Photoluminescence depending on the ZnS shell thickness of CdS/ZnS core-shell semiconductor nanoparticles

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Received 8 April 2004; accepted 25 June 2004
Available online 21 August 2004

Abstract

A core/shell type semiconductor nanoparticle of CdS/ZnS emits visible light under ultra-violet illumination, whose emission wavelength depends on the particle diameter and ZnS shell thickness. This paper describes the dependence of the shell thickness on the amount of added ZnS precursor in the synthesis process and its impact on photoluminescence. The synthesis is done by the microemulsion method in AOT surfactant reverse micelles containing water. The precursor amount is varied by two different ways (1) increasing water content, at a given precursor concentration or (2) increasing the precursor concentration at given water content. It is found that the nanoparticle diameter and the shell thickness almost linearly increase when the water content trapped in the reverse micelles increases. Similarly, the diameter increases with the precursor concentration inside the micelles. The nanoparticle size also increases with the time of aging in an inert gas because of the increase of the ZnS shell thickness.

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Keywords: Nanoparticles, CdS/ZnS; Core-shell; Reverse micelles; W/o microemulsion

1. Introduction

Semiconductor nanoparticles have attracted much attention during the last few years because of their novel optical and electronic properties, which have a great potential for many applications. For example, these are the light emitting diodes, lasers, luminescent nanocomposites and diagnostic agents in medicine. Especially, useful are the core-shell type nanoparticles composed of two kinds of semiconductors, e.g. CdS/ZnS [1], CdSe/ZnS [2] and CdSe/CdS [3,4] where the first semiconductor denotes the core while the second one is the shell that has a wider band gap than the first one. These nanoparticles are of high-efficient photoluminescence (PL) material, due to the wide band gap shell [2]. There are various synthetic methods for nanoparticles such as hot matrix methods [2,3] and microemulsion methods [1,4]. Despite of the advantages of the first method [high quality of nanocrystalline material due to the pyrolysis] [2], the second one is used in our synthesis, because of easier performance at a lower temperature and less severe conditions for the manipulation of precursors. Compared to the hot matrix method, the microemulsion method is slower with respect to the nanocrystals growth and initially gives, therefore, smaller cores. Within several days the nanoparticles grow inside the original micelles and improve their optical properties (the absorption and PL become well pronounced) due to ripening of shells.

Two different syntheses, designed as to control the shell thickness of CdS/ZnS nanoparticles were made. In the first one, the precursor concentration for the shell varied in the water droplets. In the second one, the water pool size in the micelles was varied, at a given precursor concentration. We
got different in shell thickness nanoparticles in both cases. We then measured the absorbance and photoluminescence of the particles and compared the spectra with respect to the intensity and wavelength of the excitation peak. From the absorbance spectra, we calculated the nanoparticle diameter and shell thickness as a function of the water pool size and the precursor concentration. Further changes in absorption and PL were measured after a period of time to estimate aging effects on them.

2. Experimental section

2.1. Synthesis of CdS nanoparticles

An amount of sodium bis(2-ethylhexyl) sulfosuccinate (AOT) was dissolved in heptane to prepare 0.1 M AOT solution as a surfactant solution (i). The concentration of water \([\text{H}_2\text{O}]\) added to the heptane and the concentration of surfactant [AOT] form the volume ratio, \(w = [\text{H}_2\text{O}] / [\text{AOT}]\), which is proportional to the water pool radius—the same as the core radius of a reverse micelle. The parameter \(w\) of the reverse micellar solution was controlled by adding the required amount of aqueous solution of \(\text{CdCl}_2\), \(\text{ZnCl}_2\) or \(\text{Na}_2\text{S}\). We prepared 0.2 M \(\text{Na}_2\text{S}\) (ii) and 0.2 M \(\text{CdCl}_2\) (iii) aqueous solutions. Due to the hygroscopic capacity of \(\text{Na}_2\text{S}\) the amount of \(\text{S}^{2-}\) ions is not well defined in the solution for which reason, we prefer working with excess sulfide anions. In such a way their reaction with \(\text{Cd}^{2+}\) ions is complete. We poured 100 ml of (i) into a triple neck flask. Then upon stirring with electromagnetic stirrer we added by automatic pipette 180 l of (ii), calculated in a way to get \(w = 1\). The pre-existing microemulsion droplets facilitate the distribution of precursors among them. Finally we add 180 l of (iii) to get \(w = 2\). In this way, the CdS nanoparticles were synthesized.

