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# Synthesis of Metal-Cadmium Sulfide Nanocomposites Using Jingle-Bell-Shaped Core-Shell

## Photocatalyst Particles

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## **Abstract**

Photocatalytic deposition of gold (Au) and silver (Ag) nanoparticles was investigated using a jingle-bell-shaped silica (SiO<sub>2</sub>)-coated cadmium sulfide (CdS) nanoparticles (SiO<sub>2</sub>/CdS) as a photocatalyst, which had a void space between the CdS core and SiO<sub>2</sub> shell. The size-selective photoetching technique was used to prepare the jingle bell nanostructure of SiO<sub>2</sub>/CdS. Metal nanoparticles of Au and Ag were deposited with irradiation of the photoetched SiO<sub>2</sub>/CdS in the presence of the corresponding metal complexes under deaerated conditions. The chemical etching of Au-deposited particles enabled the selective removal of CdS without any influence on the surface-plasmon absorption of Au. TEM analyses of the resulting particles suggested that some particles were encapsulated in hollow SiO<sub>2</sub> particles, while other Au particles were deposited on the outer surface of SiO<sub>2</sub> shell. Emission spectra of the photoetched SiO<sub>2</sub>/CdS showed that the metal deposition developed the broad emission with a peak around 650 nm originated from surface defects sites, the degree being dependent on the kind of metal nanoparticles and their amount of deposition. These can be explained by the formation of metal-CdS binary nanoparticles which had the defect sites at the interface between metal and CdS.

## **Key Words:**

core-shell particle, jingle bell structure, photocatalyst, photodeposition, nanoparticle, size selective photoetching, cadmium sulfide, gold, silver

## Introduction

Several synthetic methods have been used to obtain a surface coverage of nanoparticles of either metals or semiconductors in core-shell morphology, in order to modify physical and chemical properties of the core materials without their coagulation into larger particles [1-7]. For example, silica shell layer was prepared by the polymerization/precipitation of silane compounds on the particle surface [1-4]. A shell composed of polyelectrolytes and charged nanoparticles was prepared by the layer-by-layer deposition on the core surface [8]. Furthermore the partial removal of core materials in core-shell particles has been reported to generate the novel structures, such as metal or semiconductor nanoparticles-encapsulated hollow spheres that had void space between the core and shell [9-15]. These particles have attracted much attention because the void spaces are expected to be suitable for novel catalytic reactions and for the fabrication of nanostructure.

We have recently developed a novel strategy to control the size of cadmium sulfide (CdS) core in core-shell morphology [16-18]. The application of size selective photoetching to silica (SiO<sub>2</sub>)-coated CdS (SiO<sub>2</sub>/CdS) nanoparticles enabled the selective decrease of CdS core size, resulting in the formation of void spaces between the CdS core and the SiO<sub>2</sub> shell (a nanosized “jingle bell”). The size of void space could be controlled from 1.4 to 2.4 nm by adjusting the wavelength of monochromatic irradiation for CdS photoetching from 514 to 458 nm [16]. One of the significant features is that the photoetched CdS cores exposed their bare surface and their surrounding SiO<sub>2</sub> shells were sufficiently porous for permeation of small ionic species such as Cd<sup>2+</sup> and OH<sup>-</sup> to penetrate from the bulk solution to the interior of the SiO<sub>2</sub> shell [18]. Therefore, the

photoetched CdS cores behave like bare particles suspended in solution phase even if they were incorporated in the hollow SiO<sub>2</sub> particles.

In this study we report the photocatalytic activity of SiO<sub>2</sub>/CdS particles for the deposition of metal nanoparticles. The irradiation to a photoetched CdS induced the photocatalytic deposition of metal nanoparticles of gold (Au) and silver (Ag) both inside the void space of jingle-bell-shaped SiO<sub>2</sub>/CdS nanoparticles and on their outer surface. Subsequent chemical etching of CdS cores gave the metal nanoparticle-encapsulated hollow SiO<sub>2</sub> particles having a jingle-bell structure. Emission property of SiO<sub>2</sub>/CdS was greatly modified depending on the kind of metal and on their amount of deposition.

