Optical Properties and Characteristics of the CdSe Nanoparticles Synthesized at Room Temperature

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Abstract−CdSe nanoparticles were synthesized by using colloidal methods at room temperature. Nanoparticle size was controlled by the amount of stabilizer, pH, and stabilizer type and was characterized by TEM and XRD. All the synthesized CdSe nanoparticles showed the quantum confinement effect. With increased amounts of mercaptoacetic acid as a stabilizer, the size of nanoparticles decreased. The UV-VIS absorption and photoluminescence (PL) properties could also be tailored by controlling particle size. The solubility in organic solvent and the PL characteristics were enhanced through surface capping by an organic passivator.

Key words: CdSe Nanoparticle, Photoluminescence, UV-VIS Absorption

INTRODUCTION

Nanoscience is rapidly emerging field of science. The synthesis and control of materials in nanometer dimensions can lead to access to new material properties and device characteristics in unprecedented ways [Jung et al., 1997; Oh and Park, 2000; Park et al., 2001].

Semiconductor nanoparticles, which exhibit properties different from bulk materials, are a new class of materials that hold considerable promise for numerous applications in the field of electronics and photonics. Nanoscale modification of molecular design and morphology of such particles provides a powerful approach to control their electronic and optical properties as well as their processability. These properties include quantum size effects on photoreactivity and photocatalytic activity. In addition, they have applications in nonlinear optics. The physical properties of semiconductor nanocrystallites are dominated by quantum confinement, the widening HOMO-LUMO gap with decreasing particle size that directly affects the photophysics of a material. Consequently, the proper control of particle size is critical in any investigation involving these materials [Winiarz et al., 1999].

For preparation of CdSe nanocrystals, the pyrolysis of organometallic molecules and H_2Se methods have been the main methods. These methods involve, respectively, the use of complex organometallic molecular precursors and H_2Se toxic agents [Wang et al., 1999]. The nanoparticles prepared by the organometallic precursor method are of high quality, but the reaction requires harsh and difficult conditions, such as the injection of hazardous metal akyls at elevated temperatures (ca. 350 ℃), which is clearly undesirable [Green and O'Brien, 1999]. While over the past decades the limitations of these methods have been an obstacle, considerable efforts have been made to explore new solution routes to CdSe II-VI semiconductor crystals with the goal of lowering processing temperature and avoiding complex reactions and toxic precursors, as

well as searching for milder preparation conditions [Wang et al., 1999].

Recently, novel methods for the preparation of CdSe nanoparticles under milder conditions have been proposed. Nanoparticles have been synthesized from aqueous solutions while adapting the approaches of colloid chemistry in these methods. We can easily expect that the size of CdSe nanoparticles can be controlled by changing ion concentration, pH, or stabilizer concentration. However, there have been few studies in this regard. In this study, we investigated the optical properties and synthesis of CdSe nanoparticles with stabilizer concentration using an aqueous method. In addition, the optical properties of the surface passivation of the CdSe core with 4-methylbenzenethiol as an organic stabilizer were investigated.

EXPERIMENTAL

1. Aqueous Method

Colloidal CdSe nanoparticles were prepared by chemical method in an aqueous solution according to the following reactions [Xu et al., 1998]:

$$Cd^{2+}+2OH^-+SeSO_3^{2-} \rightarrow CdSe+SO_4^{2-}+H_2O \qquad (1)$$
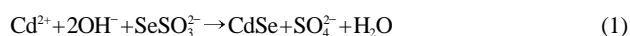
Cd^{2+} aqueous solution was made by dissolving $CdCl_2$ in deionized water. The Na_2SeSO_3 reagent was freshly prepared by dissolving Se powder in Na_2SO_3 solution under stirring. During the growth of CdSe, mercaptoacetic acid can work as a stabilizing agent. In the ethylenediaminetetraacetic acid (EDTA) stabilizer system, Cd^{2+} aqueous solution was made by dissolving $CdCl_2 \cdot 5/2H_2O$ in EDTA aqueous solution. The alkaline selenium aqueous solution was prepared as follows: 0.56 mol NaOH and 0.0025 mol of elemental Se were added to 50 ml of distilled water. Then the Cd^{2+} aqueous solution was combined with the alkaline selenium aqueous solution through rapid stirring.

