

## Fabrication and Optical Characteristics of CdS/Ag Metal-Semiconductor Composite Quantum Dots

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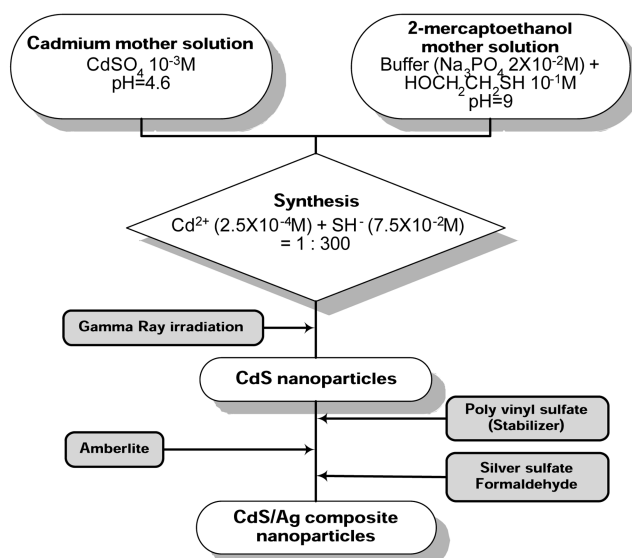
There have been great interests in the optical, electrical, and chemical properties of quantized nanoparticles, such as semiconductor quantum dots (QDs).<sup>1</sup> Semiconductor QD structures particularly have attracted attentions because of their strong three dimensional quantum confinement effects. Researches have been held to develop better methods to fabricate such semiconductor QDs, showing great progress during the past decade. One of the most early developed fabrication methods is to embed II-VI semiconductor compound QDs into glass matrices.<sup>2,3</sup> However, recently, many research groups have established chemical fabrication methods of colloidal QDs dispersed in solution, which are comparatively more stable than those in glasses.<sup>4-6</sup> In particular, a radiolysis method utilizing a gamma ray source at room temperature has been actively and successfully conducted, which allows us to monitor the size of the sample during each fabrication process.<sup>7-9</sup> These colloidal QDs are produced by chemical reactions in equilibrium states, where the solution matrices act as a stabilizer, offering fast reaction time between the atoms as well as a slow growth rate during the fabrication procedure, helping to improve stability. In general, capping ligand is usually added to avoid aggregation of the nanoparticles and increase the solubility. Along with semiconductor QDs, solid metal nanoparticles also display distinctive and potentially productive properties. Characteristics of surface enhanced Raman scattering and surface second harmonic generation due to local field enhancement associated with plasmon resonance are well known examples of such the specialties.<sup>10-12</sup> Metal nanoparticles also have a large and fast third order optical nonlinearity opening possibilities for optical switching devices.<sup>12</sup> Fabrication methods of metal nano-structured particles, like in the case of semiconductor nanoparticles, have been continuously improved to reduce inhomogeneous broadening, optimizing their optical properties.

If the metal nano-structure is incorporated into the QD system, coupling between the plasmon resonance effect and the quantum size effect of the semiconductor QD may develop new aspects of nano-composite material systems and also widen applications for noble nano-devices.<sup>13-17</sup> In this article, the fabrication and optical characteristics of CdS/

Ag semiconductor-metal composite QD structures are presented. The CdS QDs were made of cadmium sulfate and 2-mercaptoethanol by gamma ray irradiation in aqueous solution and silver was partially covered around the fabricated CdS QDs. The measured absorption spectra showed exciton peaks due to the quantum confinement effect as well as the surface plasmon resonance effect.<sup>18,19</sup> A red-shift of the CdS exciton absorption peak was observed, strongly indicating an enhancement of the local field in the semiconductor core. High Resolution Transmission Electron Microscopy (HRTEM) was also carried out to verify formation of CdS QDs and CdS/Ag composite QDs.