## **Experimental Section**

**Materials.** Sodium bis(2-ethylhexyl)sulfosuccinate (AOT), 1,1'-dimethyl-4,4'-bipyridinium dichloride (methylviologen, MV<sup>2+</sup>), and 3-mercaptopropyltrimethoxysilane (MPTS) were purchased from Tokyo Chemical Industry. Cadmium perchlorate (Kishida Reagents Chemicals) and potassium dicyanogold(I) (KAu(CN)<sub>2</sub>, Nacalai Tesque) were used as received. Other chemicals used in this study were supplied from Wako Pure Chemical Industries. Aqueous solutions were prepared just before use with water purified by a Yamato/Millipore WP501 Milli-Q system.

**Size-selective photoetching of silica-coated cadmium sulfide (SiO<sub>2</sub>/CdS) nanoparticles.** The silica (SiO<sub>2</sub>)-coated cadmium sulfide (CdS) nanoparticles were prepared using AOT-reversed-micelle method as reported in our previous papers [16-19]. The size selective

photoetching was applied to the thus-obtained particles to prepare jingle bell nanostructure. The  $\text{SiO}_2/\text{CdS}$  powder (80 mg) was suspended in a  $50 \text{ cm}^3$  oxygen-saturated water containing  $50 \mu\text{mol dm}^{-3} \text{MV}^{2+}$  and irradiated with monochromatic light until its diffuse reflectance spectra had become unchanged (typically for 8 h). The irradiation of monochromatic light at 514, 488, and 458 nm was performed by an argon-ion laser (Ion Laser Technology, model 5500A) with the intensity of ca. 60, 60, and 10 mW, respectively. The powders were washed with water and methanol several times, and dried under vacuum.

**Photochemical deposition of gold (Au) or silver (Ag) nanoparticles onto  $\text{SiO}_2/\text{CdS}$ .** The jingle-bell-shaped  $\text{SiO}_2/\text{CdS}$  nanoparticles were re-suspended in aqueous methanol (50 vol%) containing  $\text{KAu}(\text{CN})_2$  or potassium dicyanosilver(I) ( $\text{KAg}(\text{CN})_2$ ) and irradiated at  $> 300 \text{ nm}$  by a 400-W high-pressure mercury arc lamp for typically 1.5 h under an argon atmosphere. The resulting powder was isolated by centrifugation and washed with water and methanol, followed by drying under vacuum. The powder was suspended in diluted sulfuric acid ( $0.1 \text{ mol dm}^{-3}$ ) and stirred for 96 h to dissolve CdS selectively, when necessary.

**Characterization.** Samples were diluted with a powder of barium sulfate to give the content of 1 wt% and their diffuse reflectance spectra were measured using a photonic multi-channel analyzer (Hamamatsu Photonics, PMA-11) and pure barium sulfate as a reference. Emission spectra were recorded on a fluorescence spectrometer (Shimadzu RF-5300PC) with excitation wavelength at 350 nm.  $\text{SiO}_2/\text{CdS}$  powders (1.5 mg) were suspended in water ( $1.5 \text{ cm}^3$ ) and poured into a quartz cell. The suspension was vigorously stirred during the emission measurement. The structure and size

distribution of photodeposited Au nanoparticles were examined by a JEOL 2010F transmission electron microscope (TEM) with an acceleration voltage of 200 kV. The TEM samples were prepared by dropping the powder suspension onto a copper grid covered with amorphous carbon overlayers (Ouken Shoji, type B) and drying under vacuum.

