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Evolution of Luminescence with Shell's Thickness in Colloidal CdSe/CdS Core/Shell Quantum Dots *

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We synthesize colloidal CdSe/CdS core/shell quantum dots with different shell thicknesses, and there are five samples including CdSe core dots, and CdSe/CdS core/shell dots with 1–4 CdS layers. X-ray diffraction and Raman measurements indicate that the stress in CdSe core becomes stronger with the increasing shell thickness, and the optical measurements show that when the shell becomes thicker, the photoluminescence quantum yield is enhanced, and the radiative decay is also expedited. The temperature-dependent optical spectra are measured. The relation between the microstructure and the optical properties is discussed.

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In recent years, nanocrystals (NCs) of semiconductor materials have been attracting considerable interest due to their size-tunable optical and electronic properties, and they have already been used as sensors,[1] laser materials,[2] and biological labels, etc.[3,4] However, because of their high surface-to-volume ratios, their surface properties have significant effects on their electronic and optical properties. It is for this reason that the surface modification of these NCs has been the subject of extensive investigation. The growth of a shell of a higher-band-gap inorganic material on a core of another lower-band-gap material to form a heterostructure has been a successful route in the surface modification of nanostructure particles. Up to now, core/shell NCs such as CdSe/CdS[5−12] and CdSe/ZnS[11−16] have been extensively reported.

Overcoating NCs with higher band gap inorganic materials has been shown to improve the photoluminescence quantum yields[5−9,13,14] by passivating surface nonradiative recombination sites. However, the fluorescence lifetime of CdSe/CdS core/shell NCs with different shell thicknesses has not been reported. Although these core/shell NCs were largely analysed with high-resolution transmission electron microscopy (HRTEM),[5−11,13] x-ray diffraction (XRD),[5−8,11,13,15] Raman,[10,12,15] photoluminescence (PL),[5−9,11−15] optical absorption,[5−9,11−15] and time-resolved spectra,[9,16] the internal structure of the shell and the interface between core and shell, especially the dependence of their optical properties on the shell thickness, is vague yet. Raman spectra have been used to explore how the optical phonon modes vary with the shell thickness in CdSe/ZnS core/shell NCs. In this study, we synthesize bare-core CdSe NCs and CdSe/CdS core/shell NCs with 1–4 monolayers (ML) of CdS shell. The XRD and Raman measurements reveal that the stress in CdSe core becomes stronger with the increasing shell thickness, and the optical measurements show that the PL quantum yield (QY) is enhanced but the PL lifetime is decreased when the shell becomes thicker. The temperature-dependent PL QY and lifetime are also measured, and the relation between the stress and the PL properties is discussed.

Cadmium oxide (99.99%), selenium (99.5%, 100mesh), sulfur (99.98%, powder), trioctylphosphine oxide (TOPO, 90%), 1-octadecene (ODE, 90%), oleic acid (OA, 90%), octadecylamine (ODA, 97%), tributylphosphine (TBP, 97%), stearic acid (99%) were purchased from Alfa Aecscar. All chemicals were used directly without any further purification.

The bare-core CdSe NCs and CdSe/CdS core/shell NCs were prepared by an organometallic synthetic approach in two steps.[5] (1) The synthesis of bare-core CdSe NCs: A mixture of 0.0512 g (0.4 mmol) CdO, 0.4544 g (1.6 mmol) stearic acid, and 2 g ODE was heated to 200°C to make a homogeneous solution and cooled to room temperature. There were 3 g ODA and 1 g TOPO added and the solution was heated to 280°C under argon atmosphere, and a mixture of 0.158 g (2 mmol) Se, 0.472 g TBP and 1.37 g ODE was injected quickly. The solution was maintained at 250°C for 1 min to form 4.4 nm-sized CdSe cores. These CdSe NCs were purified and dispersed in hexanes for the core/shell growth. (2) The synthesis of CdSe/CdS core/shell NCs: A mixture of 0.103 g (0.8 mmol) CdO, 2.03 ml (6.4 mmol) OA and 17.97 ml ODE was heated to 250°C to make a homogeneous

