Lattice distortion and luminescence of CdSe/ZnSe nanocrystals

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Abstract
Colloidal CdSe/ZnSe core/shell nanocrystals were prepared via the conventional TOP/TOPO process and their shell thickness was controlled varying the ZnSe precursor concentration. X-ray diffraction (XRD) on the nanocrystals showed gradual peak shifts to high two-theta angles due to a decrease in the lattice parameter of CdSe cores with an increase in the ZnSe shell thickness. High-resolution transmission electron microscopy (HRTEM) images of the CdSe/ZnSe nanocrystals show a c-axis elongation with an increase in ZnSe precursor concentration and crystalline defect formation in some of the nanocrystals with 2.0 mM ZnSe precursor concentration, possibly due to high compressive strain. Photoluminescence (PL) spectra of the CdSe/ZnSe nanocrystals showed an increase in the peak intensity up to 1.0 mM ZnSe precursor concentration due to the surface passivation effect, and a decrease beyond this value, possibly due to the formation of crystalline defects such as stacking faults. The PL wavelength showed red-shifts up to 1.0 mM ZnSe precursor concentration due to the partial leakage of an electron wavefunction of CdSe cores into the ZnSe shells and blue-shifts beyond this value due to the high compressive strain from the ZnSe shells.

1. Introduction
Colloidal semiconductor quantum dots have been spotlighted as one of the most important photonic materials in nanotechnology for the last several years [1–3]. They show a specific quantum confinement effect of both the electrons and holes in all three dimensions, leading to an increase in the effective energy bandgaps of the nanocrystals with a decrease in the particle size. Among the semiconductor nanocrystals, colloidal CdSe nanocrystals have shown the visible-range light emission and thus have been intensively studied for their distinguished role in technical applications such as light-emitting diodes [4, 5], lasers [6], and biological labels [7–9].

To improve quantum efficiency, the CdSe nanocrystal core is often covered by another semiconductor shell with a high-energy bandgap such as ZnS, ZnSe, and CdS [10–14]. By introducing these shells onto the surface of CdSe cores non-radiative recombination between electrons and holes, caused by dangling bonds forming at the surface of bare CdSe nanocrystals and acting as trap sites, can be prevented, and thus the quantum efficiency of CdSe nanocrystals can be greatly improved. Examples of colloidal CdSe core/shell quantum dot structures reported so far include CdSe/CdS [10], CdSe/ZnS [11], CdSe/ZnSe [12–14], CdSe/CdTe [15], and CdSe/ZnTe [16]. Among numerous core/shell nanocrystals ZnSe-overcoated CdSe nanocrystals have shown advantages that not only is the ZnSe bandgap (2.72 eV) larger than that of CdSe (1.76 eV), forming a quantum-well structure, but also the lattice parameter mismatch relative to the CdSe core (6.3%) is lower than that of the preferred shell, ZnS (10.6%). The combination of CdSe and ZnSe into a core/shell structure is highly desirable to prevent the evolution of interfacial misfit dislocations that also act as traps for electrons and holes. Although the improved photoluminescence efficiency [13] and
the homogeneity in a size distribution [14] were reported for CdSe/ZnSe core/shell nanocrystals, the effects of ZnSe shell thickness on the crystal structures and the photoemission of CdSe cores have not been reported yet.

In this study the CdSe/ZnSe core/shell nanocrystals with a different shell thickness were synthesized controlling the concentration of shell precursors and the structural variation in CdSe/ZnSe nanocrystals was monitored using x-ray diffraction (XRD) and high-resolution transmission electron microscopy (HRTEM). Photo-emission characteristics of CdSe/ZnSe nanocrystals having different shell thicknesses were investigated using photoluminescence (PL) and discussed based upon the structural change in the CdSe cores.

2. Experimental details

Cadmium oxide (CdO, 99.99%), selenium shot (Se, 99.999%), diethylzinc ((C2H5)2Zn in 1 mol heptane), tri-n-octylphosphine (TOP, 90%), tri-n-octylphosphine oxide (TOPO, 90%), hexadecylamine (HDA, 90%), n-butanol, toluene, and chloroform were purchased from Aldrich (Aldrich Chemical, WI). Most details of the synthetic and characterizing methods were similar to those reported in the literature [13, 14].

