CdSe Quantum Shells and Wells

Colloidal Two-Dimensional Systems: CdSe Quantum Shells and Wells**

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Nanometer-sized structures with at least one dimension smaller than the critical size for a given property of a material have attracted considerable attention recently,[1–5] because of their size-dependent properties. Zero-dimensional (0D) and one-dimensional (1D) structures have recently been chemically synthesized and studied quite explicitly. On the other hand, 2D systems are rare. In fact, most of the properties of 2D semiconductor systems have not yet been demonstrated. Here we report a class of 2D colloidal semiconductor structures, ultrathin layers of semiconductors with a narrow bandgap, epitaxially grown onto a nanocrystal template with a substantially wider bandgap. The absorption and emission properties of these new structures strongly depend on the shell thickness but not on the size of the nanocrystal templates, which indicates quantum confinement only occurs along the radial direction (quantum shells).

Although there have been no reports on synthesizing colloidal semiconductor discs or sheets whose emission color is tunable in the visible color window, 2D semiconductor thin films are routinely grown onto single-crystal substrates through molecular beam epitaxy (MBE) with a precise control of the thickness.[6] This encouraged us to mimic the MBE-grown 2D semiconductor structures in solution, with the aim to grow a few monolayers of a narrow bandgap semiconductor onto a nanocrystal template with a wide bandgap. To do so, the perimeter of the shell should be larger than the diameter of the exciton of the shell semiconductor. Several research groups have attempted to grow such structures, and a significant red-shift of the absorption band edge has been observed.[7–11] The best studied system comprises one monolayer of HgS sandwiched between a CdS core and several layers of CdS overcoating.[8,9] After being activated in basic solutions, CdS/HgS/CdS emitted a red band-edge emission, which must originate from the HgS layer. Unfortunately, the poor quality of the core nanocrystals and underdeveloped growth methods for the shell layers made it difficult to observe the expected properties of 2D semiconductor structures, such as solely thickness-dependent absorption and emission, staircase-like electronic band structures (predicted by a simple model for 2D systems),[2] and good emission efficiency. In addition to the quality of the nanocrystals, the diameter of the HgS exciton may be too big to be only confined along the radial direction.

The accurate control of film thickness in MBE 2D structures and other thin film structures has been achieved through atomic layer epitaxy (ALE)[6] and successive ion layer asorption and reaction (SILAR).[12] Recently, we have demonstrated that a modified SILAR technology can be extended to the growth of core/shell semiconductor nanocrystals with precise thickness control.[13] The key feature of the newly developed SILAR method is that the precursors of the anionic and cationic components of the shell compound semiconductor are introduced in an alternating fashion. Importantly, only two subsequent additions are required for the growth of a layer of the shell semiconductor. X-ray diffraction (XRD), transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), and optical spectroscopy revealed that the shell growth of the CdSe/CdS core/shell system was nearly precisely controlled, homogeneous, and epitaxial.[13] This success motivated us to apply this new technique for growing quantum shells.

CdSe was chosen as the first quantum shell system partly because the corresponding quantum dots and rods are the most understood systems, and they exhibit tunable emission colors covering most of the visible optical window.[14,15] The diameter of the bulk exciton of CdSe is about 11 nm, which is smaller than the outer perimeter of all of the core/shell structures with more than two monolayers of the CdSe shell

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shown in this report. Thus, we suspect that the exciton should only experience quantum confinement along the radial direction. CdS nanocrystals were chosen as the nanocrystal templates since CdSe/CdS core/shell nanocrystals have been well studied, and epitaxial and uniform growth in solution between these two materials can easily be achieved by the SILAR technique.[13] In addition, CdS quantum dots with a quality that compares well with that of the standard CdSe nanocrystals can be readily synthesized using the newly developed alternative routes in noncoordinating solvents.[16]

For this specific system, SILAR temperatures between 180 and 200 °C were found to yield nanocrystals with the required thickness (about 0.7 nm increase in diameter per layer) and crystallinity, characterized by standard techniques used for the CdSe/CdS regular core/shell nanocrystals.[13] All experimental evidence indicates that the CdSe quantum shells are epitaxially grown on the CdS nanocrystal templates, similar to the reversed system, epitaxially grown CdSe/CdS core/shell nanocrystals. Figure 1 provides a selective-area electron diffraction (SAED) pattern and four TEM images that show the 3.7 nm CdS nanocrystal template before growth is initiated, and then after the growth of three (3-layer), five (5-layer), and seven monolayers (7-layer) of CdSe shells. The sizes of the dot-shaped quantum shells in Figure 1 approximately match the theoretical thicknesses predicted by the SILAR process.