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solution, cooled down to 60°C and used as 0.04 M Cd precursor solution. A mixture of 0.013 g (0.4 mmol) S and 10 ml ODE was heated to 200°C cooled down to room temperature, and used as 0.04 M S precursor solution. CdSe cores (1.01×10^{-4} mmol of particles) dissolved in hexanes was mixed with 5 g ODE and 1.5 g ODA. After removal of hexanes and air under vacuum, the mixture was heated to 240°C under argon atmosphere, some cadmium precursor was injected and some sulfur precursor was injected subsequently to form the first CdS shell, then cadmium and sulfur precursors were injected to form the next monolayer of CdS shell. The amounts of the injected precursors were calculated by assuming that the average thickness of one CdS ML was taken as 0.35 nm.[5] We synthesize four core/shell NCs with the same core size and 1, 2, 3 and 4 ML of CdS shells.

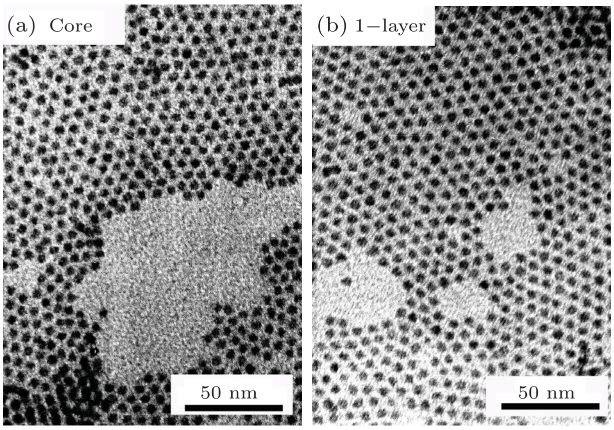

Fig. 1. TEM images of the bare-core CdSe NCs and the corresponding core/shell NCs with CdS thickness of 1 ML.

Absorption spectra were measured with a UV-3600 spectrophotometer, PL spectra and PL lifetime were measured using an F900 fluorescence spectrophotometer. TEM images were taken with a JEOL JEM-2000EX transmission electron microscope. XRD spectra were obtained using a Rigaku D/max 2500VL/PC x-ray diffractometer. Raman spectra were recorded with the 514.5 nm line of an Ar^+ laser as the excitation source in a backscattering configuration at room temperature.

Figure 1 shows the typical TEM images of the bare-core CdSe NCs and CdSe/CdS core/shell NCs with shell thickness of 1 ML. It can be seen that the obtained NCs are almost spherical in shape. TEM images indicate that the diameter of the CdSe cores is 4.4 nm (±5%), and those of the four CdSe/CdS core/shell NCs are 5.1 nm (±6%), 5.7 nm (±6%), 6.2 nm (±7%) and 6.8 nm (±7%), respectively. According to one CdS monolayer with 0.35 nm mentioned in experimental synthesis, the four CdSe/CdS core/shell NCs should be 5.1 nm, 5.8 nm, 6.5 nm, 7.2 nm, respectively, which is close to the TEM results.

Figure 2 shows the absorption and PL spectra. The growth of CdS shell results in a considerable shift of the emission peak from about 602 nm (bare-core NCs) to about 620 nm (core/shell NCs, 4 ML), and a corresponding shift of the first exciton absorption peak from about 593 nm to about 609 nm. The red-shifts are induced by the partial leakage of exciton into the shell.[13] The inset in Fig. 2 shows the PL quantum yield (QY) and the PL full width at half maximum (FWHM) of these NCs. As the CdS shell thickness on the CdSe surface increases, we can see a dramatic increase of the PL QY. The PL QY starts at about 3% for the bare-core CdSe NCs and increases with the addition of CdS, approaching a value of about 33% at 4 ML coverage. This is due to the increasing passivation of the core surface with the shell growth. In other words, non-radiative recombinations of excitons, caused by dangling bonds formed at the surface of bare-core CdSe NCs and acting as trap sites, can be prevented, and thus the PL QY can be greatly improved. On the other hand, the PL FWHMs of the bare-core CdSe NCs and the corresponding core/shell NCs vary between 24 nm and 27 nm, and the latter is slightly larger than the former, which indicates that the size distribution of core/shell NCs is worse than the bare-core NCs.