Typically, 128 mg (0.1 mM) of CdO was dissolved in 5.75 g of TOP and 14.25 g of HDA in a three-neck flask inside an N2-filled glove-box. The mixture was heated to 320 °C under an Ar flow until it became a clear solution. A TOPSe stock solution containing 395 mg (0.5 mM) of Se was dissolved in 10 ml of TOP at room temperature. A TOPSe stock solution was quickly injected into the reaction flask. Immediately after the injection the temperature dropped to 290 °C and then the mixture was cooled to 290 °C under an Ar flow until it became a clear solution. A TOPSe stock solution containing 395 mg (0.5 mM) of Se was dissolved in 10 ml of TOP at room temperature. A TOPSe stock solution was quickly injected into the reaction flask. Immediately after the injection the temperature dropped to 290 °C and then the mixture was cooled to 290 °C under an Ar flow until it became a clear solution.

The CdSe/ZnSe core/shell nanocrystals were synthesized in a stabilizing mixture containing HDA, TOPO, and TOP. HDA played a major role not only in the control of the size-elective precipitation in methanol and then redispersed in hexane. To overcoat the CdSe cores with ZnSe shells, a colloidal solution with 30 mg of CdSe nanocrystals was dispersed in 7 g of TOP and 4.5 g of HDA under an Ar flow, and then the mixture was heated to 200 °C. Diethylzinc (Et2Zn) and Se were used as Zn and Se precursors, respectively. Equimolar amounts of the precursors were mixed in 10 ml of TOP inside an N2-filled glove-box. The ZnSe precursor solution was continuously injected into the flask containing CdSe cores with a different amount at a flow rate of 0.66–0.15 ml min⁻¹. After the addition was completed the mixture was annealed at 190 °C and then n-butanol was again added to the mixture. CdSe/ZnSe quantum dots were rinsed with methanol several times to remove the extra solvent (HDA and TOPO). At room temperature methanol was evaporated and CdSe/ZnSe quantum dots were collected from the dried powder.

Powder x-ray diffraction (XRD: Rigaku Ultima 2000, Tokyo, Japan) was performed for the CdSe/ZnSe nanocrystals using Cu Kα radiation at 40 kV and 40 mA. High-resolution transmission electron microscopy (HR-TEM: JEM 4010, Tokyo, Japan) was operated at 400 kV to identify the crystallinity and morphologies of the nanocrystals. Photoluminescence (PL: Hitachi F-4500, Tokyo, Japan) was employed to analyse photoemission properties of nanocrystals.

3. Results and discussion

3.1. XRD and HRTEM analyses

The CdSe/ZnSe core/shell nanocrystals were successfully synthesized in a stabilizing mixture containing HDA, TOP, and TOP. HDA played a major role not only in the control of growth rate of nanocrystals, but also in the stabilization of the surface ligands of TOPO [17, 18]. Figure 1(a) shows powder XRD patterns of CdSe and CdSe/ZnSe core/shell nanocrystals. The CdSe/ZnSe core/shell nanocrystals were synthesized using 0.5–2 mM concentrations of ZnSe precursors, which caused the differences in the overall diffraction patterns. According to our inductively coupled plasma (ICP: Perkin-Elmer, Optima 2000 DV, Boston, MA) analysis results, increased concentrations of the ZnSe precursors must have led to the enhanced amount of ZnSe shell, proving the linear dependence of the shell thickness on the precursor concentration. The increasing ZnSe concentration caused gradual diffraction peak shifts to the higher reflection angles. The intensities of CdSe diffraction peaks decreased with ZnSe precursor concentration, which is probably due to the decreased crystallinity of the CdSe core caused by a high level of compressive strain from ZnSe shells. At a high ZnSe precursor concentration of 1.5 mM a new peak showing the pure ZnSe(112) reflection started to appear at around 54° and it also seems that the ZnSe(002) reflection started to appear.
at around 27.3°. Thus, the increased and broadened XRD peak, locating at around 24°–29° in the nanocrystals with 1.5 and 2.0 mM ZnSe precursor, may result from the diffraction from the ZnSe shell, which is thick enough to affect diffraction peak intensities. The gradual peak shifts in the nanocrystals may rule out the possibility of phase separation or separated nucleation of CdSe or ZnSe nanocrystals. This result is in good agreement with that of CdSe/ZnS nanocrystals by Dabbousi et al [11] and that of CdS/ZnS nanorods by Manna et al [19]. Among the XRD peaks the characteristic (110) and (112) CdSe peaks were worthy of notice with increasing concentrations of shell since each peak was not overlapped on the other peaks. The change in the positions of (110) and (112) peaks with the ZnSe precursor concentration was monitored and used to determine the variation in a- and c-axes, respectively. The peaks showed apparent shifts to high two-theta values with the ZnSe precursor concentration due to the relatively small lattice parameter values of ZnSe (a = 3.974 Å, c = 6.506 Å) compared to CdSe (a = 4.299 Å, c = 7.01 Å). The CdSe/ZnSe core/shell nanocrystals with the ZnSe precursor concentration of 2.0 mM showed apparent diffractions from (002) and (112) planes of the ZnSe shells since the thickness is large enough for diffraction. The lattice parameter variations were determined chasing the XRD peak shifts and plotted in figure 1(b). A gradual decrease in both the lattice parameter values was observed as the concentration of ZnSe precursor increases. The lattice parameter values of the CdSe cores were decreased by 1.234 and 1.511% for the a- and c-axes, respectively. Thus, it is obvious that the CdSe cores were strained by a compressive manner due to the relatively small lattice parameter of ZnSe shells. The slightly higher shrinkage in the c-axis can be explained as more ZnSe was attached to the c-direction of the CdSe cores, thus giving a higher compressive strain to it.