2. Inverse Micelle Method

CdSe nanoparticles were prepared in micelles according to the above reaction (1). Two separate solutions were prepared by dis-

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solving surfactant AOT (sodium dioctyl sulfosuccinate) in heptane. Then deionized water was added to the above solutions. Stirring gave two homogeneous micelle solutions with W=6.7([H$_2$O]/[AOT]). Under quick stirring, a standard solution of Cd^{2+} was added to one of the above micelle solutions, while SeSO$_3^{2-}$ solution was added to the second micelle solution. Then the Cd^{2+} micelle solution was slowly transferred to SeSO$_3^{2-}$ solution, resulting in an orange or red solution. The size of CdSe nanocrystals could be controlled by changing the Cd^{2+} concentration, SeSO$_3^{2-}$ concentration, or W value of the micellar solution.

3. Characterization

X-ray diffraction patterns were obtained by using a Rigaku X-ray diffractometer equipped with CuKα radiation and a curved graphite crystal monochromator. Optical absorption spectra were collected at room temperature on a Jasco V-530 UV/Vis spectrophotometer. The samples for transmission electron microscopy (TEM) were prepared by placing a drop of solution of a sample on a copper grid. Bright field images were obtained with a JEOL JEM-2010 transmission electron microscope operating at 200 kV. The photoluminescence (PL) spectra were obtained by using a Perkin-Elmer Luminescence Spectrometer LS 50.

RESULTS AND DISCUSSION

1. Aqueous Method

Fig. 1 shows the UV-VIS absorption spectra at room temperature for colloidal CdSe made with different mercaptoacetic acid concentrations. With increased content of mercaptoacetic acid as a stabilizer [from (a) to (d)], the pH of the reaction medium has lower values, while pH of sample (d) is controlled to 8.9 by adding NaOH aqueous solution. With increased mercaptoacetic acid concentration, the color of the solution changes from orange-red to orange, yellow and light yellow. The range of the absorption edge lies between 630 nm to 520 nm, which is a pronounced blue shift from 712 nm of the bulk CdSe band gap [Xu et al., 1998]. By increasing

Fig. 2. Photoluminescence spectra of the CdSe nanoparticles shown in Fig. 1.
(a) pH 10.7, (b) pH 7.9, (c) pH 7.2, (d) pH controlled to 8.9

the mercaptoacetic acid concentration or decreasing quantum dots size, the range of absorption edges is blue shifted to high energy. This result is evidence of a quantum confinement effect in the CdSe quantum dots. It is also worth noting that an obvious absorption transition (1S-1S transition) has been observed in all absorption spectra, indicating that our samples have a relatively narrow size distribution [Brus, 1986].