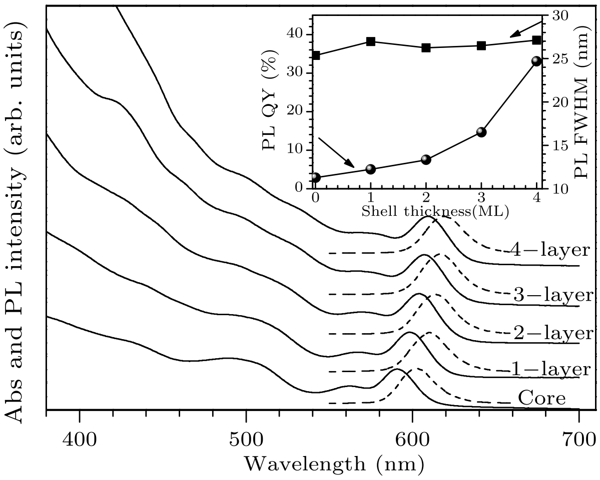

Fig. 2. Absorption (solid line) and PL spectra (dashed line) for bare-core CdSe NCs and CdSe/CdS core/shell NCs with different shell thicknesses. Inset: PL QY (circle) and PL FWHM (rectangle) of the CdSe/CdS core/shell NCs versus the number of CdS ML.

Figure 3 shows the typical PL decay curves at room temperature. The PL decay of CdSe NCs was not single exponential but multi-exponential. All the PL decays could be well fitted by a tri-exponential decay $\sum_{i=1}^{3} B_i e^{-t/\tau_i}$ (the reduced chi-square χ^2 is smaller than 1.2), and the inset of Fig. 3 shows the average lifetimes τ_{av}, where the τ_{av} value is equal to $\sum_{i=1}^{3} B_i \tau_i^2 / \sum_{i=1}^{3} B_i \tau_i$. With the increasing CdS shell thickness, the fluorescence lifetime is decreased. The reason is that the capping simplifies the recombination kinetics because the surface defects have been greatly decreased after capping.[14] The probability of excitons captured by the surface defects is decreased, so the probability of lingering luminescence due to the recombination via the radiative surface traps is decreased, and thus the fluorescence lifetime is decreased.[14] However, compared to the sample with shell thickness of 3 ML, the fluorescence lifetime of the sample with shell thickness of 4 ML is increased. This may be resulted from the high stress, as shown in the XRD patterns, in the CdSe core with the thicker CdS shell. Such crystalline imperfection makes the recombination rate become lower.

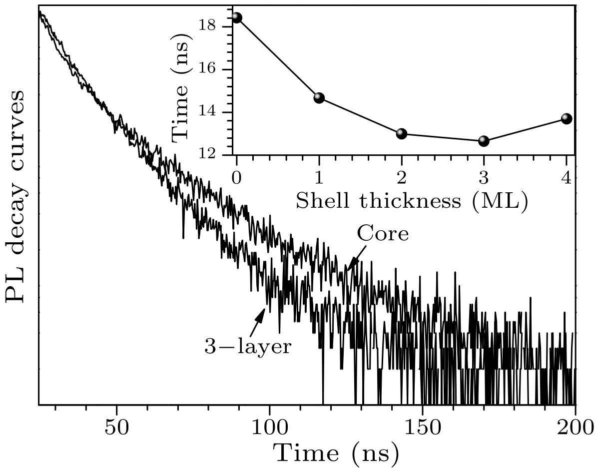

Fig. 3. PL decay curves for the bare-core CdSe NCs and CdSe/CdS core/shell NCs with the shell thickness of 3 ML at room temperature. The inset shows the fluorescence lifetime with the evolution of the shell thickness at room temperature.