## **Results and Discussion**

### **Photodeposition of Gold Nanoparticle**

Figure 1 shows the changes in diffuse reflectance spectra of SiO<sub>2</sub>/CdS. Original particles exhibited an absorption onset at ca. 550 nm. Since the energy gap of bulk CdS has been reported to be 2.4 eV [20] (corresponding to the absorption onset of ca. 520 nm), most of the CdS nanoparticles had an energy gap similar to that of the bulk materials. The monochromatic irradiation at 488 nm caused its blue shift to ca. 490 nm. This indicates that CdS core in SiO<sub>2</sub>/CdS was successfully photoetched to the size expected from the wavelength of irradiation light, resulting in formation of a void space between CdS core and SiO<sub>2</sub> shell as reported in our previous paper [16]. When the photoetched SiO<sub>2</sub>/CdS powders were irradiated in the presence of the gold complex under deaerated conditions, a new broad absorption band assignable to a surface plasmon (SP) band of Au particles [21] appeared in the range of wavelength longer than 500 nm. The irradiation with the time longer than 1.5 h caused almost no change in the diffuse reflectance spectra, indicating that the photodeposition of Au nanoparticles was completed within 1.5 h. A marked decrease in CdS absorption in the wavelength range of 300-500 nm was observed after the deposition of Au,

probably due to electronic interaction between them and/or changes in degree of scattering of the resulting particles, suggesting that the photodeposition of Au nanoparticles occurred to give an Au-CdS binary particles incorporated in the SiO<sub>2</sub> shell (SiO<sub>2</sub>/CdS-Au), as shown in Scheme 1. Furthermore, when the amount of Au loading increased, the intensity of SP band linearly increased without changes in the spectral shape up to at least 5 wt % Au loading as shown in Fig. 1b.

The absorption assigned to CdS nanoparticles in SiO<sub>2</sub>/CdS-Au disappeared by the chemical treatment with diluted sulfuric acid, suggesting the formation of SiO<sub>2</sub>/Au. The resulting powders had the SP band position of Au nanoparticles similar to that of corresponding SiO<sub>2</sub>/CdS-Au. TEM images of these particles were shown in Fig. 2. We could not obtain clear evidence in TEM images showing connection between CdS and Au in SiO<sub>2</sub>/CdS-Au, due to overlapping of particles. The complete removal of CdS was confirmed by the EDX analyses. Almost spherical Au nanoparticles were observed in the aggregation. The high magnification image of a particle (Fig. 2b) clearly shows that Au nanoparticles had the lattice fringes with interplanar spacing of 0.20 nm assigned to the (200) lattice plane of the face-centered cubic structure of gold crystal [22]. Furthermore it was clearly seen in Fig. 2b that the Au nanoparticle with size of ca. 4 nm was surrounded by an SiO<sub>2</sub> hollow shell (the size of ca. 6 nm), a jingle bell structure, as depicted in the schematic illustration. The void space between Au core and SiO<sub>2</sub> shell was calculated to be ca. 2 nm from the size difference between the Au nanoparticle and the hollow SiO<sub>2</sub> particle. Consequently Au nanoparticle was photodeposited in the void space of jingle bell-shaped SiO<sub>2</sub>/CdS and the surrounding SiO<sub>2</sub> shell prevented the coalescence of the Au nanoparticles during the chemical treatment. However the

average size ( $d_{av}$ ) of CdS core photoetched at 488 nm was determined to be 3.4 nm with the standard deviation ( $\sigma$ ) of 0.40 nm by TEM observation, which was larger than the void space in SiO<sub>2</sub>/Au observed in Fig. 2b. A possible explanation for this difference is change in the shape of Au deposits; the deposition must occur to cover the CdS surface, but they might transform to spherical particles of least surface energy during and/or after the CdS dissolution. The total volume of particles with diameters of 3.4 (CdS) and 4 nm (Au) does not exceed the volume of the inner space of hollow SiO<sub>2</sub> (6 nm).

