Optical properties of CdS and CdS/ZnS quantum dots synthesized by reverse micelle method

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Abstract. The CdS and CdS/ZnS semiconductor quantum dots have been synthesized by reverse micelle method using sodium bis (2-ethylhexyl) sulfosuccinate (AOT) surfactant agent. The quantum dot diameter is about 2.5 to 4 nm depending on the concentration of the surfactant agent. It is interesting that, in contrast to other colloidal methods, the size of quantum dots does not depend on the growth time. The absorption spectra of CdS quantum dots show the narrow size distribution. The photoluminescence (PL) spectra include two bands, the intrinsic emission of CdS nanocrystals and the emission of surface states. There is noticeable increase of the PL intensity and subsequent photostability of CdS/ZnS core-shell quantum dots in comparison with CdS quantum dots without the ZnS shell.

Keyword: CdS, CdS/ZnS, quantum dots, semiconductor, reverse micelle method.

1. Introduction

Nowadays semiconductor nanocrystal quantum dots have been investigated in different aspects from physical properties of low-dimensional systems to their potential applications [1]. Efficient luminescent quantum dots form an important and interesting class of luminescent materials. They have demonstrated excellent optical properties and higher photochemical stability than most organic emitters [1, 2]. Their broad absorption spectrum and narrow emission band would be tunable by changing their size. One of the most interesting applications is the use of quantum dots as luminescent labels for optical sensors or fluorescent label sources for biological imaging applications [3-5].

Among approaches to prepare nanocrystals, the direct solution chemical routes have widely been used for synthesis of semiconductor quantum dots because these methods allow us to create the quantum dots with a narrow size distribution [1]. In the reverse micelle method, a solution is created by three components, surfactant molecules, water and a non-polar organic solvent. The polar heads of the surfactant molecules are directed toward the interior of a water-containing sphere, whereas the aliphatic tails are oriented toward the non-polar organic phase. The size of the quantum dots obtained by the method can be controlled by changing the ratio of water to the surfactant agent. In this work, we have studied the optical properties of CdS and CdS/ZnS core/shell semiconductor nanocrystal quantum dots synthesized by the reverse micelle method. The core/shell nanocrystal structures show the enhanced luminescence and photostability.
2. Experimental

The CdS quantum dots were synthesized by the reverse micelle method with sodium bis (2-ethylhexyl) sulfosuccinate (AOT) used as the surfactant agent and heptane used as the solvent [1, 2, 6]. To obtain two micellar solutions with the aqueous solution encapsulated within the reverse micelles formed by the surfactant in oil, we prepared two identical mixtures of heptane and AOT and then added an aqueous solution of Cd(CH₃COO)₂·2H₂O to one of the mixtures and an aqueous solution of Na₂S·9H₂O to the other. After addition of one micellar solution containing Cd²⁺ ions into the other micellar solution containing S²⁻ ions in a vigorously stirring condition, CdS nanocrystal quantum dots were yielded in the nanometer-sized water pool within the reverse micelles. The size of the nanocrystals was changed by the molar ratio \( W = [\text{H₂O}]/[\text{AOT}] \). The value of \( W \) was chosen of 2.5, 5, 7.5 and 10.

To synthesize CdS/ZnS core/shell quantum dots, a ZnS shell layer was grown on CdS core nanocrystals by using two aqueous solutions of Zn²⁺ and S²⁻ ions which were obtained by dissolving the compounds Zn(CH₃COOH)₂·2H₂O and Na₂S·9H₂O into water. The aqueous solutions of Zn²⁺ and S²⁻ were mixed separately with two identical AOT/heptane stock solutions. Then two micellar solutions containing Zn²⁺ and S²⁻ ions were injected at a very slow rate into the CdS nanocrystal micellar solution which had been prepared before. The obtained solution was then stirred vigorously, so that ions Zn²⁺ and S²⁻ could hang on the drops containing CdS quantum dots, forming the ZnS shell layer. The CdS/ZnS core/shell quantum dots were dispersed in organic solvents such as methanol and heptane.