Figure 2 shows HRTEM images of the (a) bare CdSe and (b)–(d) CdSe/ZnSe core/shell nanocrystals with increasing ZnSe precursor concentration. Each nanocrystal shows growth of the distinct (002) atomic planes along [001] direction.

3.2. PL analyses
Photoluminescence (PL) spectra were collected from the nanocrystals with different ZnSe shell concentrations as shown in figure 3(a). The PL peak from each nanocrystal showed a different wavelength and intensity according to the shell concentration, which is presented in figures 3(b) and (c), respectively. The wavelength of CdSe with 0.5 mM ZnSe precursor shows a sudden red-shift possibly due to the partial leakage of an electron wavefunction into the ZnSe shell [20–22]. The red-shift continued up to 1.0 mM ZnSe and the blue-shift occurred beyond this concentration. The ZnSe shell, that is thick enough to give a compressive strain to the CdSe core, can cause the blue-shift of the CdSe core since the compressive strain can increase the energy bandgap of semiconductors. Thus, it can be stated that until 1.0 mM ZnSe the leakage of an electron wavefunction to the shell dominates (red-shift) and beyond this value a compressive strain to the CdSe core dominates (blue-shift). However, the CdSe with 2.0 mM ZnSe shell still shows a longer PL wavelength than that of the bare CdSe core, which indicates that the leakage of the electron wavefunction to the shell still predominates over the compressive strain. The PL intensity also varied with the ZnSe concentration and it showed a maximum value at 1.0 mM ZnSe. The ZnSe shell can effectively remove surface dangling bonds at the surface of the bare CdSe nanocrystals up to a ZnSe concentration of 1.0 mM. Beyond this value the PL intensity decreases and this would originate from the evaluation of crystalline imperfection such as stacking faults in the CdSe cores due to the high compressive strain along the c-axis as shown in figure 2(d).

4. Summary
CdSe/ZnSe core/shell nanocrystals were synthesized using a TOP/TOPO approach. Their structural variations were analyzed though XRD and HRTEM. With increase of ZnSe concentration XRD peaks of the CdSe cores gradually shifted to high reflection angles due to the compressive strain by the ZnSe shells and their intensities decreased, possibly due to the decreased crystallinity. The lattice parameters of the a- and c-axes showed 1.234 and 1.511% shrinkage, respectively. HRTEM analyses showed formation of the ellipsoidal shape nanocrystals having apparent stacking faults along the c-axis at a high ZnSe precursor concentration. PL spectra showed...
Figure 3. Photoluminescence (PL) spectra of bare CdSe and CdSe/ZnSe core/shell nanocrystals with a different ZnSe precursor concentration (a). PL peak intensity (b) and wavelength (c) variations with ZnSe precursor concentration.

the red-shifts at a low ZnSe concentration, originating from the partial leakage of an electron wavefunction into the ZnSe shells, and the blue-shifts, coming from the compressive strain from the ZnSe shell having a smaller lattice parameter. PL intensities showed a maximum value at 1.0 mM ZnSe due to the surface passivation effect at a low ZnSe concentration and the crystalline defect formation at a high ZnSe concentration, respectively.

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