The size distribution of Au nanoparticles was obtained by measuring the size of more than 80 particles in TEM images, as shown in Fig. 3. The Au nanoparticles had a broad size distribution with an average  $d_{av}$  of 7.6 nm and  $\sigma$  of 2.2 nm. The original CdS nanoparticles had the size in the range from 3.5 to 7 nm with  $d_{av}$  of 5.0 nm and  $\sigma$  of 0.79 nm and the inner diameter of SiO<sub>2</sub> was equal to the diameter of CdS before photoetching as reported in our previous paper [16], so that it might be expected that Au nanoparticles photodeposited had the size less than ca. 7 nm. However, this was not the present case; large part of Au nanoparticles had the size in the range from 7 to 14 nm. The photodeposition of Au nanoparticles might occur on the outer surface of SiO<sub>2</sub> shell as well as inside the void space. This explanation was supported by the photodeposition of Au using original SiO<sub>2</sub>/CdS as a photocatalyst: the broad SP band of Au nanoparticles appeared in the range of wavelength longer than 500 nm with the irradiation. The SiO<sub>2</sub> shell thickness was estimated to be ca. 0.3 nm from the elemental analyses of original SiO<sub>2</sub>/CdS. Since original particles had no void

space inside the SiO<sub>2</sub> shell, this fact indicated that the shell was thin enough to induce the electron transfer through it and to drive the photodeposition on the outer surface of SiO<sub>2</sub> shell.

### **Photodeposition of Silver Nanoparticle**

Figure 4 shows the changes in the diffuse reflectance spectra of SiO<sub>2</sub>/CdS particles before and after 0.5 wt% Ag deposition. The irradiation of the original or photoetched particles caused the appearance of the broad absorption band of Ag nanoparticles in the wavelength from 500 to 800 nm, suggesting that the Ag nanoparticles was also photodeposited both on the outer surface and inside the void space of SiO<sub>2</sub> shell. It should be noted that the absorption onset of SiO<sub>2</sub>/CdS photoetched at 488 nm was almost the same, irrespective of the Ag photodeposition, so that negligible changes in CdS size occurred during the present procedures of metal nanoparticle deposition under deaerated conditions.

### **Emission Properties of Metal-loaded SiO<sub>2</sub>/CdS**

Figure 5 shows the emission spectra of 488 nm-photoetched SiO<sub>2</sub>/CdS powders before and after metal photodeposition. The photoetched SiO<sub>2</sub>/CdS without metal deposition exhibited the band gap emission at 468 nm, while a broad emission appeared from metal-deposited samples in the range of wavelengths from 500 to 800 nm with a peak around 650 nm, which were attributed to the recombination of photogenerated charge carriers at the surface defect sites in CdS nanoparticles [23,24]. The emission intensity was greatly dependent on the kind of metal nanoparticles and their

amount. With an increase in the amount of Au deposition, the emission originated from the surface defect sites was enhanced while the band gap emission became small. The photodeposition of Ag nanoparticles considerably enhanced the emission at 650 nm rather than those observed for Au deposition. These results show that the metal nanoparticles deposited on the surface of CdS cores, i.e. Au-CdS or Ag-CdS binary nanoparticles in hollow SiO<sub>2</sub> particles, produced surface defect sites at the interface between the CdS core and metal nanoparticles, the degree being dependent on the kind of metal nanoparticle.

## **Conclusion**

The void space of the jingle-bell-shaped SiO<sub>2</sub>/CdS has been proved to work as a reaction space for the metal photodeposition. The removal of CdS by chemical etching enabled the preparation of Au-encapsulated hollow SiO<sub>2</sub> particles (SiO<sub>2</sub>/Au). The emission property of the photoetched CdS in the jingle bell structure was modified by the formation of metal-semiconductor binary structure, the degree depending on the kind of metal and their amount. Since metal deposition on the outer surface of SiO<sub>2</sub> shell could not be prevented due to the thin shell layer, the selective preparation of metal-semiconductor binary nanoparticles incorporated in SiO<sub>2</sub> shell or metal-encapsulated SiO<sub>2</sub> hollow particles could not be achieved in the present study. The metal nanoparticles will be deposited on a desired site in the jingle-bell-shaped SiO<sub>2</sub>/CdS by changing the SiO<sub>2</sub> shell morphology such as thickness and coverage. Study along this line is currently in progress.