Photoluminescence (PL) spectra of colloidal CdSe nanocrystals made with the same conditions as those outlined in Fig. 1 are shown in Fig. 2. All spectra show visible PL peaks in the range of 550 nm to 700 nm. With increased mercaptoacetic acid concentration, the peak was blue shifted to short wavelength. But for all samples, they show a small Stokes shift. These broad bands are mostly attributed
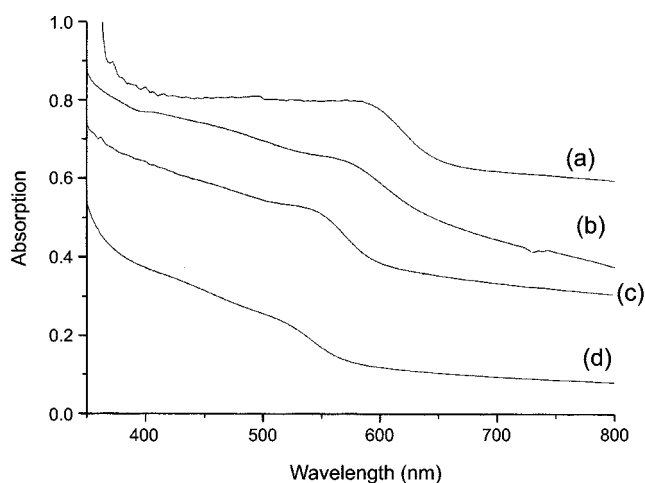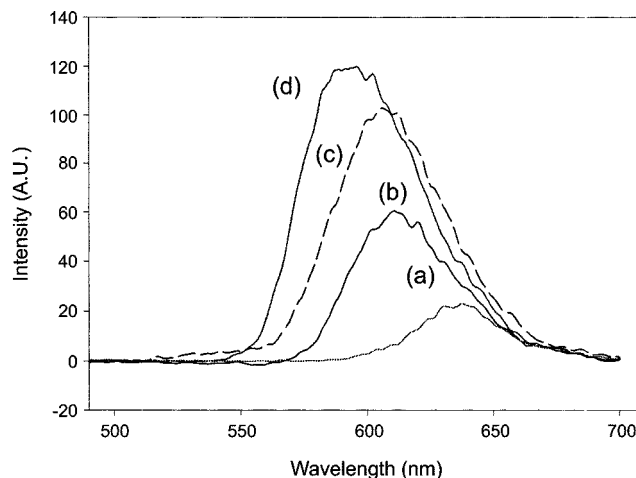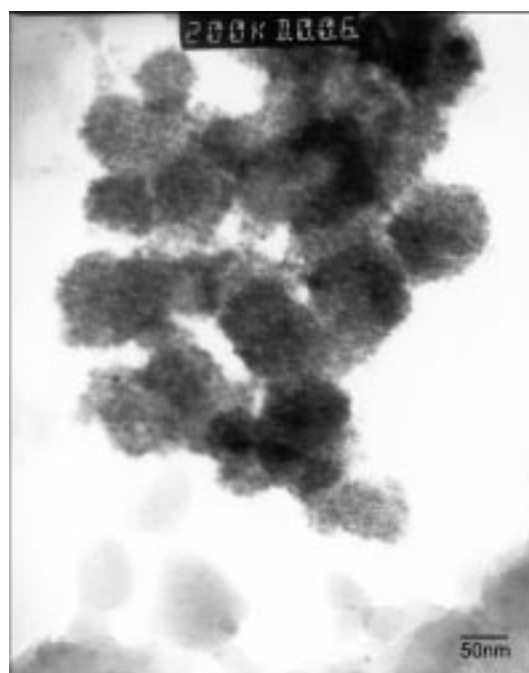

Fig. 1. UV-VIS absorption spectra for colloidal CdSe made with different mercaptoacetic acid concentrations. With increased mercaptoacetic acid, the pH of the reaction medium has a lower value.
(a) pH 10.7, (b) pH 7.9, (c) pH 7.2, (d) pH 8.9 (pH controlled by adding NaOH)

Fig. 3. Transmission electron microscope (TEM) image of CdSe nanoparticles by using aqueous method [(d) in Fig. 1].
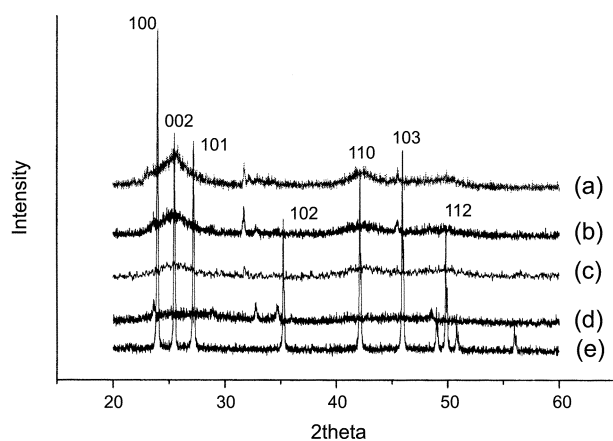
Fig. 4. X-ray diffraction patterns of the CdSe nanoparticles shown in Fig. 1; (a) pH 10.7, (b) pH 7.9, (c) pH 7.2, (d) pH controlled to 8.9. Sizes calculated by Scerrer's equation are (a) 29.3 Å, (b) 28.2 Å, (c) 21.6 Å, and (d) 10.5 Å, respectively. (e) 10 μm commercial CdSe powder for reference.

