Quantum Dots

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Color-Saturated Green-Emitting QD-LEDs**

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Semiconductor nanocrystals (NCs) or quantum dots (QDs) show great promise for use in QD-LED (quantum dot light-emitting device) displays, owing to their unique optical properties and the continual development of new core and core–shell structures to meet specific color needs.[1–10] This in combination with the recent development of more efficient and saturated QD-LEDs as well as new QD-LED fabrication techniques,[11,12] suggests that QD-LEDs have the potential to become an alternative flat-panel display technology. The ideal red, green, and blue emission spectrum of an LED for a display application should have a narrow bandwidth and a wavelength such that its color coordinates on the Commission Internationale de l'Eclairage (CIE) chromaticity diagram lie outside the current National Television System Committee (NTSC) standard color triangle (see Figure 2). For a Gaussian emission spectrum with a full width at half maximum (FWHM) of 30 nm and a maximized perceived power, the optimal peak wavelength for display applications is $\lambda = 610$–620 nm for red, $\lambda = 525$–530 nm for green, and $\lambda = 460$–470 nm for blue. For the red pixels, wavelengths longer than $\lambda = 620$ nm become difficult for the human eye to perceive, while those shorter than $\lambda = 610$ nm have coordinates that lie inside the standard NTSC color triangle. Optimization of wavelength for the blue pixels follows the same arguments as for the red pixel, but at the other extreme of the visible spectrum. For green pixels, $\lambda = 525$–530 nm provides a color triangle with the largest area on the CIE chromaticity diagram (and therefore the largest number of colors accessible by a display). Wavelengths longer than $\lambda = 530$ nm make some of the blue/green area of the triangle inaccessible. Wavelengths shorter than $\lambda = 525$ nm compromise the yellow display emissions.

To date, efficient red-emitting QD-LEDs with a peak emission wavelength optimized for display applications have been realized using (CdSe)ZnS core–shell NCs,[11,13] while blue QD-LEDs with a peak wavelength of emission optimized for display applications have been realized with a (CdS)ZnS core–shell material.[10] To date, although efficient green-emitting core–shell semiconductor NCs that emit at $\lambda =$ 525 nm have been synthesized, they have not been successfully incorporated into a QD-LED suitable for display applications. Previous work using (CdSe)ZnS core–shell NCs gave QD-LEDs that emit at wavelengths no shorter than $\lambda = 540$–560 nm.[13,14] Using (CdSe)ZnS core–shell NCs to achieve $\lambda = 525$ nm emission requires making small CdSe cores (≈ 2.5 nm in diameter).[15,16] Such small CdSe semiconductor NCs can be difficult to synthesize with narrow size distributions and high quantum efficiencies, and are also more difficult to process and overcoat with a higher-band-gap inorganic semiconductor, which is necessary for incorporation into solid-state structures. A core–shell composite, rather than an organically passivated NC, is desirable in a solid-state QD-LED device owing to the enhanced photoluminescence and electroluminescence (EL) quantum efficiencies of core–shell NCs and their greater tolerance to the processing conditions necessary for device fabrication.[13,15–20] Larger NCs are also more desirable for use in QD-LEDs because the absorption cross section of NCs scales with size. Larger NCs with larger absorption cross sections lead to an increase in the efficiency of Förster energy transfer from electroluminescing organic molecules to NCs in a working QD-LED, which in turn leads to more efficient devices.

Herein, we report the synthesis of a $Cd_xZn_{1-x}Se$ alloy core on which we then grew a $Cd_yZn_{1-y}S$ shell to create a core–shell NC material with the ideal spectral characteristics for green emission in a QD-LED display and with a size large enough for fabricating a working QD-LED. Our $Cd_xZn_{1-x}Se$ core synthesis was based on work recently published, in which Cd and Se precursors were slowly introduced into a growth solution of ZnSe NCs.[1,2] A three-step synthetic route was employed to prepare the $(Cd_xZn_{1-x}Se)Cd_yZn_{1-y}S$ core–shell NCs. In the first step, ZnSe NCs were prepared by rapidly injecting 0.7 mmol of diethylzinc (Strem) and 1 mL of tri-*n*-octylphosphine selenide (TOPSe; 1M) dispersed in 5 mL of tri-*n*-octylphosphine (TOP; 97% Strem) into a round-bottom flask containing 7 grams of degassed hexadecylamine (distilled from 90% Sigma–Aldrich) at 310°C and by then growing the NCs at 270°C for 90 min. The second step consisted of transferring 8 mL of the above ZnSe NC growth solution, at 160°C, into a degassed solution of 16 grams of tri-*n*-octylphosphine oxide (TOPO; distilled from 90% Sigma–Aldrich) and 4 mmol of hexylphosphonic acid (HPA; Alfa Aesar), also at 160°C. A solution of 1.1 mmol of dimethylcadmium (Strem) and 1.2 mL of TOPSe (1M) dispersed in 8 mL of TOP (97% Strem) was then introduced dropwise