Optical (UV-VIS) absorption measurements for nanocrystal samples were performed in the wavelength range of 300 - 750 nm using a Jasco V-600 (Japan). Photoluminescence (PL) and photoluminescence excitation (PLE) measurements were carried out at room temperature with a monochromatized light source (200 nm < \( \lambda_{\text{exc}} < 900 \) nm) from a 450 W Xe lamp of a FS 920 Edinburgh (England).

3. Results and discussion

The prepared CdS and CdS/ZnS core/shell quantum dots were clusters which were protected by the surfactant agent (AOT) layer and dispersed in the heptane solvent. Figure 1 presents the absorption spectra of CdS quantum dots prepared with different values of the molar ratio of water to surfactant agent (W). There is an evident shift of the absorption peak towards lower wavelengths (or higher energy) compared to that of bulk CdS crystal (\( \lambda_{\text{bulk}} \sim 500 \) nm corresponding to \( E_g = 2.482 \) eV at room temperature [7]). This blue shift is in connection with a decrease of the particle size.

![Figure 1. Absorption spectra of CdS quantum dots prepared with different values of the molar ratio of water to surfactant agent.](image)

Various theoretical approaches have been employed to account for the variation in the electronic structure of nanocrystal quantum dots as a function of their size [3]. In the strong confinement regime, when the quantum dots radius \( R \) is much smaller than the Bohr exciton radius \( a_B \), the electron-hole
individual confinement model is applied. We used the Brus’ formula [8] to estimate the mean radius of the CdS nanocrystals from the absorption peak energy. The observed peak values are 3.875 eV (320 nm), 3.594 eV (345 nm), 3.38 eV (378 nm) and 3.024 eV (410 nm) for the samples with the value W of 2.5, 5, 7.5 and 10, respectively. The mean radius of CdS quantum dots are estimated to be 1.2, 1.4, 1.6 and 2.0 nm, respectively. It is evident that increasing the molar ratio W of water to the surfactant agent leads to the increase of the mean quantum dots radius.

Figure 2. Absorption spectra of CdS quantum dots in the condition of W = 2.5 with different growth times.

Figure 3. Absorption spectra of CdS quantum dots in the condition of W = 5 with different growth times.

Figure 4. Absorption spectra of CdS quantum dots in the condition of W = 7.5 with different growth times.

Figure 5. Absorption spectra of CdS quantum dots in the condition of W = 10 with different growth times.
The observation of the clear absorption peaks indicates the narrow size distribution of the CdS quantum dots. The size distribution width $\sigma$ can be estimated from the line shape analysis. Following Kim et al. [1], the total absorption spectrum $F_{\text{abs}}(E)$ is given by the contributions from all quantum dots, i.e., $F_{\text{abs}}(E) = \int A(R, E) N(R) \, dR$, where $A(R, E)$ is the absorption of an individual quantum dot with a given radius $R$, $N(R)$ represents a quantum dot size distribution assumed to be Gaussian. The shape of $A(R, E)$ as a function of $R$ is also assumed to be Gaussian to take into account the inhomogeneous broadening due to differences in the shape and/or surface morphology of the quantum dots.

To calculate the width $\sigma$, the spectral width $\Gamma$ of $A(R, E)$ has to be referred to the experimental results of single-dot spectroscopy, but there have been no reported data at room temperature. Here, we assume the peak area to be Gaussian and determine the full width at half maximum (FWHM).

Figure 6 presents the absorption spectra of CdS quantum dots with Gaussian fitting of the peak area (circle-symbol curves). The FWHM of the curves is 40, 55, 45 and 52 nm for $W = 2.5$, 5, 7.5 and 10, respectively. The size distribution width $\sigma$ is estimated to be about 10-15%, showing the narrow quantum dot size distribution.

The narrow size distribution of the CdS quantum dots is also shown in photoluminescence (PL) spectra. Figure 7 presents the room temperature PL spectrum of CdS quantum dots of $W = 5$ dispersed in a heptane solution. The PL emission is a narrow band peaked at 409 nm and has the FWHM of 26 nm.

