Quantum Dots

Blue Luminescence from (CdS)ZnS Core–Shell Nanocrystals**

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The ability to synthesize semiconductor nanocrystals with narrow size distributions and high luminescent efficiencies has made quantum dots an attractive alternative to organic molecules in applications such as optoelectronic devices[1,2] and biological fluorescence labeling.[3–5] Not only are quantum dots (QDs) more stable to photooxidation relative to organic molecules, but their fluorescence is also more saturated (narrow emission bandwidths). Their size-tunable optical properties, which are independent of their chemical

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properties, along with their stability and saturated color emission, have made them particularly interesting as the active materials in large-area (cm^2) hybrid organic/inorganic QD light-emitting devices (QD-LEDs).[6–8] To date, efficient red- and green-light-emitting QD-LEDs have been realized with (CdSe)ZnS core–shell nanocrystals, but QD-LEDs that emit blue light have remained elusive due to a lack of appropriate core–shell materials. The ideal blue emission spectrum of an LED for a flat panel display application would have a narrow bandwidth and a wavelength such that its coordinates on the Commission International d'Eclairage (CIE) chromaticity diagram would lie to the outside of the current National Television System Committee (NTSC) standard color triangle. For a Gaussian emission spectrum with a full-width at half-maximum (FWHM) of 30 nm and a maximized perceived power, the ideal wavelength of blue emission for display applications is ≈ 470 nm. Wavelengths shorter than 470 nm become difficult for the human eye to perceive, while those longer than 470 nm have coordinates that lie inside the standard NTSC color triangle. In this work, we synthesize a core–shell QD material with these ideal spectral characteristics, and show its potential as the active material in a blue-light-emitting QD-LED.

The best-characterized semiconductor QD system to date is CdSe, whose optical tuning range spans the visible region of the spectrum.[9] Blue emission can be obtained from CdSe particles smaller than 2 nm, which are difficult to synthesize with narrow size distributions and good quantum efficiencies. They are difficult to process, manipulate, and overcoat with a higher-band-gap inorganic semiconductor, all of which are necessary for incorporation into solid-state structures. A core–shell-type composite rather than an organically passivated QD is desirable in a solid-state QD-LED device due to their enhanced photoluminescence (PL) and electroluminescence (EL) quantum efficiencies and greater tolerance to the processing conditions necessary for device fabrication.[2,10–12] In addition, QDs < 2 nm in diameter have a small absorption cross section, which leads to a small Förster energy transfer radius. All of these factors combine to make CdSe a poor choice for blue QD-LEDs.

The largest high-quality ZnSe[13] nanocrystals recently reported exhibit band-edge fluorescence up to 440 nm, which is too short a wavelength.[14] Both ZnTe and CdS have appropriate band gaps.[15] To date, it has been difficult to grow large (> 4.5 nm diameter) particles of ZnTe with narrow size distributions. We show in this work that (CdS)ZnS core–shell nanocrystals can be made to emit in the 460–480 nm range with relatively narrow size-distributions, making them ideal blue-light-emitters for display applications.

A recent report has detailed the synthesis of high-quality bare CdS QDs.[16] However, bare CdS cores tend to emit deep-trap white luminescence that overwhelms the blue emission. We report a procedure for the growth of CdS nanocrystal cores of appropriate size, with narrow size distributions, and a robust, reproducible method for overcoating these cores with ZnS. The resulting core–shell (CdS)ZnS nanocrystals exhibit bright blue (quantum efficiencies = 20–30 %) and narrow-band-edge luminescence (FWHMs ≤ 28 nm) from 460 to 480 nm. We also demonstrate preliminary results of blue EL from these core–shell nanocrystals by embedding them in an organic thin-film device.

The synthesis of the (CdS)ZnS core–shell nanocrystals is a two-step procedure. The CdS cores are synthesized and processed from a growth solution, and the shell of ZnS is grown onto the CdS cores in a separate reaction. The synthesis of the CdS nanocrystal core material is based on the well established colloidal methods of preparing nanocrystals, in which the precursors are rapidly injected at high temperatures into a flask of high-boiling organic solvents.[9] Here the cadmium and sulfur precursors are injected into a mixture of oleylamine and trioctylphosphane in the presence of a dialkyl phosphinic acid, which provides controlled growth and leads to large particles with narrow size distributions. Figure 1 shows the optical absorption spectra for a size series of CdS cores, demonstrating their narrow size distributions. The largest particles with a first absorption feature at 448 nm (core diameter 5.2 ± 0.4 nm) still exhibit secondary and even tertiary absorption features. The crystallinity of the core material is seen clearly in the inset of Figure 2a, in which the HRTEM micrograph shows the atom columns of a ≈ 4.9 nm particle. The low-resolution TEM image (Figure 2a) illustrates the relatively good size distribution and morphology of the particles. PL quantum efficiencies for these CdS core nanocrystals after processing were 3–6 %. The PL of the CdS core nanocrystals contains a noticeable quantity of deep-trap emission (Figure 3), which gives the core materials a violet appearance when excited with a UV lamp.