### Experiments

The CdS QDs were prepared in water under the following five step processes as depicted in Figure 1. All processes were held under N<sub>2</sub> gas environment to prevent oxidation. First, cadmium sulfate (CdSO<sub>4</sub>, M.W. = 78.13) was dissolved into super pure water to make a Cd<sup>2+</sup> mother solution of 10<sup>-3</sup> M at pH 4. Next, 0.1 M HOCH<sub>2</sub>CH<sub>2</sub>SH mother solution of



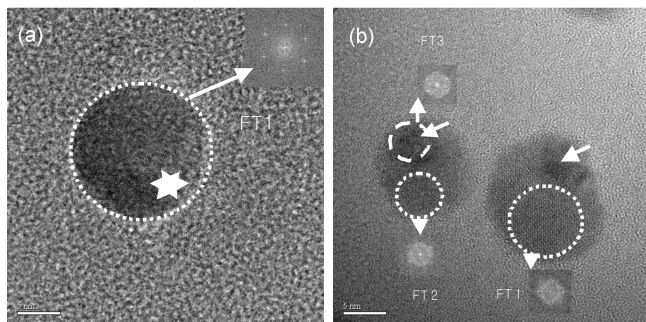
**Figure 1.** Five step fabricate processes of CdS quantum dots.

pH 9 was produced by combining 2-mercaptoethanol ( $\text{HOCH}_2\text{CH}_2\text{SH}$ , M.W. = 208.46) in a buffer solution made by dissolving sodium phosphate ( $\text{Na}_3\text{PO}_4$ ) in water. Third, both solutions were mixed by adding the mother solution of  $\text{Cd}^{2+}$  and  $\text{HOCH}_2\text{CH}_2\text{SH}$  solution with the ratio of concentration as 1 : 100, 1 : 200 and 1 : 300 at pH 7.5. Fourth,  $^{137}\text{Cs}$  facility of 2500Ci was used to irradiate the solutions in the steady-state regime with a gamma-ray dosage of 0.3 kGy, 0.6 kGy, and 0.9 kGy, to produce CdS QDs using the hydrated electron  $e_{\text{aq}}^-$  as reducing species. Finally, in order to fabricate metal coated CdS/Ag with the previously made CdS QDs, the excess of 2-mercaptoethanol had to be removed. Then, a poly vinyl sulfate mother solution of  $2 \times 10^{-4}$  M was added to stabilize the CdS QDs, while resin and amberlite were used to remove the excess of 2-mercaptoethanol. 1 ml of the silver mother solution of  $1.6 \times 10^{-3}$  M using silver sulfate ( $\text{Ag}_2\text{SO}_4$ ) was also annexed into the solution for the silver capping process. Finally, formaldehyde solution of  $10^{-3}$  M was added to reduce the silver sulfate at the surface of the CdS QDs.

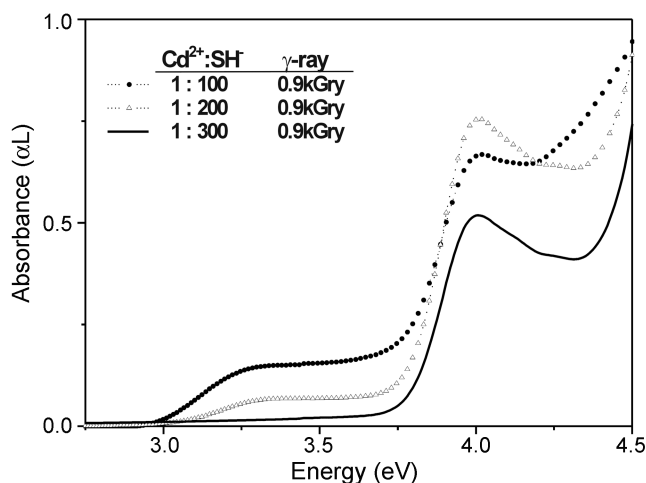
HRTEM investigations were performed using a Philips CM30 electron microscope, equipped with a high resolution stage to get information not only of the structure, but also of the texture of the materials at a nanometric scale. The spatial resolution in HR mode was 0.18 nm (point to point). The CM30 is equipped with a Low Illumination Digital camera which can directly catch the numerical micrograph, providing a Fourier Transform (FT) operation of the images on a full scale or on a selected Region of Interest (ROI).