Figure 8 exhibits the absorption spectra of the CdS and core/shell nanocrystal dispersed in a solution with the molar ratio of water to surfactant agent $W = 5$. In the case of CdS/ZnS quantum dots charge carriers can penetrate into the ZnS layer, leading to lowering the confinement energy of the charge carriers in the CdS core. This results in a red shift of the absorption peak in the absorption spectrum of CdS/ZnS quantum dots in comparison with bare CdS quantum dots. This red shift is more pronounced in smaller dots where the leakage of the charge carriers into the ZnS shell has a more dramatic effect on their confinement energies [3]. In our experiment the shift is of about 294 meV (31 nm) for the core size of 2.8 nm (corresponding to $W = 5$).

The photoluminescence (PL) measurements of the CdS nanocrystal quantum dots were carried out under continuous excitation with 330, 350, and 370 nm wavelengths. Figure 9 shows the PL spectra of CdS and CdS/ZnS quantum dots with $W = 5$. The emission of CdS quantum dots without the ZnS shell (curve 1) includes two bands, a narrow band peaked at 410 nm and a broad band peaked at 620 nm. The 410 nm emission band is attributed to the intrinsic emission of CdS quantum dots (or the band-to-band transition in CdS nanocrystals), while the other band centered at 620 nm is attributed to the emission of surface states due to the small size of nanocrystals. When the CdS quantum dots are
overcoated with a ZnS shell, the intensity of intrinsic emission of CdS quantum dots increases significantly and is stronger than the emission of surface states (curve 2). This fact shows the passivation of the ZnS shell. It makes the emission of the surface states decrease, so that the intrinsic emission is enhanced. However, the emission of surface states is quite strong for CdS/ZnS quantum dot samples. This may result from a surplus of some compounds that did not take part in reaction and some CdS quantum dots were not passivated, so that the density of surface states is high.

![Figure 8. Absorption spectra of CdS and CdS/ZnS quantum dots samples with W=5.](image1)

![Figure 9. PL spectra of CdS and CdS/ZnS core/shell quantum dots with excitation wavelength of 330 nm at room temperature.](image2)

In order to obtain only the intrinsic emission of CdS quantum dots in PL spectra, besides passivating the quantum dots by ZnS shells, the prepared quantum dots were precipitated and then washed and centrifuged by methanol. Figure 10 presents the PL spectrum of CdS/ZnS core/shell quantum dots after washing and centrifugation. It can be seen that the emission of surface states is diminished significantly.

![Figure 10. PL spectra of CdS/ZnS core/shell nanocrystals quantum dots after washing and centrifugation with excitation wavelength of 330 nm at room temperature.](image3)

![Figure 11. The absorption spectra of CdS quantum dots with W = 7.5 as grown and after the preparation 7 days.](image4)

To estimate the stability of CdS quantum dots, the prepared samples were protected by surfactant agent (AOT) layer and dispersed in heptane or methanol solvent. The samples were kept in condition of dark at room temperature. Figure 11 shows the absorption spectra of CdS quantum dots with W = 7.5 measured just after the preparation and after 7 days. The curves seem to be nearly the same: no significant change in the absorption peak energy and the spectrum width is observed. These features are necessary for the practical applications of quantum dots.
4. Conclusion
The CdS and CdS/ZnS nanocrystals quantum dots were synthesized by the reverse micelle method. The diameters of the CdS nanocrystals have a narrow distribution and their mean value is about from 2.5 to 4 nm depending on the molar ratio W of water to surfactant agent. The absorption spectra show that the size of prepared nanocrystals does not depend on their growth time and can be controlled by changing the ratio W. This shows the role of the surfactant agent AOT in preventing the aggregation of nanocrystals.

The photoluminescence spectra include two bands, the intrinsic emission of CdS nanocrystals and the emission of surface states. There is a noticeable increase of the photoluminescence intensity and the photostability of CdS/ZnS quantum dots in comparison with CdS quantum dots without the ZnS shell.

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