Several CdS nanocrystal templates with diameters between 2.5 and 5.0 nm were used for the growth of the quantum shells, with the absorption peak ranging from 380 (3.26 eV) to 440 nm (2.82 eV). It should be noted that the amounts of cadmium and selenium precursors added for the growth of a monolayer of a CdSe shell on differently sized CdS templates varied significantly. For example, for the growth of the second monolayer of CdSe onto 2.5, 2.7, 3.7, and 5 nm CdS templates, 0.21, 0.23, 0.36, and 0.58 mL of the cadmium and selenium injection solutions (0.04 mol L^{-1}) were respectively injected into growth solutions with the same particle concentration. This shows that the volume increase of a monolayer of a dot-shaped crystal is strongly associated with the diameter of the dots.

Despite the large difference in the energy bandgap, the size of the templates used, and the volume increase of the CdSe shells on differently sized templates, the resulting CdSe quantum shell nanocrystals with the same shell thickness on differently sized templates have great similarities in their photoluminescence (PL) and absorption properties. For all quantum shells with a thickness equal to or greater than two monolayers, the position of the PL peak and the color of the emission were all strongly dependent on the thickness of the quantum shells (Figure 2). As a comparison, the influence of the size and the energy bandgap of the template nanocrystals on the PL position of a given shell thickness was found to be small, within ± 8 nm or ± 0.03 eV (Figure 2). The highest PL quantum yield (QY) of the band-edge emission of the CdSe quantum shells was about 20 %.

The absorption onset and the overall contour of the absorption spectra of the quantum shells are also mainly determined by the shell thickness (Figures 2 and 3). In addition, multiple staircase-like states in the absorption spectra were resolved in the absorption and photoluminescence excitation (PLE) spectra (Figures 2 and 3) if the shell thickness was two or more monolayers. The energy bandgap of the CdS template nanocrystals showed some local influence at the energy window close to the original absorption peak of the CdS templates, especially for thin layers. Furthermore, this influence increased as the size (energy gap) of the nanocrystal templates increased (decreased). When the shell thickness reached five monolayers, this influence became insignificant for all cases (Figure 2) due to the dominant volume fraction of the shell material. This fact is further demonstrated by the PLE spectra (Figure 3). The

