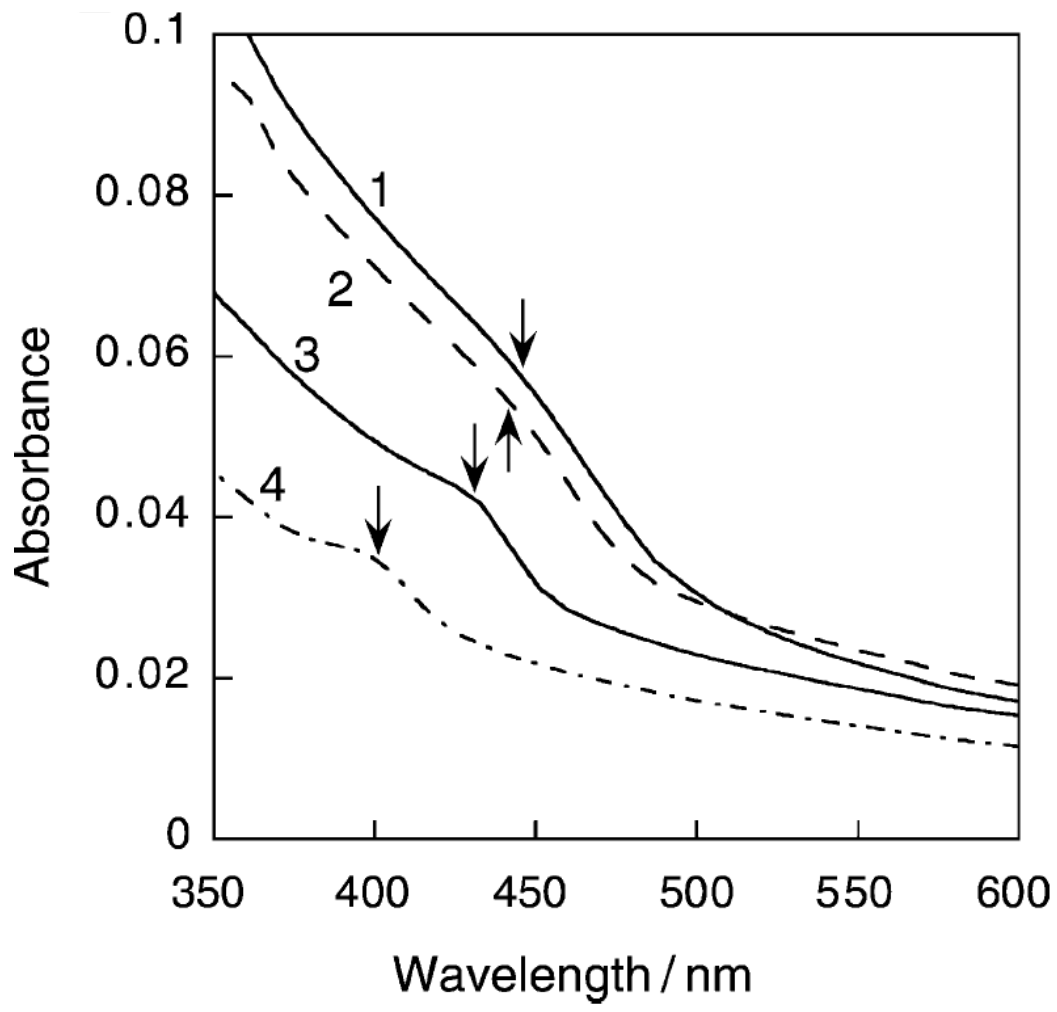
**Figure 6** The absorbance difference ( $\Delta A$ ) between exciton peak and absorption onset of silica-coated CdS nanoparticle films before (1) and after irradiation at (2) 488, (3) 458, and

(4) 436 nm as a function of curing temperature. The results in Fig. 5 were used for calculation. The films were as prepared (open symbols) and after heat-treatment (solid symbols).

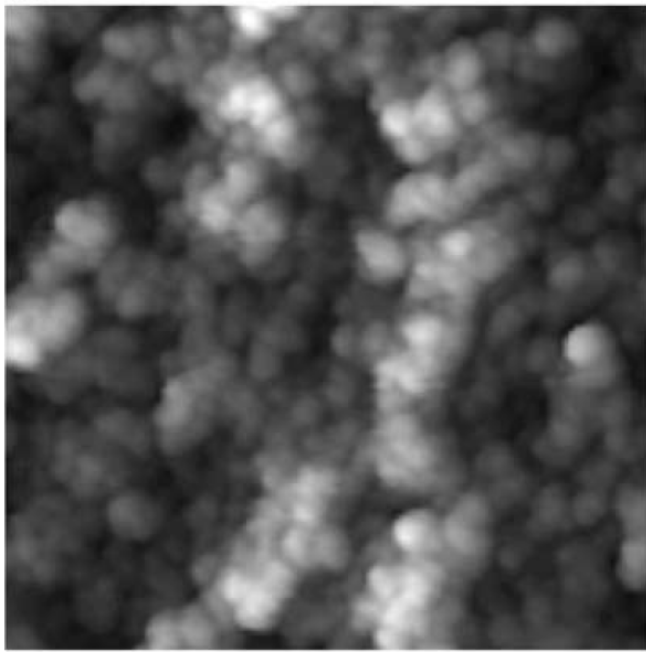






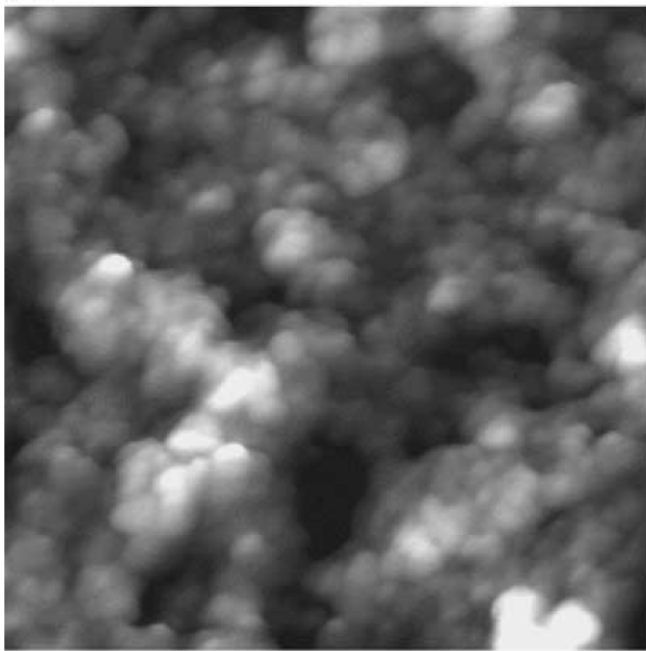


(a)



100 nm

(b)



100 nm