## Acknowledgment

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## Figure Captions

**Fig. 1.** (a) Diffuse reflectance spectra of various SiO<sub>2</sub>/CdS samples: (1) original, (2) after photoetching at 488-nm laser light irradiation, (3) after 2 wt% Au photodeposition, and (4) after chemical etching of CdS. (b) The intensity of SP peak of Au as a function of the amount of Au loading.

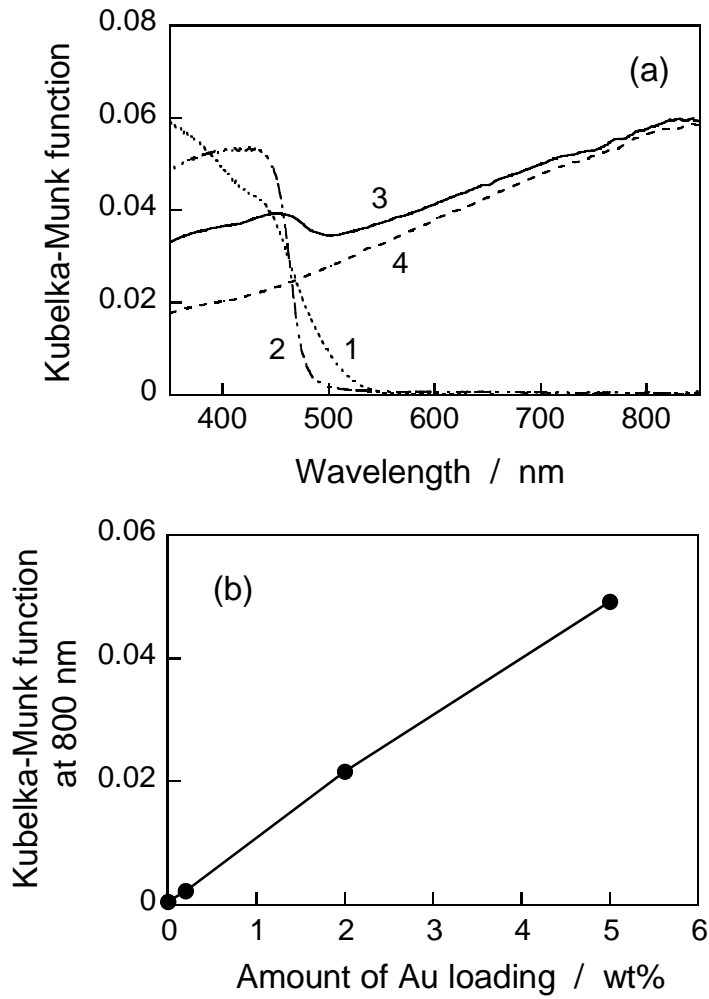
**Fig. 2.** TEM images of Au nanoparticles incorporated in SiO<sub>2</sub> shell. A picture (b) is a high magnification image of a particle shown in the picture (a). The schematic illustration of the structure is also shown.