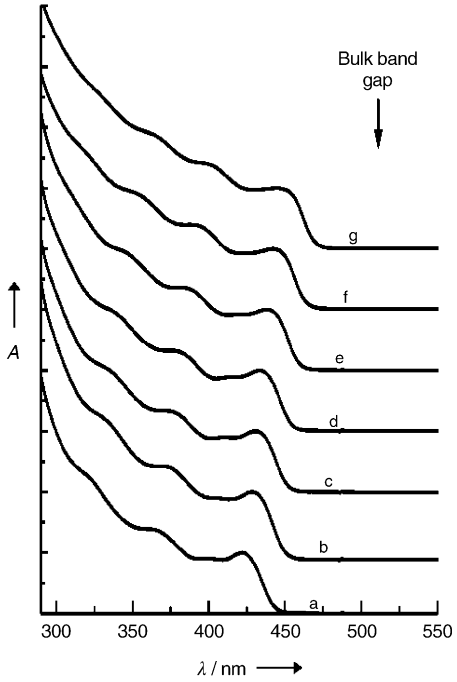

Figure 1. Absorption spectra of a size-series of large CdS nanocrystals ranging from 3.7 ± 0.4 nm to 5.2 ± 0.4 nm in diameter. The longest wavelength absorption feature occurs at a) $\lambda = 422$, b) 427, c) 432, d) 435, e) 439, f) 444, and g) 448 nm.

Growth of the ZnS shell is based on the prior overcoating procedure for (CdSe)ZnS core–shell nanocrystals.[11,12] ZnS

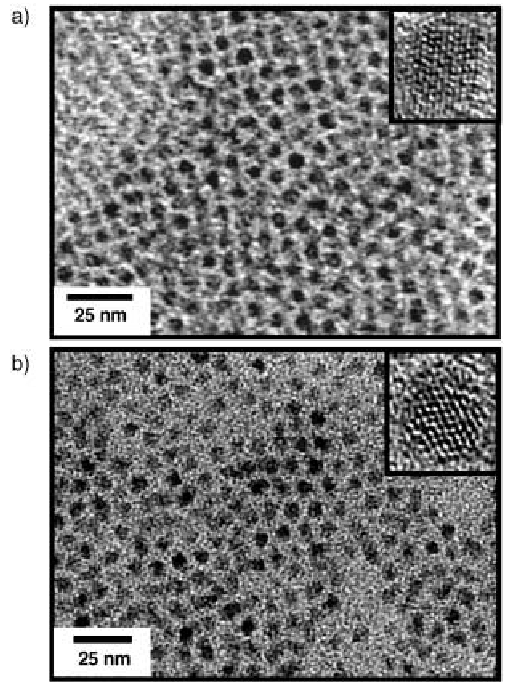

Figure 2. TEM images of CdS core and (CdS)ZnS core–shell nanocrystals. a) Micrograph showing bare, 4.9 ± 0.4 nm CdS nanocrystals (inset: corresponding HRTEM image); b) the same nanocrystal sample overcoated with ≈3 monolayers (3.1 Å per monolayer) of ZnS (inset: corresponding HRTEM image).