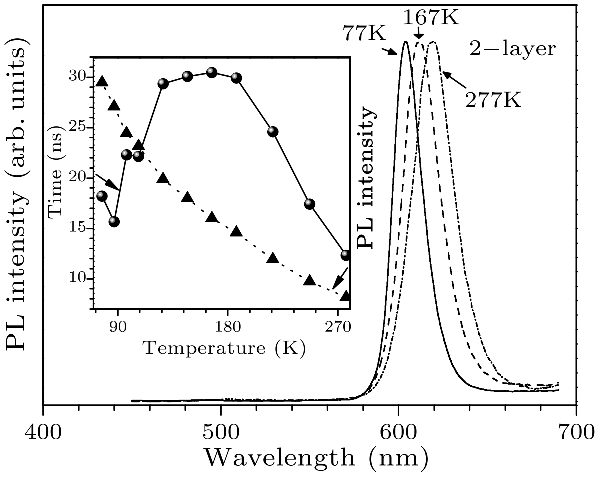

Fig. 4. PL spectra (normalized) at various temperatures (77, 167 and 277 K) for the CdSe/CdS core/shell NCs with shell thickness of 2 ML. The inset shows the temperature dependence of PL intensity (triangles) and fluorescence lifetimes (circle).

Figure 4 shows the typical temperature-dependent PL spectra. The PL peak exhibits a redshift when the temperature is increased from 77 K to 277 K. The redshift is because the band gap of the NCs is narrowed duo to thermal lattice expansion.[17] The inset in Fig. 4 shows the temperature dependence of PL intensity and fluorescence lifetime. The PL intensity is in inverse proportion to temperature because there are thermally activated nonradiative relaxation channels that are frozen at low temperature.[18] The fluorescence lifetime is increased with the increase of temperature towards 167 K, and then it is decreased. The similar phenomenon has been reported previously for CdSe/ZnS.[16] The increase of the fluorescence lifetime at temperature below 167 K is probably due to a finite spatial phase-coherence effect.[19,20] According to Citrin's calculation, the spatial coherence of excitons in NCs produces a mixing of the large-wavevector nonradiative states and the small-wavevector radiative states.[20] As the temperature increases, a larger number of excited states of the centre-of-mass motion are occupied and thus the radiative lifetimes increase further. On the other hand, the decrease of the fluorescence lifetime at temperature above 167 K is attributed to the predominance of nonradiative recombination due to thermal activation.

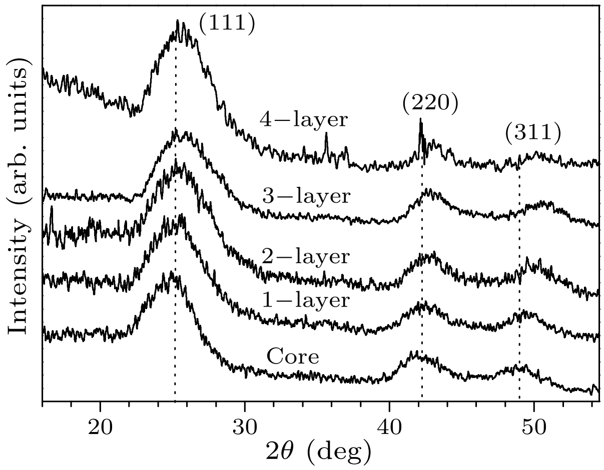

Fig. 5. X-ray diffraction patterns from the bare-core CdSe NCs and CdSe/CdS core/shell NCs.

