Size and Shell Effects on CdSe Quantum Dots in Binary Ligand System

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ABSTRACT

We synthesized various-sized CdSe quantum dots (QDs) capped with a binary ligand system using oleic acid (OA) and trioctylphosphine (TOP), as well as high-quality CdSe/CdS core/shell structured QDs using Cd-oleate and TOP as shell precursors. The energy of the fluorescence (FL) peak for the CdSe QDs shifted from 2.475 to 2.064 eV with increasing growth time, which resulted in increasing the size of QDs. Upon an increase in the size of QDs, the electron and hole level energies decreased due to the quantum confinement effect. The full width at half maximum (FWHM) of the FL peaks for the CdSe QDs decreased with increasing growth time because of the Se-rich surface and low OA molar ratio. In particular, the FWHM of FL peaks from the CdSe/CdS core/shell-structured QDs is smaller than that of the CdSe core QDs owing to the improved size uniformity resulting from slow continuous shell deposition and high reaction temperature. An enhanced light absorption capacity was also observed for the CdSe/CdS core/shell structure QDs.

Keywords: Quantum dot, Core/shell structure, Binary ligand system, Optical property, Electronic transition

1. Introduction

Engineering nanomaterials have been highlighted across many scientific fields, and recent progress in nanotechnology has enabled various approaches for the fabrication of semiconductor nanomaterials that exhibit different electronic properties compared with the bulk states. Therefore, the design and engineering of high-quality quantum dots (QDs) are beneficial to solar cells, light-emitting diodes, lasers, biotechnology, and medical applications [1-5]. In particular, II-VI QDs including CdSe, CdS, and CdTe provide high and efficient photoluminescence by quantum confinement effects at the nanometer scale [6]. QDs have broad wavelength tunability owing to their size-dependent properties; additionally, they offer various advantages such as narrow emission spectra and high photochemical stability [7]. Surface modification with deliberately selected capping agents can improve their luminescence but offers no long-term stability. Furthermore, the surface passivation of QDs can improve the quantum yield, as well as the photochemical and thermal stability of core QDs [8]. Depositing shells with a larger bandgap on another material with a smaller bandgap can be a solution for the formation of nanoheterostructures and facilitate surface passivation [9-11]. The nanoheterostructure type is determined by the band alignment of the core and the shell material [12]. In type-I core/shell QDs, shells with larger bandgaps passivate the core QD-surface and improve its optical Properties. To reinforce the production of core/shell structure QDs, a binary ligand system involving fatty acid and phosphine is important for facilitating the solubility of anions and cations within a solvent [13]. In particular, chain length can affect fatty acids like oleic acid (OA), stearic acid, and lauric acid. These acids decelerate the growth of QD as their chain lengths increase [14]. OA can affect the binding of surface Cd atoms from shell deposition and allows complex metal ions. Furthermore, trioctylphosphine (TOP) with high electron affinities enables the binding of chalcogenides and prevents high conversions of monomers into CdS shells [13]. Therefore, it is important to investigate the growth kinetics and the effects of surface ligands on the optical properties of core and core/shell QDs.

In this study, we investigated the effect of size and shell on the optical properties of CdSe and CdSe/CdS core/shell QDs in a binary ligand system. Fluorescence (FL) and absorption measurements were performed to investigate the effects of the size of CdSe QDs and compare the optical properties of CdSe core QDs and CdSe/CdS core/shell structure QDs. In addition, theoretical calculations for the quantum-size levels of CdSe QDs were performed for an appropriate band model based on experimental results.