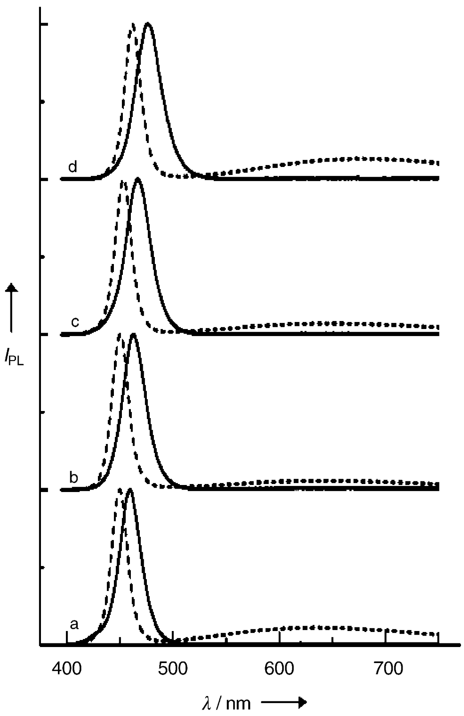

Figure 3. Normalized PL spectra of bare CdS nanocrystals (-----) and the corresponding PL of the (CdS)ZnS core–shell nanocrystals (——). a) Bare CdS nanocrystals emitting at 450 nm (4.7 ± 0.4 nm diameter core, FWHM = 18 nm) and overcoated with ≈2 monolayers emitting at 460 nm (FWHM = 24 nm); b) bare CdS nanocrystals emitting at 450 nm (4.7 ± 0.4 nm diameter core, FWHM = 18 nm) and overcoated with ≈3 monolayers emitting at 465 nm (FWHM = 25 nm); c) bare CdS nanocrystals emitting at 454 nm (4.9 ± 0.4 nm diameter core, FWHM = 18 nm) and overcoated with ≈3 monolayers emitting at 469 nm (FWHM = 27 nm); d) bare CdS nanocrystals emitting at 463 nm (5.2 ± 0.4 nm diameter core, FWHM = 18 nm) and overcoated with ≈4.5 monolayers emitting at 480 nm (FWHM = 28 nm). I_{PL} = photoluminescence intensity.

was chosen as the shell material because of its large band gap (3.7 eV corresponding to $\lambda = 335$ nm), which aids confinement of the exciton on the CdS core, accompanied by the relatively small, 8 % lattice mismatch between CdS and ZnS. As the zinc and sulfur precursors are added, the weak violet fluorescence changes gradually over the course of the overcoating process to a bright blue emission. Figure 3 shows the emission spectra of CdS cores before overcoating and the corresponding (CdS)ZnS core–shell emission spectra after overcoating. Consistent with previous overcoating studies, suppression of deep-trap emission is achieved with the growth of the ZnS shell, as well as increased PL stability (see Supporting Information). The relatively good size distribution and crystallinity of the (CdS)ZnS core–shell nanocrystals is seen in Figure 2 b. The core–shell nanocrystals exhibit quantum efficiencies of 20–30 %.[17] The quantum efficiency peaks at an average ZnS shell thickness of ≈3 monolayers (3.1 Å per monolayer). No change in the quantity of deep-trap emission from the cores was seen in the presence of amine. We believe that the amine enables the controlled growth of the ZnS shell based on the fact that in the absence of amine in the overcoating solution not all of the deep-trap emission is suppressed.[18] These observations make it difficult to distinguish how the amine independently affects shell thickness (amine concentration was always held constant) and quantum yield. As thicker shells of ZnS are grown onto the core CdS nanocrystals, an expected increase in the emission FWHM occurs. The band-edge emission FWHM of the CdS core particles is 17–19 nm. After overcoating with 2–3 monolayers[19] the FWHM increases to about 24–26 nm accompanied by red shifts of about 10 nm in emission and about 5 nm for the first absorption feature (see Supporting Information for the shift in absorption based on different ZnS shell thicknesses). Similar red shifts in absorption have been observed for the overcoating of CdSe with ZnS and are due to the leakage of the exciton into the shell.[12] Figure 4 shows the absorption and emission spectrum of 5.4 ± 0.4 nm (CdS)ZnS core–shell nanocrystals. The inset demonstrates (CdS)ZnS core–shell EL. At low currents (●, 1 mA cm^{-2} at 14 V) the FWHM of the QD-LED spectral peak is 30 nm centered at 468 nm, while at higher currents (——, 60 mA cm^{-2} at 21 V) the EL from organic layers begins to dominate (seen as the shoulders in the UV and the green regions of the spectrum). Organic and QD luminescence occur simultaneously in the working device, and as more current is applied the ratio of QD to organic emission changes. At high currents, excitons are created deeper in the organic transport layers, which causes the width of the exciton-generation region to exceed the organic-QD Förster energy transfer radius, which results in an increased contribution of organic luminescence to the EL spectrum.[10] These preliminary results demonstrate the potential of (CdS)ZnS core–shell nanocrystals as blue-light