Fig. 5. XRD patterns of CdSe nanoparticles using different stabilizers, (a) mercaptoacetic acid, and (b) ethylenediaminetetraacetic acid (EDTA).

to the recombination of the carriers trapped in the surface states of bare CdSe quantum dots. These surface defects are mostly associated with Cd^{2+} and Se^{2-} vacancies (such as unstoichiometric defects and dangling bonds), which can induce nonradiative or radiative emission [Liu et al., 2000], resulting in the degradation of luminescence properties. Since the trap energies changed with the band gap of CdSe nanocrystals, the PL peaks blue shifted with decreased CdSe size. This result is consistent with the theory reported by Chestnoy and Brus [Chestnoy et al., 1986].

The structure of CdSe nanoparticles is characterized by transmission electron microscopy (TEM) and X-ray diffraction. Fig. 3, a TEM image of (d) in Fig. 1, shows that the agglomerated particles of 20-30 nm scale are composed of spherical particles with an average diameter of about 1 nm. This implies that a series of nanosized CdSe colloidal particles were successfully produced and that the size distribution could be controlled. This result coincided with the XRD data in Fig. 4. However, the CdSe nanoparticles formed agglomerates with a size of about several tens nm due to coagulation in the aqueous system.

To confirm that the blue shift observed in these samples was accompanied by the expected reduction in average size, size determination was conducted through XRD in conjunction with the Scherrer formula [Kakudo and Kasai, 1972; Azaroff and Buerger, 1958],

$$d = \frac{0.9\lambda}{\beta(2\theta)\cos\theta} \qquad (2)$$

where λ is the wavelength of the scanning radiation, $\beta(2\theta)$ is the full width at half-maximum of the peak in question, and θ is the angle at which the peak is centered. This formula quantitatively relates the observed broadening of X-ray diffraction lines with the finite size of the sphalerite crystalline particles. Fig. 4 shows XRD patterns of CdSe nanoparticles. Using Eq. (2), it was calculated that the size of the particles is (a) 29.3, (b) 28.2, (c) 21.6, and (d) 10.5 Å, respectively. XRD obtained for 10 μm commercial CdSe powder is included for the purpose of comparison. The selected area electron diffraction pattern furthermore identifies that the nanocrystalline CdSe is a wurtzite crystal structure. From the pattern, the re-
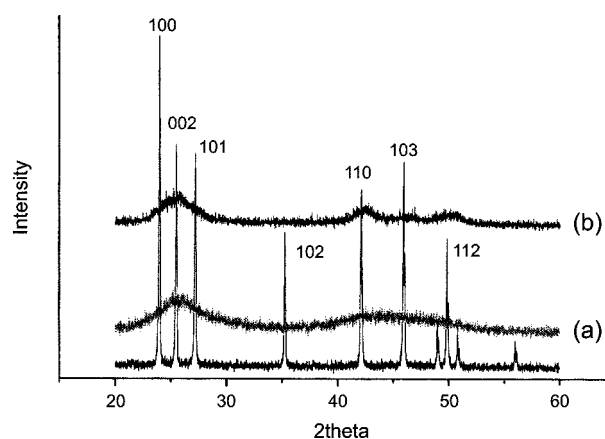
flections of planes 002, 110, and 112 are clearly seen.

To investigate stabilizer effects, two kinds of stabilizer, mercaptoacetic acid and EDTA, were used. Fig. 5 shows XRD patterns of CdSe nanoparticles by using different stabilizers. The broadening of the X-ray diffraction line in mercaptoacetic acid system was more pronounced than that of the EDTA system. Mercaptoacetic acid has a stronger stability that EDTA since the sulfur group can form a strong bond with the Cd of CdSe to prevent CdSe from growing large.