2. Experimental details

Cadmium oxide powder (CdO), selenium powder (Se), sulfur, TOP, and 1-octadecence (ODE) were obtained from Sigma-Aldrich. OA, methanol, acetone, and chloroform were purchased from Daejung. All chemicals were used as received, without any further purification. To synthesize CdSe QDs, a mixture of CdO (10 mmol, 1.28 g), OA (20 mmol, 6.5 ml), and ODE (70 ml) was heated to 120 °C for 60 min in a 100-ml three-neck flask and then further heated at 180 °C for 30 min.
The growth of CdSe QDs was carried out under N₂ gas flow. Subsequently, a stock solution including Se (20 mmol, 0.156 g) dissolved in ODE (3 ml) and TOP (3 ml) was quickly injected into the heated flask at 220 °C. After the injection, CdSe QDs were extracted at different growth times [30 s (S1), 45 s (S2), 170 s (S3), and 30 min (S4)] at 208 °C. To prepare the CdSe/CdS core/shell structure QDs (S5), sulfur (0.192 g) was dissolved in TOP (4 ml) and ODE (6 ml) solvents. After preparing the CdSe QDs (S3), sulfur was dissolved in TOP, and ODE was added dropwise to the solution of CdSe QDs at 213 °C for 40 min. To improve the stability of the CdSe/CdS core/shell structure QDs, the mixture was maintained at 120 °C for 60 min under the N₂ gas flow. All samples were precipitated with acetone and methanol and then dispersed in chloroform. Figure 1 shows the digital photographs of CdSe QDs at different growth times (S1, S2, S3, and S4) and CdSe/CdS core/shell structure QDs under a single 365 nm UV light source. The emission color of the CdSe QDs under UV light shows various colors when the emission wavelengths of the CdSe QDs were tuned from blue to red. The deposition of CdS shell was completed at a temperature higher than the CdSe core growth temperature, and a bright red emission light was observed, as depicted in Fig. 1(b). The UV-vis absorption and FL measurements of the CdSe QDs and CdSe/CdS core/shell structure QDs were performed using a FLAME-S spectrophotometer (Ocean Optics) at room temperature.

### 3. Results and discussion

Figure 2 shows the FL and absorption spectra of CdSe QDs (S1, S2, S3, and S4) capped with OA ligands at room temperature. As the growth time increased, the energies of the FL and absorption peaks of the CdSe QDs decreased due to the increased QD size. In the smallest CdSe QDs (S1), a band edge emission peak accompanied with a broad shoulder peak near 1.959 eV (633 nm) was observed. This behavior is attributed to the high surface-to-volume ratio owing to the extremely small size of the QD and the dangling bond-derived states of the surface [15].

Figures 3(a) and 3(b) show the FL and first excitonic absorption peak positions of CdSe QDs at different growth times (S1, S2, S3, and S4). The FL peak position of the CdSe QDs at a growth time of 30 s...
(S1) was 2.475 eV (501 nm). When the growth time was 30 min (S4), the FL peak energy shifted to 2.064 eV (601 nm), resulting in a redshift of 411 meV (100 nm). The first excitonic absorption peaks of the CdSe QDs correspond to the transitions involving the lowest electron state (1S−1S0) [16]. The energies of the first excitonic absorption peak for S1, S2, S3, and S4 were observed at 2.636, 2.412, 2.184, and 2.098 eV, respectively. The energy of the FL and first excitonic absorption peaks of the CdSe QDs decreased with an increase in the QD size owing to the quantum size effects [7]. The initial CdSe and Cd:OA molar ratios were crucial during the QD synthesis [7,14]. The molar ratios of Cd:Se (1:2) and Cd:OA (1:2) were chosen for the Se-rich surface and low OA molar ratio. The FWHM of the FL spectra for the CdSe QDs at different growth times (S1, S2, S3, and S4) is shown in Fig. 3(c). The CdSe QDs had two different growth kinetic regimes [17]. When the growth time increased up to 170 s in the case of S3, the FWHM of the FL spectra gradually decreased due to the improved uniformity resulting from Ostwald ripening. After 170 s of growth, the distribution was defocused by depletion in monomer concentration. The FWHM of the FL spectra for the CdSe QDs with a growth time of 30 min (S4) increased slightly to 123 meV.