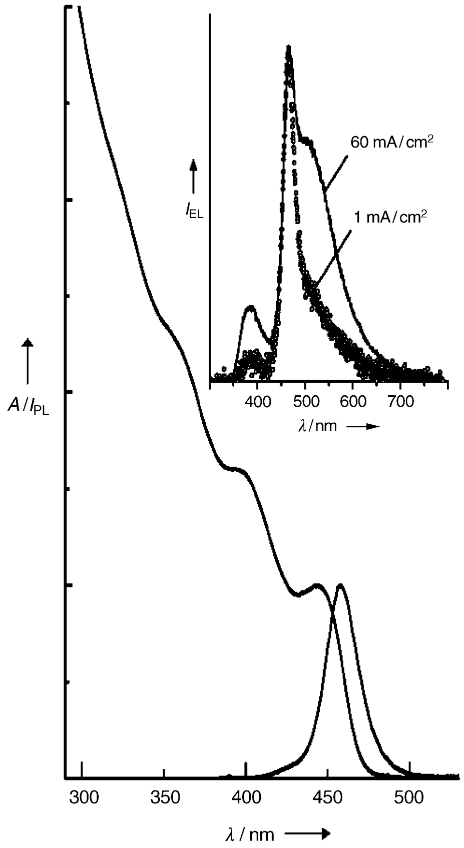

Figure 4. Absorption and emission spectra of (CdS)ZnS core–shell nanocrystals. The (CdS)ZnS core–shell nanocrystals have a 4.7 ± 0.4 nm diameter core, with a ZnS shell thickness of ≈ 2 monolayers. The emission peaks at 459 nm with a FWHM of 24 nm and the first absorption feature is at 445 nm. The inset shows the EL spectra, at two different current densities, of (CdS)ZnS core–shell nanocrystals embedded in a QD-LED. The layered device structure, based on that reported in ref. [6], consists of ITO/CBP/(CdS)ZnS QD monolayer/TAZ/Alq_3/Mg:Ag/Ag[22] and exhibits an external quantum efficiency of 0.1 % (see Supporting Information for I–V curve and efficiency plot). I_{PL} = photoluminescence intensity; I_{EL} = electroluminescence intensity.

emitters for display applications, but further optimization of the device and the materials will be required to obtain saturated blue EL. Figure 5 a shows the X-ray powder pattern for 4.9 ± 0.4 nm bare CdS nanocrystals, which appears to be a wurtzite structure with zinc blende stacking faults along the [002] direction.[9] The X-ray powder patterns of core–shell nanocrystals with ZnS coverages of ≈ 2 monolayers (Figure 5 b) and ≈ 3 monolayers (Figure 5 c) show a noticeable influence of the wurtzite ZnS shell on the overall diffraction pattern. Little evidence of small ZnS particles was seen with TEM or optical spectroscopy, but nonetheless care was taken during sample preparation to ensure that no ZnS particles were present for the XRD and WDS measurements.

In conclusion, we have detailed the synthesis of blue-light-emitting (quantum efficiencies = 20–30 %) (CdS)ZnS core–shell nanocrystals. The procedure is a two-step synthesis, in which CdS core nanocrystals 4.7 ± 0.4 to 5.2 ± 0.4 nm in diameter are overcoated with ZnS to yield stable core–shell particles emitting from 460 nm to 480 nm. Blue electroluminescence from the (CdS)ZnS core–shell nanocrystals is also demonstrated. Access to this region of the spectrum has been realized with stable, processible core–shell nanocrystals, which make applications such as blue QD-LEDs and blue QD-biological fluorescence labeling possible.

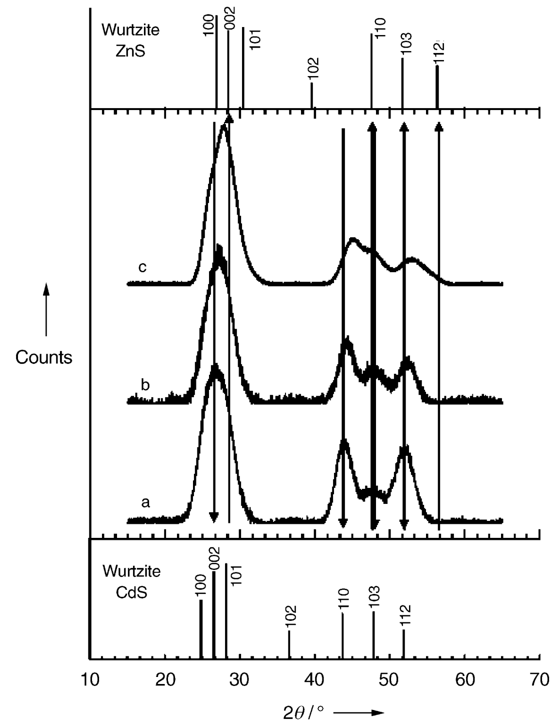

Figure 5. XRD patterns for a) 4.9 ± 0.4 nm bare CdS nanocrystals and ZnS overcoated samples with a coverage of b) ≈ 2, and c) ≈ 3 monolayers, respectively. The powder patterns for wurtzite CdS and ZnS are shown for comparison in the bottom and top insets, respectively. The lines with arrows are included to help guide the eye to the respective bulk material powder peaks.