### Experimental Results

Figure 2 shows typical HRTEM pictures of a CdS QD and CdS/Ag composite QDs, which were fabricated by using the aforementioned method. As shown in Figure 2(a), an almost perfectly circular CdS QD can be fabricated, which has three different systems of fringes (3 crossed white arrows). The FT of a ROI indicated by a white dashed circle on the micrograph gives the following inter reticular distances between the fringes:  $2.41 \pm 0.12$  Å,  $2.36 \pm 0.11$  Å and  $2.035 \pm 0.10$  Å. Figure 2(b) displays the micrograph of CdS QDs (low contrast) doped by Ag (high contrast). The ROI



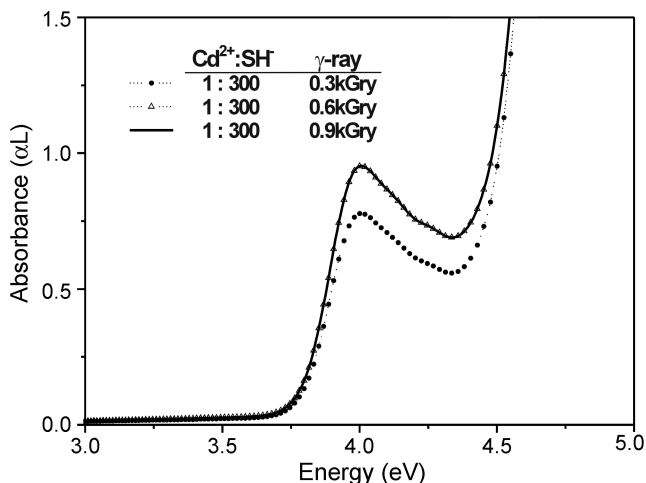
**Figure 2.** High-Resolution TEM image of (a) a CdS quantum dot and (b) CdS/Ag composite quantum dots. (The white small dashed circle corresponds to the ROI of the FT<sub>1</sub> and FT<sub>2</sub> and the white large dashed circle to the FT<sub>3</sub>).



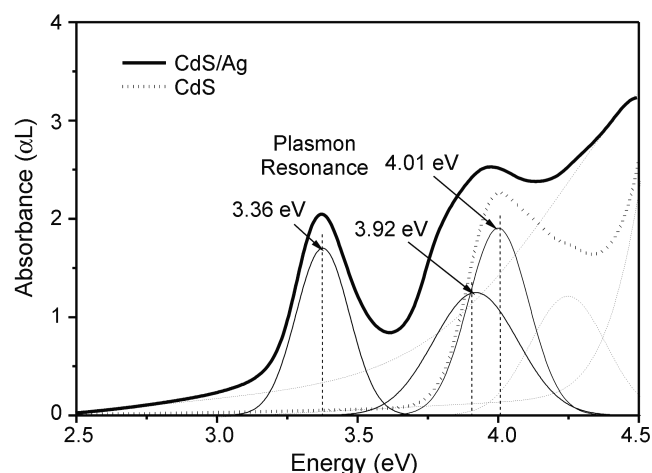
**Figure 3.** Absorption spectra of CdS quantum dots for varying concentration ratios of 2-mercaptoethanol.

selected presents two different systems of atomic fringes. The FT<sub>1</sub> and FT<sub>2</sub> for the ROI<sub>1</sub> and ROI<sub>2</sub> reveals the formation of CdS with inter reticular atomic distance of  $3.417 \pm 0.15$  Å,  $3.042 \pm 0.15$  Å,  $2.410 \pm 0.12$  Å,  $2.35 \pm 0.11$  Å, and  $2.035 \pm 0.10$  Å, which are in accordance with value corresponding to CdS crystals in JCPDF files. The FT<sub>3</sub> of the ROI<sub>3</sub> exhibits a Debye-Scherrer pattern with fringes at  $2.41 \pm 0.12$  Å and  $2.213 \pm 0.11$  Å, indicating the partial growth of Ag hexagonal nano-crystals on the surface of the CdS QDs.