**Fig. 3** Size distribution of Au nanoparticles obtained from TEM images.

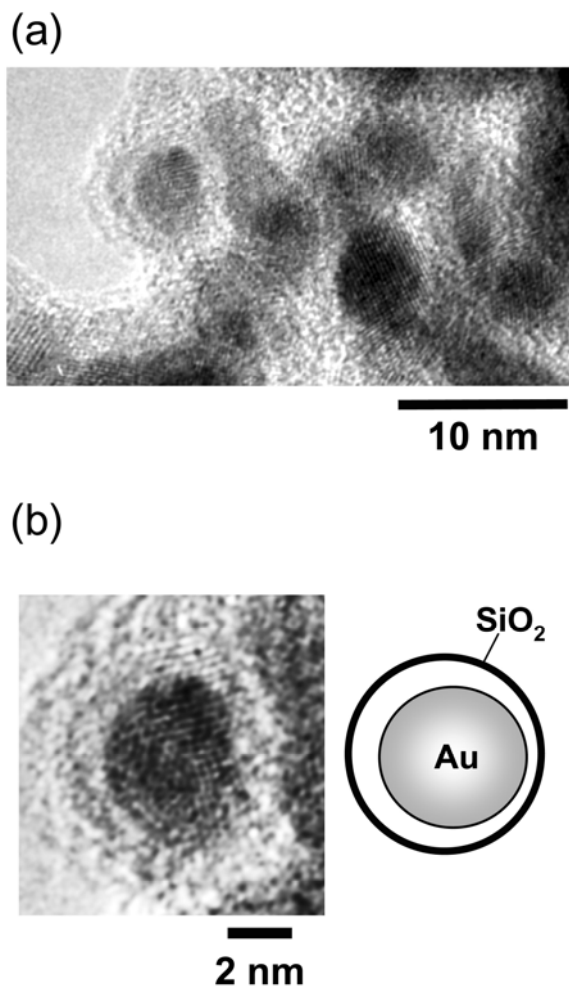
**Fig. 4.** Diffuse reflectance spectra of SiO<sub>2</sub>/CdS particles before (dotted lines) and after 0.5 wt% Ag deposition (solid lines). SiO<sub>2</sub>/CdS used were original (a) and photoetched with 488nm irradiation (b).

**Fig. 5.** Emission spectra of 488 nm-photoetched SiO<sub>2</sub>/CdS powders. Samples were before (a) and after metal photodeposition of 0.2 wt% Au (b), 5.0 wt% Au (c), and 0.5 wt% Ag (d). The excitation wavelength was 350 nm.

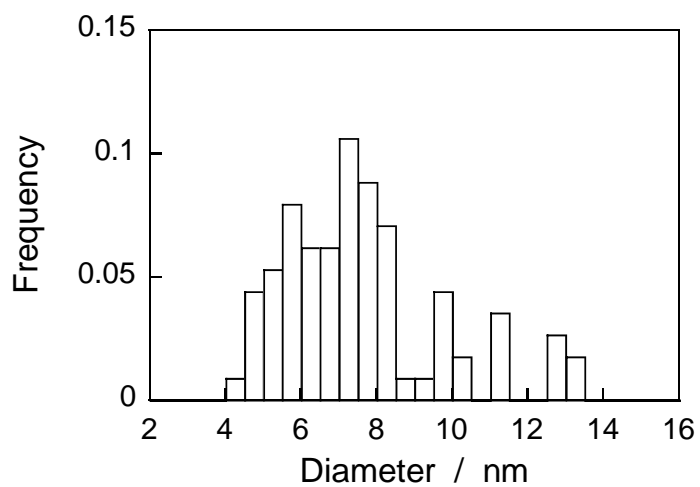
**Scheme 1** Schematic illustration of photodeposition of metal nanoparticle to SiO<sub>2</sub>/CdS and its chemical etching. The procedures used in this process were size-selective photoetching (1), photodeposition (2), and chemical etching (3).