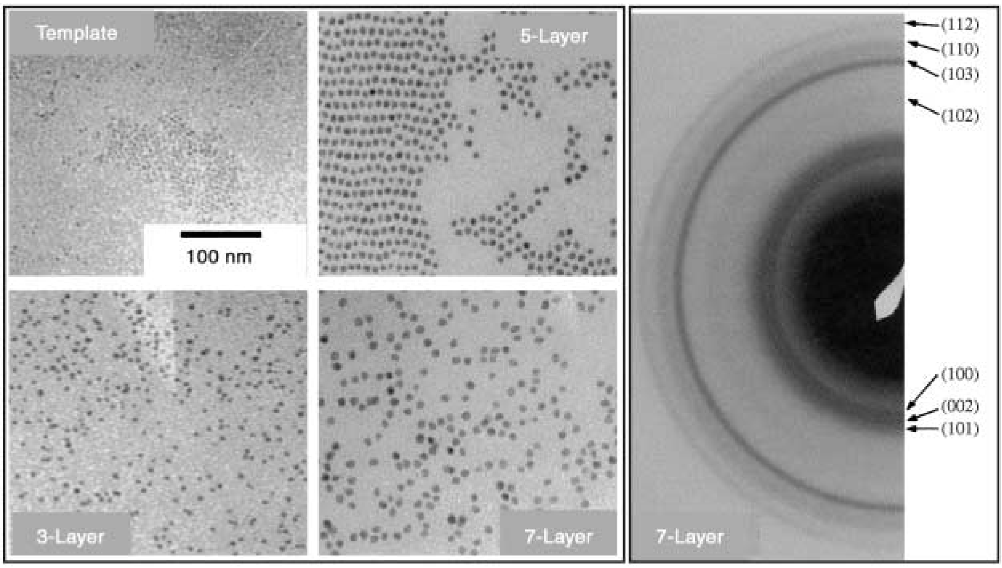

Figure 1. Left: TEM images of CdSe quantum shells with different thickness grown on 3.7-nm CdS nanocrystal templates; right: a SAED pattern of the 7-layer CdSe quantum shells and the indices of each diffraction ring, which are indicative of a wurtzite structure.

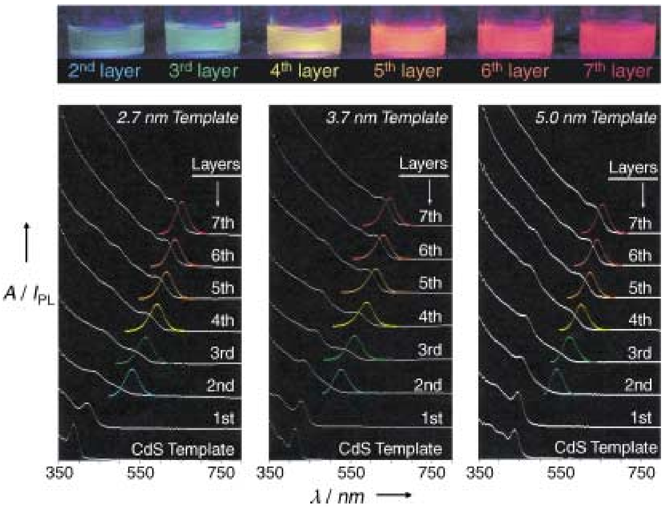

Figure 2. Bottom: Absorption and PL spectra of the CdSe quantum shells grown on three different-sized CdS templates, 2.7 nm (left), 3.7 nm (middle), and 5.0 nm (right). The number of CdSe monolayers is marked on the right for each sample; top: emission colors of CdS/CdSe quantum shells with different shell thicknesses.