2.2. Synthesis of CdS/ZnS nanoparticles

After 1 h from the beginning of CdS cores formation, we add 9 l of 0.2 M \(\text{ZnCl}_2\) aqueous solution (iv) to 10 ml of the CdS nanoparticle suspension. This amount of (iv), together with the already added precursors, would correspond to auxiliary microemulsion droplets of \(w = 3\). Next 9 l of 0.2 M \(\text{Na}_2\text{S}\) aqueous solution (ii) was added to get droplets with \(w = 4\). Upon stirring the suspension color changes to dark yellow, indicating a ZnS shell covering (Fig. 1).

2.3. Particle characterization

The obtained nanoparticle suspensions were characterized by absorbance spectroscopy 1 h after the synthesis (Model 6400 Vis, Jenway, Felsted, UK). The effect of aging was examined by taking the absorbance spectra within several days after the preparation of nanoparticles. The photoluminescence spectra were measured approximately one day after the synthesis using SPEX 1403 double spectrometer equipped with a photomultiplier working in photon counting mode. Spectral slit width was 50 cm⁻¹. UV-lamp (365 nm) was used as exciting source. Some aged samples were also recorded. As seen from Fig. 2, the PL of the specimen is overlapped with a peak coming from the second-order diffraction maximum of the excitation light in the spectrometer. Transmission electron micrographs (TEM) of CdS/ZnS nanoparticles were taken few weeks after their preparation.

In Appendix A are derived the equations for calculating the particle size and shell thickness.
3. Results

The existence of nanoparticles can be recognized from the light yellow color of the suspension liquid. Upon excitation with UV-lamp (wavelength $\lambda = 365$ nm) the dispersion shows yellow or orange photoluminescence depending on the nanoparticle size. The photoluminescence changes upon coating of nanoparticles from yellow (CdS nanoparticles) to orange (CdS/ZnS nanoparticles).

3.1. Effect of the water pool size on the PL

Increasing the pool size, i.e. $w$, shifts the peak of CdS absorbance spectra to larger wavelengths (Fig. 3a), i.e. towards bigger nanoparticles (Fig. 3c). The nanoparticle diameter $D$ increases linearly with $w$ because we add more precursors which are going to increase the shell thickness. This result is comparable with the linear dependence of the water pool radius $R_w$ on $w$.[6]

Similar trend is observed also in the case of core-shell nanoparticles CdS/ZnS (Fig. 3b and c). The slope of the line in Fig. 3c turns out proportional to the shell thickness $\delta$. Since the slope for CdS/ZnS is smaller, the ZnS shell should be thinner than the respective increase of the diameter of pure CdS nanoparticles.

3.2. Effect of the precursor concentration on the PL

The absorbance of the samples (Fig. 4a and b) is similar to that obtained previously at a constant $w$. The absorbance increases with the precursor concentration, $C_m = [\text{Zn}^{2+}] + [\text{S}^2-]$. The peak wavelength is also increasing due to increasing nanoparticle diameter (Fig. 4c). The core-shell CdS/ZnS nanoparticles are smaller than the pure CdS nanoparticles. This is because of smaller cores in the former case and better adhesion of CdS to the core in the latter case. The intensity of photoluminescence increases with $C_m$ (Fig. 4d).

3.3. Effect of the aging of the nanoparticles on the PL

The nanoparticles slowly grow in the suspension, which is called "aging" [7,8]. This comes from two reasons: First, non reacted material accumulates in the water pools; Second, mass transfer occurs from small to large particles (Ostwald
Fig. 4. Absorption spectra of (a) CdS nanoparticles and (b) CdS/ZnS nanoparticles taken at different molar concentration \( C_m \). (c) Dependence of the particle diameter on the molar concentration—data from (a) and (b). (d) Photoluminescence spectra of CdS/ZnS nanoparticles at different precursor concentration.

1. **Absorption Spectra:**
   - In the case of CdS, the absorption spectra shift to larger wavelength—Fig. 5a. The initial nuclei grow as shown in Fig. 5c. The intensity of absorption can decrease with the time, because of the growth of nanoparticles, which decreases their number in turn—Fig. 5b. The same effect can come from the oxidation of the nanoparticles surface and creation of defect traps for the emitted photons [2]. An improvement in the nanoparticle crystallinity can also make the PL intensity large.

   - For CdS/ZnS nanoparticles, the intensity of absorption also decreases with the time—Fig. 5b. The absorption peak moves to larger wavelength due to the increase of the nanoparticle size—Fig. 5c. This linear increase is mainly a result from the shell thickness growth—Fig. 6 below.