The quantum confinement energy in the strong confinement regime is given by \( h^2/8m_a^2 \pi^2 \), where \( m \) is the electron effective mass, \( a \) is the QD radius, \( h \) is the Plank constant, and \( a_n \) is the nth zero of the spherical Bessel function, and \( f \) and \( s \) are the orbital and principal quantum numbers, respectively [18]. A parabolic approximation can facilitate the analyses of the electronic transition states as well as the size and energy levels of the electronic transition of QDs in the strong confinement regime. It is a fundamental approach for understanding simple parabolic band structures. No semiconductor can easily satisfy this approach because parabolic approximation can only be used with parabolic conduction and valence bands [19]. Therefore, energy band parameters are required to analyze the electronic transition between electron and hole quantum size levels. Eq. (1) indicates the energy of the hole level without spin-orbit coupling [19]. The energies of the hole level (1S3/2, 2S3/2, 1P3/2) with \( j \) (total angular momentum) = 3/2 and hole level (1S1/2) with \( j = 1/2 \) are expressed as Eq. (1), where \( m_{hk} \) and \( m_l \) denote the heavy and light hole effective masses, respectively. To account for the spin-orbit coupling, the quantum size levels of the hole and electron were determined using Eq. (2).

\[
\Delta E_p (1S_{3/2}, 2S_{3/2}, 1P_{3/2}) = \frac{h^2}{2m_{hk} \pi^2} a_n^2
\]

\[
\Delta E_p (1S_{1/2}) = \frac{h^2}{2m_{lh} \pi^2} a_n^2
\]

\[
E_{p \alpha} = \left[ 1 + 2f + \frac{2}{3} \left( \frac{2}{E_{p \alpha} + E_p + E_q + \Delta} \right) \right] \frac{h^2}{8m_{lh} \pi^2} a_n^2
\]

where \( f \) is a parameter contributing to the electron effective mass, \( E_p \) is the energetic band parameter, \( \Delta \) is the spin-orbit coupling of CdSe QDs, and \( m_l \) is the electron effective mass [18]. The fitting of energy levels of electronic transition for the CdSe QDs was obtained using the following energy band parameters: \( f = -0.42 \), \( E_p = 17.5 \) eV, \( E_q = 1.74 \) eV, and \( \Delta = 0.42 \) eV. Figure 4 shows the calculated hole and electron level energies for the different-sized CdSe QDs. The results demonstrate that the electron and hole level energies decreased when the QD size increased owing to the quantum confinement effects. Considering the ground state level, the gap energy of CdSe bulk must be added to the electronic transition energy.

Figure 5 shows the fluorescence and absorption spectra of the CdSe QDs with growth time 170 s (S3) and CdSe/CdS core/shell structure QDs (S5). A small redshift (< 50 meV) in the FL and first excitonic absorption peaks is typically observed in CdSe QDs by the growth of CdS shell due to a partial leakage of excitons into the shell material, which has a larger bandgap (2.42 eV for bulk CdS) than the core material (1.74 eV for bulk CdSe) [20]. However, the FL and first excitonic absorption peaks for the CdSe/CdS core/shell structure QDs
exhibited a large redshift (~100 meV). This large redshift can be related to the extensive delocalization of the electrons into the CdS shell and predicts a redshift in the FL and first excitonic absorption peaks during reactions such as the growth of CdSe QDs capped with binary ligands [13]. Compared with the CdSe core QDs, the FWHM of the FL peak of the CdSe/CdS core/shell structure QDs using Cd-oleate and TOP as shell precursors decreased from 120 to 102 meV owing to the slow continuous shell deposition and high reaction temperature [21]. The absorption intensity of the CdSe/CdS core/shell structure QDs was higher than that of the CdSe core QDs due to the increased light absorption capacity associated with the 2S transition (1S−2S3/2). This behavior is attributed to a decrease in the overlap of electron and hole wave functions owing to shell deposition [13].

4. Conclusions

We synthesized different-sized CdSe QDs capped with binary ligands and high-quality CdSe/CdS core/shell QDs via hot injection. We observed a redshift in the FL and absorption peaks of the CdSe QDs as their size increased. With the increasing size of the QDs, the electron and hole level energies in the s- and p-symmetries decreased because of the quantum confinement effect. The FWHM of the FL peaks of the CdSe QDs decreased gradually with the increase in the QD size. In addition, the FWHM of the CdSe/CdS core/shell structure QDs with slow continuous shell deposition and high reaction temperature was smaller than that of the CdSe core QDs because of improved size uniformity. The absorption intensity of the CdSe/CdS core/shell structure QDs was higher compared with that of the CdSe core QDs because of the increased light absorption capacity. These results provide further insights into the band model of CdSe QDs with energy band parameters and ligands to understand the growth kinetics of core and core/shell structure QDs.

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