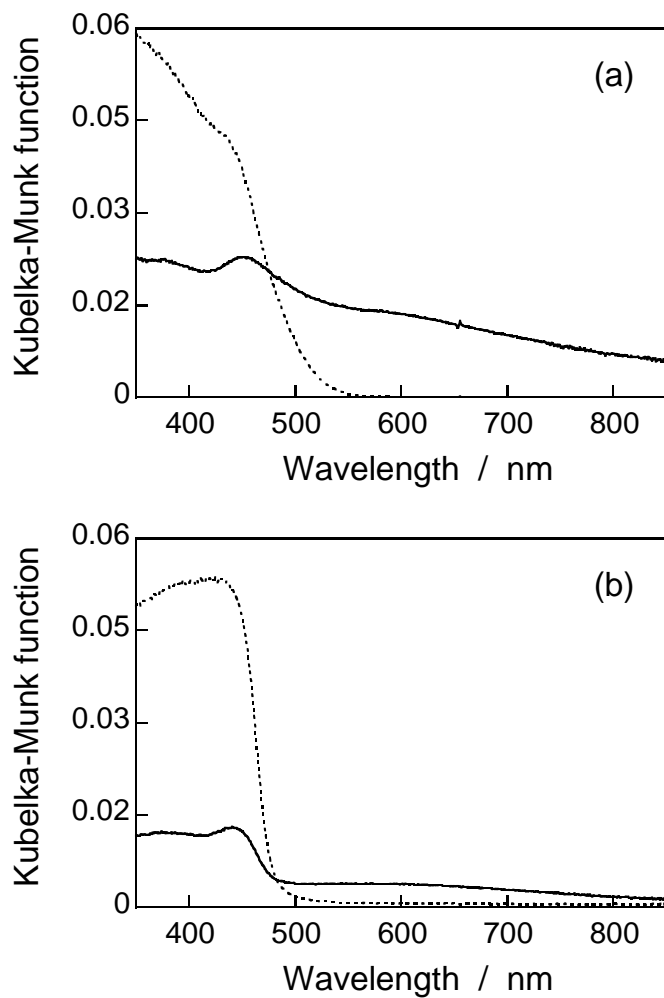
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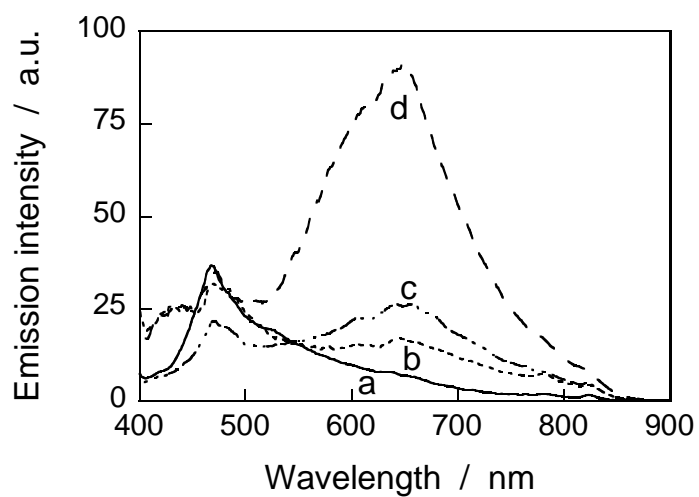
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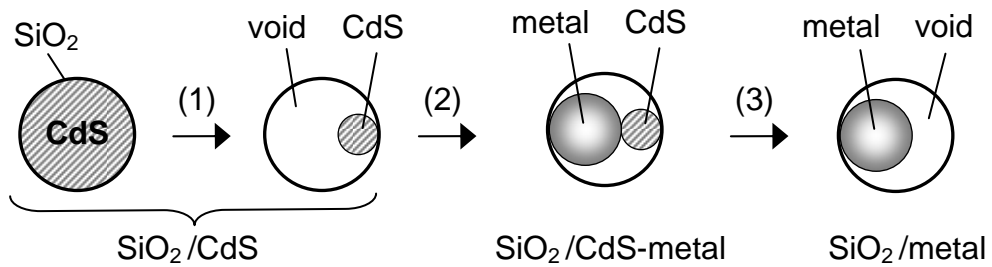
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**Scheme 1** Schematic illustration of photodeposition of metal nanoparticle to  $\text{SiO}_2/\text{CdS}$  and its chemical etching. The procedures used in this process were size-selective photoetching (1), photodeposition (2), and chemical etching (3).