2. **Discussion:**
   - Despite of the broad interest to microemulsion synthesis of core-shell nanoparticles (for a recent review of the methods see reference [9]), there are not so many attempts in making of semiconductor core-shell nanoparticles, for example CdS/ZnS [1]. Here, we go to the next step of synthesis—the control of the nano-shell thickness, which determines in turn the optical properties of the nanoparticles. On this purpose, two parallel syntheses have been made: the first one is of CdS nanoparticles by adding CdS “shells” on the pre-existing CdS cores and the second one is by adding ZnS shells on the CdS cores. More material goes for the “shell” of CdS on CdS cores than for the shell of ZnS on the cores of CdS. The ZnS shell thickness increases with the amount of precursor added to the solution. The ZnS shell increase generally leads to an increase of the absorption and photoluminescence intensity, because of a better quantum efficiency of the core-shell nanoparticles [2]. Possibly, in both cases certain amount of precursor is spent also for obtaining of new nanoparticles cores or remains trapped in the non-reacted water pools.

   - In each synthesis, two types of procedures have been utilized. In the first procedure, the water pool number is varied at a fixed precursor concentration in order to achieve different supply of the shell with material. In both cases, the nanoparticles grow in the same fashion which means that their growth depends on the total mass of precursor rather than on the way it is added to the solution.
Fig. 5. Absorption spectra of: (a) CdS nanoparticles and (b) CdS/ZnS nanoparticles at a different time of aging. (c) Time dependence of the nanoparticle diameter $D$: data taken from (a) and other experiments for CdS and from (b) for CdS/ZnS. The water pool size is $w = 6$, the precursor concentration is $C_m = 0.2$ M.

The average nanoparticle diameter calculated from the absorption spectra by means of the quantum confinement theory is 3.2 nm ($\pm 0.3$ nm) for CdS and 2.36 nm ($\pm 0.11$ nm) for CdS/ZnS nanoparticles. The CdS nanoparticles are generally bigger than the CdS/ZnS nanoparticles because the latter are prepared by capping of rather small CdS cores soon after their synthesis. These results are in agreement with a TEM observation of aged CdS/ZnS samples which gives 3.6 nm ($\pm 1.2$ nm).

Based on the above considerations we plot the ZnS shell thickness of CdS/ZnS in Fig. 6. The shell thickness $\delta$, calculated by Eq. (A.7), linearly increases with the total amount of precursor given by the concentration $C_m$, as well as with the water pool size $w$. It shows that both methods control the shell thickness in a similar way. About 40% of the precursors compose the nanoparticles; the rest should remain as ions in the water pools.

Increasing the water pool size makes the PL intensity larger (Fig. 3d). The peak wavelength decreases from 709 to 694 nm as $w$ increases (red photoluminescence). Fig. 7 shows the luminescence of CdS/ZnS nanoparticles aged for several weeks in the original suspensions.

With the time, the nanoparticles are found to increase in size. The CdS/ZnS nanoparticle diameter linearly increases with the time due to the shell thickness increase. The CdS cores also increase in size with the time at a bigger growth rate than the shells. The characteristic growth time seems several days and more which should be taken into account in the practical utilization of the nanoparticle suspension.

Acknowledgement

The authors thank to Mr. J. Jechev (Faculty of Mathematics and Informatics) for preparing the software for absorption data acquisition.
Appendix A

A.1. Calculation of the nanoparticles radius

Below we will derive a formula relating the nanoparticle radius \( R \) to the wavelength at the exciton peak of absorption measured experimentally. It is known that the excitonic peak energy \( E \) corresponding to HOMO–LUMO transition is given as \([5,6,7]:\)

\[
E(R) = E_0 + \frac{\hbar^2 \pi^2}{2R^2} \left( \frac{1}{m_{\text{e}}^*} + \frac{1}{m_{\text{h}}^*} \right) - \frac{1.79\hbar^2}{\epsilon_2 R} + 0.248 E_{\text{Ry}}\nonumber
\]

(A.1)