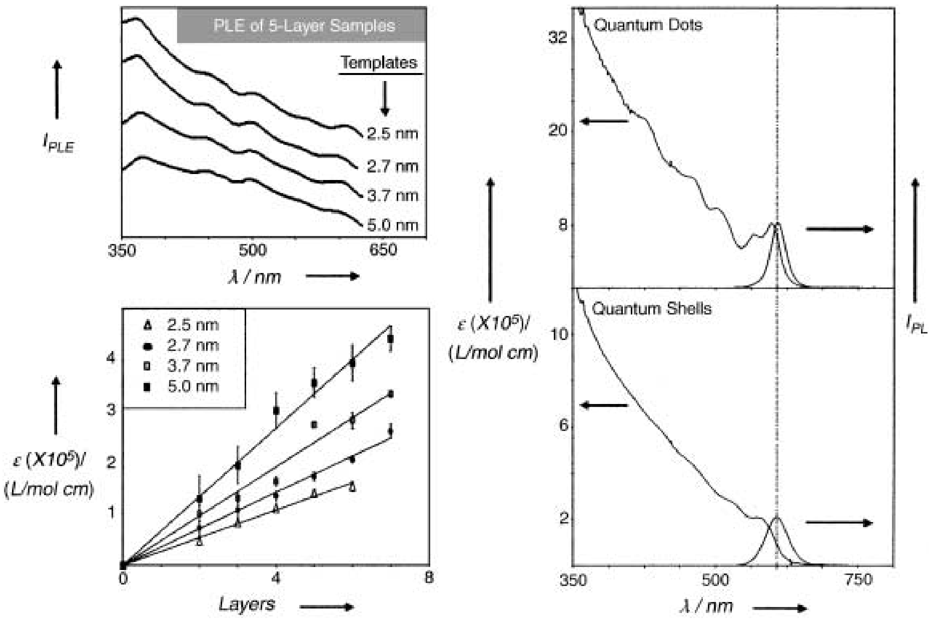

Figure 3. Top left: A collection of photoluminescence excitation (PLE) spectra for the 5-layer CdSe quantum shells grown on four different-sized CdS nanocrystal templates; bottom Left: a plot of the extinction coefficients (ε) at the first absorption feature of the quantum shells versus the number of monolayers of CdSe grown on four different-sized CdS nanocrystal templates. The error bars account the uncertainty of the peak position of the first absorption feature. The solid lines are a linear fit of the experimental data for the four series of CdSe quantum shells; right: a spectroscopic comparison between CdSe quantum shells (below) and high-quality CdSe quantum dots (above). Note: The scales of the y axis for the two plots are different.

overall size (including the CdS templates) of the four 5-layer quantum shells shown in Figure 3 ranged approximately from 6.0 to 8.5 nm depending on the size of the templates.

The extinction coefficient per mole of the nanocrystals (ε) at the first absorption feature position was found to be approximately proportional to the shell thickness for a given sized template (Figure 3, bottom left). Regardless of the template sizes, the ε values were found to be proportional to the CdSe units per particle (see Supporting Information). This is similar to some of the results reported in literature.[17–19] In addition, all four straight lines shown in the plot go through the origin, which indicates that the absorption feature is indeed caused by the CdSe shells. The ε values of the CdSe quantum shells at the emitting peak position are significantly lower than that of CdSe quantum dots with the same PL peak position (Figure 3), which makes the quantum shells potentially ideal emitters when a high concentration of particles is needed, such as for LEDs,[20,21] lasers,[22] and multiple or high-density bio-labeling.[23,24] Under these circumstances, reabsorption and Forster energy transfer may cause serious quenching of the PL[14] and electroluminescence (EL)[20] since the particles are in close proximity with each other.

The optical properties of the 1-layer structures have typically not fully developed into 2D systems, in contrast to those with thicker layers. This was true for CdS/CdSe and other systems (see Supporting Information) with a variety of template sizes. Typically, the absorption spectra are dominated by the slightly red-shifted absorption of the CdS template nanocrystals with a tail on the low energy side (Figure 2). PL spectra of all 1-layer structures display mainly the deep-trap emission of the nanocrystals. If the ε value of the first absorption feature of the 1-layer structure falls onto the linear trend lines shown in Figure 3, the oscillator strength of the narrow bandgap semiconductor is extremely low in comparison to that of the CdS template nanocrystals. As a result, the energy states contributed by the single monolayer of the narrow bandgap semiconductor may mostly act as the deep-trap states of the core CdS structures, causing deep-trap emissions.

The emission properties of quantum shells can be improved through inorganic passivation by additional epitaxial growth of a high-bandgap semiconductor on the surface of the quantum shells in a one-pot approach. The resulting nanocrystals structurally and electronically resemble the MBE quantum wells, thus we denote those structures as colloidal quantum wells. Figure 4 shows the optical spectra before and after the epitaxial growth of four monolayers of CdS onto a CdSe quantum shell sample. As expected, the PL QY increased

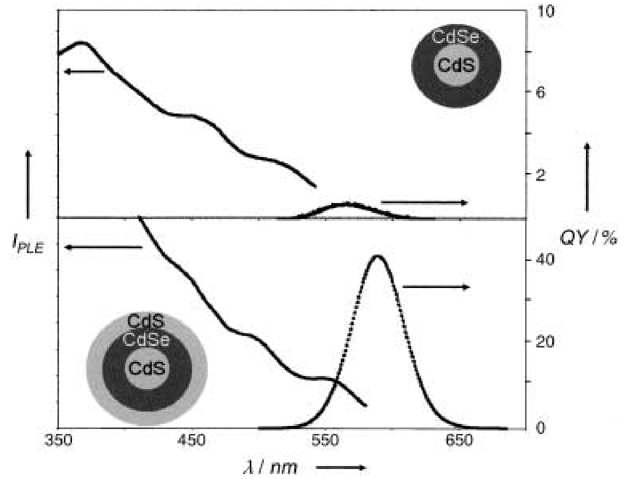

Figure 4. PLE and PL spectra of CdSe quantum shells before (top) and after (bottom) the expitaxial growth of four monolayers of CdS shell on the outer surface. Note: The scales for PL quantum yield (QY) for the quantum shells (top) and the colloidal quantum wells (bottom) are different.