The effect of the concentration of 2-mercaptoethanol has been investigated on the preparation of smaller sized CdS QDs. In Figure 3, the absorption spectra for different ratios of  $[\text{Cd}^{2+}]/[\text{SH}^-]$  is displayed. One can distinguish two bands at  $\sim 4.00$  eV and  $\sim 3.35$  eV corresponding to CdS QDs having an average radius of  $\sim 1.29$  nm and  $\sim 1.75$  nm, respectively. As the concentration of 2-mercaptoethanol, which acts as a stabilizer for the CdS QDs increase, the absorption band around 3.35 eV decrease in intensity and disappear



**Figure 4.** Absorption spectra of CdS quantum dots for different  $\gamma$ -ray dosage.



**Figure 5.** Absorption spectra after capping CdS quantum dots with silver ( $[\text{Cd}^{2+}]/[\text{SH}^-] = 1/300$ ,  $\gamma\text{-ray} = 0.9 \text{ kGy}$ ).

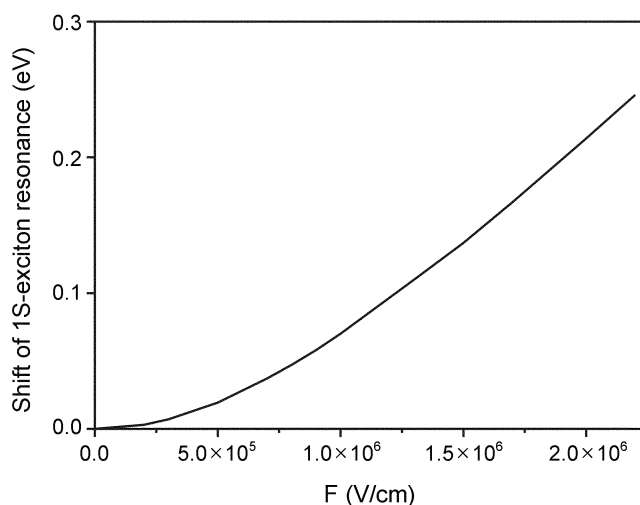
completely for a ratio  $[\text{Cd}^{2+}]/[\text{SH}^-]$  of 1/300. This effect indicates that for stabilizing the particles, large amounts of 2-mercaptoethanol is necessary.

In Figure 4, the effect of the dose on the growth of CdS QDs is presented. Above a dose of 0.6 kGy, the maximum absorption at 4 eV remains constant indicating a complete reaction and a complete use of the cadmium concentration to form CdS QDs. For capping silver on the surface of the particles, therefore, a dose of 0.9 kGy and a concentration ratio  $[\text{Cd}^{2+}]/[\text{SH}^-]$  of 1/300 has been used.

After the silver is added into the colloidal solution, two absorption peaks are apparent between 3.0 eV and 4.25 eV, as shown in Figure 5. Gaussian fitting of the absorbance reveals that a new peak is observed at 3.36 eV, which arises from the plasmon resonance of silver nanostructures originating from silver structures coating the CdS semiconductor QDs. In addition, the Gaussian fitting of exciton and plasmon resonance peaks shows that the pre-existent absorption peak at 4.01 eV has shifted to a lower energy by 0.09 eV to 3.92 eV. The red-shift of the absorption peak is attributed to be an effect due to the local-field enhanced by a metal structure surrounding the semiconductor core.

We have calculated the Stark shifts based on the effective-mass Hamiltonian in the presence of an external electric field, as shown in Figure 6. From this calculation, the local field is estimated to be approximately  $1 \times 10^6 \text{ V/cm}$  for the observed red-shift of 0.09 eV. The calculations are determined by the electron-hole pair energy levels and the dipole moment matrix elements, which are obtained by the results of the numerical matrix diagonalization method.<sup>20</sup> Thus, we conclude that the red-shift of the absorption peak corresponding to the semiconductor core implies the strong local field effect in metal-coated semiconductor composite QD systems. The red-shift of the exciton peak as a function of the silver thickness is under investigation.

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**Figure 6.** Calculated Stark shifts for a CdS QD of radius 1.29 nm as a function of external electric field based on the effective-mass Hamiltonian.

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