2. Inverse Micelle Method

Bare CdSe quantum dots prepared by colloidal methods have many surface defect states, such as surface nonstoichiometry, unsaturated bonds, etc., which act as nonradiative recombination or radiative luminescence centers, as shown in Fig. 2. The luminescence yield is reduced due to the recombination of carriers on these defect states. Applications of bare structure nanoparticles have been limited due to their surface instability when exposed to light and air. Because these defect states are located at the surface of colloidal quantum dots, surface passivation with various organic or inorganic groups by using chemical methods can modify them and consequently raise quantum yield as well as improve the luminescence properties. For applications such as optoelectronic devices using a polymer/semiconductor nanocomposite, the surfaces of the CdSe nanoparticles should be treated to be organophilic. Therefore, the CdSe quantum dots were synthesized by the inverse micelle method and their surfaces were treated with 4-methylbenzene thiol as an organic modifier in this section.

Fig. 6 shows a TEM image of CdSe before and after surface modification with an organic thiol. It shows that most particles are spherical with an average diameter of about 4 nm before the surface treatment. After the surface treatment, however, the particles have a broader size distribution than the bare CdSe particles, ranging from 4 to 10 nm. However, the majority of particles maintain their initial size, while only some particles show much bigger size. This could be a result of coagulation of CdSe particles due to the interaction of the shell part in the process of surface treatment, washing, and ultracentrifugal separation. The phenyl capping reaction effectively changes the crystallite surface from hydrophilic to hydrophobic. The crystallites leave the water pools and then precipitate. Therefore, the ul-
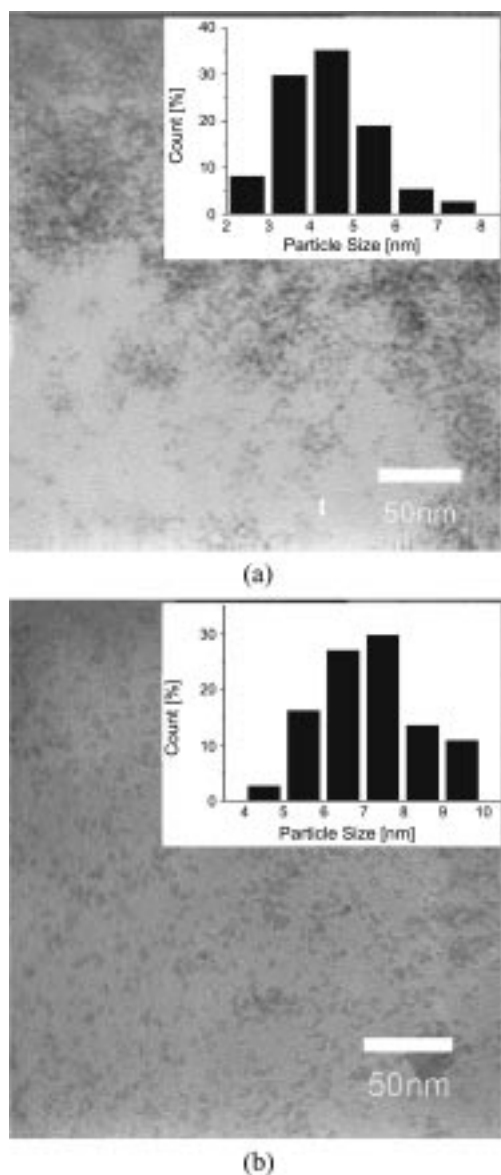
Fig. 6. TEM image of CdSe nanoparticles (a) before and (b) after surface modification with an organic thiol. Graphs in inset show the size distribution of each case.

tracentrifugal separation is easier. Furthermore, the hydrophobic cluster molecules obtained are completely soluble in pyridine.