Figure 5 shows the XRD patterns for bare-core CdSe NCs and CdSe/CdS core/shell NCs with different shell thicknesses. Figure 5 indicates that the CdSe cores are of zinc-blende phase. Compared with bare-core CdSe NCs, the XRD peaks of the CdSe/CdS NCs match with those of the CdSe cores with slight shift towards large angles. The gradual shifts of XRD peaks may rule out the possibility of phase separation or separated nucleation of CdSe or CdS NCs. The lattice parameter calculated from the (111) peak is 6.057, 6.050, 6.041, 6.034, and 5.963 Å for the five samples, respectively. It is noted that the lattice parameters for the zinc-blende phase of bulk CdSe and CdS are 6.077 and 5.818 Å, respectively. Figure 5 indicates that the lattice parameter of the CdSe core is gradually decreased with the increase of the CdS shell thickness. Because there is only about 5–6% lattice mismatch between CdSe and CdS crystals, and the lattice parameter of CdSe is smaller than that of CdS, the CdSe core is strained by a compressive manner when it is overcoated with the CdS shell. Therefore, the presence of the lattice contraction in the CdSe core is induced from the compressive strain from the CdS shell, and the compressive strain becomes stronger with the increase of the shell thickness.

Figure 6 shows the Raman spectra of the five NCs samples. The bare-core CdSe NCs exhibit clearly the longitudinal optical (LO) and 2LO phonons at 207 cm^{-1} and 413 cm^{-1}, respectively. Compared to the LO peak of bulk CdSe at 210 cm^{-1},[21] the LO peak of the CdSe core shows a downward shift due to the spatial confinement of phonons in NCs.[22] With the CdS shell overcoated onto the CdSe core, the line of LO phonon of CdSe core shows a slight shift to 208.5 cm^{-1}, which is caused by the lattice contraction caused by the compressive strain from the CdS shell.[15]

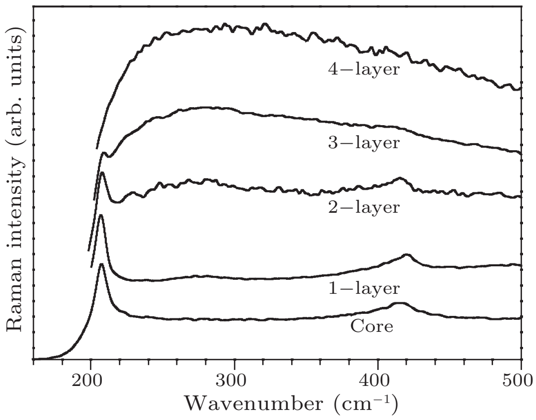

Fig. 6. Optical Raman spectra for the bare-core CdSe NCs and CdSe/CdS core/shell NCs.

If a 1 ML CdS shell is coated onto the CdSe core, a new peak appears at 276.5 cm^{-1}, which is related to the LO phonons of the CdS shell.[12] With 2 ML of CdS shell, the peak shifts to higher frequency (277.5 cm^{-1}), and its intensity becomes stronger. With 3 or 4 ML of CdS shell, this peak becomes broader, and the LO and 2LO peaks of the CdSe core are submerged. This large broadening of Raman peak was considered as disorder-related effects.[23] Disorder is inevitable during the growth of nano-structured materials due to the random spatial positions and sizes.[23] The shape of interfaces, which produce quantum confinement, can also contain random irregularities.[23] The lattice mismatch between the CdSe core and the CdS shell results in some tensile strain in the shell besides the compression strain in the core. Due to such imperfect crystalline quality, the inter-atomic distances and bond angels are fluctuated during the growth of the CdS shell.[23] Consequently, all these facts induce the broadened Raman peak.

In conclusion, the microstructure and optical properties of CdSe/CdS core/shell NCs are studied systemically. The red shifts in absorption and PL peaks of the CdSe NCs after passivation with CdS are accompanied with an improvement of their emission efficiency. After the capping of the CdS shell, the fluorescence lifetime of the colloidal NCs is decreased at room temperature. For all the bare-core CdSe NCs and CdSe/CdS core/shell NCs, the fluorescence lifetime is temperature-dependent, which is increased with the increase of temperature towards 167 K, and then is decreased. With the increase of the CdS shell thickness, the XRD peaks of CdSe cores are gradually shifted to higher angles due to the compressive strain from the CdS shell. There are no XRD peaks related with the CdS shell, and the Raman peak related with the CdS LO phonons is widely broadened, the crystalline structure is of high disorder in the CdS shell.

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