significantly after inorganic overcoating and the PL peak position was red-shifted. To inorganically passivate quantum shells with CdS, it was seen that using fatty acids (such as oleic acid) as ligands yielded nanocrystals with higher quantum yields than when using amines. When fatty acids were used as the ligands, the CdSe quantum shells before inorganic passivation did not emit well but did grow the desired monolayers on the CdS templates. This is consistent with the observation that fatty acids are better passivation ligands for CdS surfaces, while amines are better for CdSe surfaces.[13,16,25,26] However, one issue became apparent when fatty acids were employed: There was a possibility that the nanocrystals might become insoluble during or after growth. Typically, reactions performed with short fatty acids had a strong tendency to form insoluble species but did yield CdS/CdSe/CdS colloidal quantum wells with the highest quantum yields.

In summary, CdSe quantum shells with necessary control over the shell thickness and the size distribution of the nanocrystals have been synthesized. Preliminary results revealed that other quantum shells, such as CdS/InP (see Supporting Information), can also be grown in a similar manner. The experimental results of the inorganically passivated quantum shells reveal that even more complex systems can be conveniently built with the SILAR technique. The synthesis of quantum shells and other complex systems will eventually add many new materials to the colloidal semiconductor nanocrystal family. The unique properties described above and the ones to be discovered for such new systems should greatly promote the fundamental understanding of semiconductor nanocrystals, especially for 2D systems. High-quality quantum shells and colloidal quantum wells are optically comparable to high-quality quantum dots and rods, with reasonably high PL quantum yields (over 20% for the CdSe quantum shells and over 40% for the CdS/CdSe/CdS colloidal quantum wells), relatively narrow emission bands, and tunable emission colors from about 520 to 650 nm. These optical features coupled with their low extinction coefficients at the emission position warrant their potential applications as desired emitters when high densities of nanocrystals are needed, such as for LEDs, lasers, and certain biomedical applications.

Experimental Section

High-quality CdS nanocrystals of a size ranging between 2.5 and 5 nm were synthesized and purified using a scheme modified from previously reported methods.[16] The growth of CdSe quantum shells was achieved by following the established SILAR method.[13] For a typical SILAR process, the Cd injection solution (CdO dissolved with oleic acid in octadecene (ODE)) and the Se injection solution (Se powder dissolved with tributylphosphane in ODE) were injected in an alternate fashion at 185 °C. The quantity of shell precursors added into the growth solution for each monolayer was based on the size of the nanocrystal templates, the concentration of the nanocrystals, and the lattice constants of the crystal system. Control experiments without the presence of CdS nanocrystal templates revealed that a trace amount of CdSe nanocrystals with a peak at around 550 nm were slowly formed under the reaction conditions, which typically did not show any noticeable photoluminescence. The extinction coefficient per particle (ε) at the first absorption feature of the quantum shells was obtained by diluting a certain amount of reaction mixture in a given volume of solvent. Since the concentration of the CdS nanocrystal templates in the reaction mixture was known, the concentration of the quantum shells in the diluted solution could be readily determined for the calculation of ε. For the quantum shells grown on different sized templates, the emission color of samples with the same shell thickness was observed to be approximately the same. The emission for taking PL images was generated while the nanocrystals were illuminated by a handheld UV lamp (365 nm). The formation of CdS/CdSe/CdS colloidal quantum wells was achieved by alternating injections of Cd (0.04 M) and S (0.04 M in ODE) precursor solutions after growth of the quantum shells by using fatty acids as the ligands. It was found that a higher reaction temperature (230–240 °C) was necessary for the formation of the outer CdS layers than for the CdSe layers. Up to five layers of CdS were found to give the best emission efficiencies for the nanocrystals; purification of the nanocrystals always led to an increase in the emission efficiency of the nanocrystals.

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