Fig. 7 shows the UV-VIS absorption spectra at room temperature for colloidal CdSe made by the inverse micelle method. The absorption edge lies at about 550 nm, both before and after surface treatment, which is a pronounced blue shift from the bulk CdSe absorption edge. However, the UV-VIS absorption of coated CdSe nanoparticles with an organic capping agent has not changed significantly compared with that of uncoated CdSe. This suggests not only that the first electronic states of CdSe core have been little modified but also that the coagulation of CdSe nanoparticles does not take place between CdSe cores.

Fig. 8 shows the PL spectra of the CdSe nanoparticles before and after surface treatment. The effects of surface treatment are greatly pronounced in PL behavior. PL behavior before surface treatment shows a broad emission peak because of the unstable surface state.
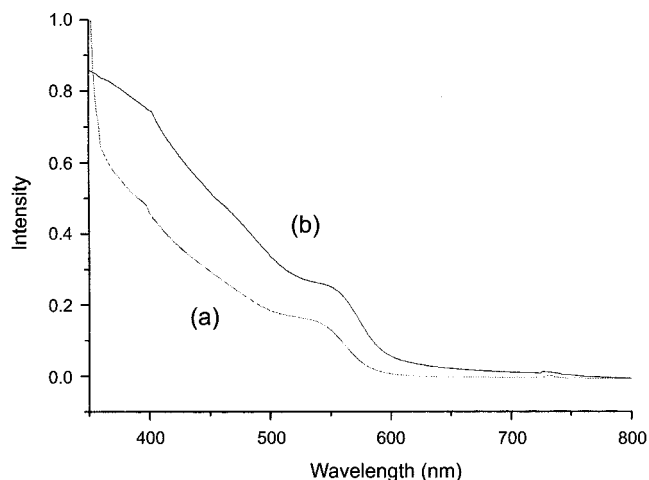

Fig. 7. UV-VIS absorption spectra of colloidal CdSe made by the inverse micelle method; (a) before and (b) after the surface treatment.
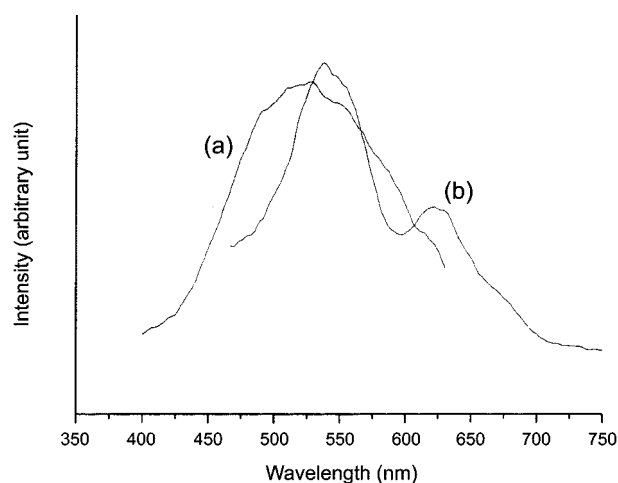

Fig. 8. Photoluminescence spectra of colloidal CdSe made by the inverse micelle method; (a) before and (b) after the surface treatment.

Fig. 8(b) exhibits two peaks, a low-wavelength peak arising from band-edge emission and a high-wavelength peak caused by surface states. This figure shows the decrease of surface-state emission by the surface capping with a thiol. Two emission peaks in PL behavior mean that the surface of CdSe nanoparticles was incompletely covered. These partially capped nanoparticles have advantages for applications of charge transfer devices. On the other hand, it is expected that the greater amount of surface capping agent would lead to a complete capping of the CdSe surface and the enhancement of the band-edge emission [Xu et al., 2000].

CONCLUSIONS

In summary, CdSe nanoparticles and organically capped nanoparticles were successfully synthesized by using colloidal methods at room temperature. The size of nanoparticles could be controlled by the amount of stabilizer, pH, and stabilizer type. The UV-VIS absorption and the PL properties could also be tailored by control-

ling particle size. The surface characteristics and PL stability were enhanced through surface capping by an organic passivator. This not only gives solubility to common organic solvents and polymers but also has potential benefits in applications such as photonic devices and optoelectronic devices.

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