Here, the parameters are: \( R \) is the nanoparticle radius (m); \( m_{\text{e}}^* \) the effective electron mass (kg); \( m_{\text{h}}^* \) the effective hole mass (kg); \( \hbar \) the Planck constant \((1.05 \times 10^{-34} \text{ J s})\); \( \epsilon_2 \) the dielectric constant of the semiconductor core; \( \epsilon \) the electron charge \((1.60 \times 10^{-19} \text{ C})\); and \( E_{\text{Ry}} \) is the Rydberg energy (it is neglected in the subsequent calculations). The constants for CdS are: \( E_0 = 2.58 \text{ eV}\); \( m_{\text{e}}^* = 0.19 m_0 \); \( m_{\text{h}}^* = 0.8 m_0 \) \((m_0 = 9.10 \times 10^{-31} \text{ kg})\) is the free electron mass); \( \epsilon_2 = 3.86\epsilon_0 \); \( \epsilon_0 = 5.5 \) \((\epsilon_0 = 8.85 \times 10^{-12} \text{ F/m})\) is the permittivity of vacuum). By substituting of the parameters in Eq. (1) with the values of constants for CdS we get \( R \) as a function of \( \lambda \):

\[
R = \frac{7.29 \times 10^{-20} + \sqrt{6.43 \times 10^{-53} + (3.12 \times 10^{-41})/\lambda}}{-8.27 \times 10^{-19} + (3.97 \times 10^{-21})/\lambda}.
\]

(A.2)

Here, \( \lambda \) (nm) is the peak of the absorbance wavelength in a medium. Eq. (A.2) is strictly valid for CdS nanoparticles and will be used below to calculate the nanoparticle radius from the absorbance spectra.

In the case of the core–shell particles one can calculate the effective mass of the electron as:

\[
m_{\text{e}}^* = \psi m_{\text{e,CdS}}^* + (1 - \psi)m_{\text{e,ZnS}}^*
\]

(A.3)

Here, \( \psi = V_{\text{CdS}}/V \) is the volume fraction of CdS core, \( V_{\text{CdS}} = (4/3)\pi R^3 \) is the volume of the CdS core, \( V = (4/3)\pi(R + \delta)^3 \) is the total volume of the core–shell nanoparticle. Assuming that the shell is thin, \( \delta \ll R \), one gets \( \psi \approx 1 - 3\delta/R \). Therefore, Eq. (3) becomes:

\[
m_{\text{e}}^* = \left( 1 - \frac{3\delta}{R} \right) m_{\text{e,CdS}}^* + \frac{3\delta}{R} m_{\text{e,ZnS}}^*
\]

(A.4)

By noting that \( m_{\text{e,ZnS}}^* = 0.4 m_0 \approx m_{\text{e,CdS}}^* \) [10] and \( \delta/R \ll 1 \), Eq. (4) gives \( m_{\text{e}}^* \approx m_{\text{e,CdS}}^* \). Similar results can be obtained also for the effective mass of the hole, \( m_{\text{h,ZnS}}^* \approx 0.6 m_0 \) (since we did not find respective data for ZnS, that of ZnSe was used for the estimate) and the dielectric constant \( \epsilon_{\text{ZnS}} = 8.9 \) [11]. In view of these findings, one can use Eq. (A.2) also for the processing of core-shell nanoparticles since the shell contribution to the exciton energy is negligible.

A.2. Thickness of the nanoparticle shell

Assuming that the core–shell nanoparticle is spherical, one can write for the ZnS shell volume with thickness \( \delta \)

\[
V_{\text{ZnS}} = 4\pi R^2(\delta^2 + R^2)
\]

(A.5)

where the term \( \delta^2 \) has been neglected. Written by volumes of core and shell this becomes:

\[
\delta^2 + R^2 = \frac{V_{\text{ZnS}}}{V_{\text{CdS}}} = 0
\]

(A.6)

Here \( V_{\text{ZnS}} = (m_{\text{ZnS}}/\rho_{\text{ZnS}})\delta V_{\text{CdS}} \) and \( V_{\text{CdS}} = (m_{\text{CdS}}/\rho_{\text{CdS}})\delta V_{\text{CdS}} \) are the volumes of compounds. \( m_{\text{CdS}} \) and \( m_{\text{ZnS}} \) are the weights of Cd+S and Zn+S, respectively. \( \rho_{\text{CdS}} \) and \( \rho_{\text{ZnS}} \) are the material densities in crystal forms. \( \epsilon_{\text{CdS}} \) and \( \epsilon_{\text{ZnS}} \) are the ratios between the material weights in crystal and precursor forms. Then \( \delta \) is

\[
\delta = R \left( \frac{1}{2} - \sqrt{\frac{1}{2} + \frac{4\rho_{\text{CdS}}\rho_{\text{ZnS}}}{m_{\text{CdS}}\rho_{\text{ZnS}}}} \right)
\]

(A.7)

This is calculated at a given \( \alpha = \rho_{\text{CdS}}/\rho_{\text{ZnS}} \), which gives the efficiency of the transition of precursors into cores and shells.

References