Experimental Section

A two-step synthetic route was employed to prepare (CdS)ZnS core–shell nanocrystals. In the first step, the CdS cores were prepared by rapidly injecting the precursor solution into a round-bottomed flask containing degassed (under vacuum at 100 °C for 1 h) oleylamine (7 mL, 98 %; Pfaltz & Bauer Inc.)[20] and trioctylphosphane (TOP) (8 mL, 97 %; Strem) stirring rapidly at 250–280 °C and then growing at 250 °C for 15 to 30 min. The precursor solution was made by mixing a degassed (under vacuum at 100 °C for 1 h) mixture of cadmium acetate hydrate (1–2 mmol), TOP (6 mL), and bis(2,4,4-trimethylpentyl) phosphinic acid (BTMPPA) (1–2 mmol, Cyanex$^+$ 272 Extractant, Cytec Canada Inc.)[21] with a degassed (under vacuum at room temperature for 1 h) solution of elemental sulfur (1–2 mmol) in oleylamine (3 mL). The size was tuned by changing the injection temperature, growth time, and concentration of precursors, while maintaining the sulfur-to-cadmium-to-BTMPPA ratio at 1:1:1.

Before overcoating, the CdS cores were precipitated out of the growth solution and then one more time out of hexane to remove unreacted precursors and excess capping ligands. The particles were flocculated from the growth solution by adding 0.4 equiv of hexane, 0.8 equiv of butanol, and 3 equiv of methanol to 1 equiv of growth solution and centrifuging for 5 min. The particles were then dispersed in 0.15 equiv of hexane and flocculated by adding one drop of butanol per equivalent of original growth solution and 0.5 equiv of methanol, and then centrifuging for 5 min.

In the second step, the ZnS shell was grown. Trioctylphosphane oxide (TOPO) (8–14 g, 99%; Strem), oleylamine (3 mL), hexadecylamine (2 g, 98%; Aldrich), and BTMPPA (0.3–2.0 mmol) were degassed under vacuum for 2 h in a four-necked flask at 100 °C. The CdS cores dispersed in hexane were then added to the degassed solution and the hexane was removed at 80 °C under vacuum. Under a flow of argon, the nanocrystal solution was heated to 180 °C and the ZnS shell precursor solution (diethylzinc (min. 95%); Strem) and hexamethyldisilthiane (> 97%; Fluka) dissolved in TOP (7 mL)) was added dropwise. After addition was complete the solution was kept at 180 °C for 5 min and then left stirring overnight at 75 °C to promote annealing of the shell. The (CdS)ZnS core–shell nanocrystals were obtained by precipitation using a mixture of butanol and methanol, similar to the core-processing procedure.

Optical absorption spectra were acquired on a Hewlett Packard 8453 diode array spectrometer. Photoluminescence spectra were acquired using a SPEX Fluorolog-2 spectrometer in a right-angle collection configuration. The core CdS absorption spectra were collected with samples prepared by diluting the as-grown nanocrystal solutions in hexane, while all (CdS)ZnS core–shell optical characterization was carried out with samples that had been precipitated out of solution at least one time and redispersed in hexane. High-resolution transmission electron microscopy (HRTEM) carried out to determine the shell thickness, crystallinity, and particle-size distributions was performed on a JEOL-2010 electron microscope operated at 200 kV. Low-resolution TEM was carried out on a JEOL 2000FX microscope operated at 200 kV. Elemental analysis of the core–shell material was obtained using wavelength dispersive spectroscopy (WDS) on a JEOL JXA-733 Superprobe. Powder X-ray diffraction (PXRD) patterns were obtained on a Rigaku Ru300 X-ray diffractometer.

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[22] ITO = indium tin oxide; CBP = 4,4′-*N*,*N*′-dicarbazolyl-biphenyl; TAZ = 3-(4-biphenylyl)-4-phenyl-5-*tert*-butylphenyl-1,2,4-triazole; Alq_3 = tris-(8-hydroxyquinoline)aluminum.