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(1 drop/ ≈ 2 s) into the ZnSe NC growth solution/TOPO/HPA mixture at 150 °C. The solution was then stirred at 150 °C for 46 h. Before overcoating the $Cd_xZn_{1-x}Se$ cores with $Cd_yZn_{1-y}S$, the $Cd_xZn_{1-x}Se$ cores were isolated by precipitation out of solution twice with a miscible non-solvent. In the third step, the $Cd_yZn_{1-y}S$ shell was grown by introducing dropwise a solution of dimethylcadmium (20 % of total required moles of cation; Strem), diethylzinc (Strem), and hexamethyldisilathiane (Fluka) in 8 mL of TOP into a degassed solution of 10 grams of TOPO (distilled from 90 % Sigma–Aldrich) and 2.4 mmol of HPA (Alfa Aesar), which contained the core $Cd_xZn_{1-x}Se$ NCs, at 150 °C (the $Cd_xZn_{1-x}Se$ cores dispersed in hexane were added to the degassed TOPO/HPA solution and the hexane was removed at 70 °C under vacuum prior to the addition of the shell precursors).

To fully characterize our $Cd_xZn_{1-x}Se$ core material, aliquots were sampled from the growth solution at time $t =$ 7, 60, and 2760 min (46 h) and analyzed with transmission electron microscopy (TEM), wavelength dispersive spectroscopy (WDS), and absorption and fluorescence spectrophotometry. Figure 1 a shows the absorption and emission spectra of these three aliquots as well as the absorption spectrum of the starting ZnSe NCs (2.6 ± 0.5 nm in diameter, as determined by TEM). Over time the absorption and emission spectra shift to the red and the broad trap emission diminishes after 46 h of growth (Figure 1 a, spectrum 4), yielding particles approximately 3 nm in diameter. Upon overcoating the cores of $Cd_xZn_{1-x}Se$ with $Cd_yZn_{1-y}S$, the trap emission was completely suppressed, yielding an efficient (quantum yields of 50–60 %),[21] saturated (FWHM = 30 nm), green-emitting core–shell material (≈ 4 nm in diameter) suitable for QD-LED display applications (Figure 1 b). An alloyed material for the shell was used to minimize lattice mismatch with the $Cd_xZn_{1-x}Se$ core.

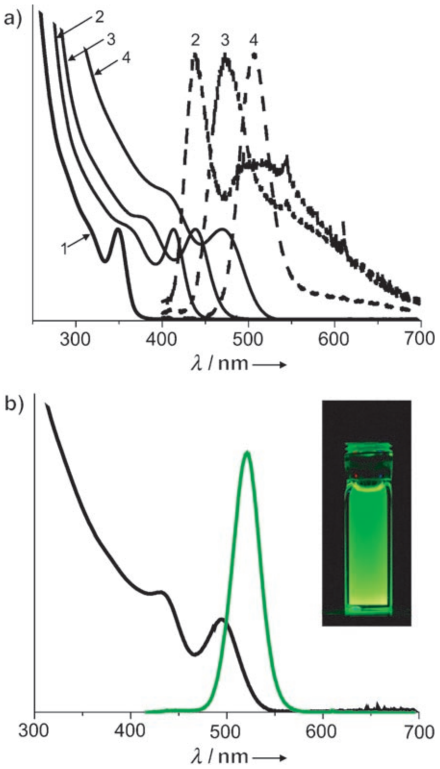

Figure 1. a) Normalized absorption (solid) and emission (dashed) spectra of the core NCs over time: 1) Starting ZnSe NCs (first absorption peak at 350 nm); 2) Aliquot taken out after 7 min of growth (first absorption peak at 413 nm; emission peak at 439 nm); 3) Aliquot taken out after 60 min of growth (438 nm; 475 nm); 4) Aliquot taken out after 46 h of growth (470 nm; 506 nm (FWHM = 34 nm)). b) Absorption (black) and emission (green) spectra of $(Cd_xZn_{1-x}Se)Cd_yZn_{1-y}S$ core–shell NCs. The emission peaks at 520 nm with a FWHM of 30 nm, and the first absorption feature is at 495 nm. The inset shows the bright, color saturated, green emission from the NCs upon excitation with a UV lamp.

Table 1 shows the growth time ($t = 0$, 7, 60, and 2760 min) of each aliquot, the average outer diameter determined by TEM, the Zn to Cd ratio determined by WDS, the measured first absorption peak, and calculated alloy ($Cd_xZn_{1-x}Se$) and core–shell ((ZnSe)CdSe core-shell) wavelengths based on the observed Zn to Cd ratios. We see from the raw data that as the reaction proceeds, the first absorption peak shifts to the red, the Zn to Cd ratio decreases, and the diameter of the particles increases. It is important to note that there is a relatively large increase in particle diameter from $t = 7$ to $t = 60$ min of growth, followed by a negligible increase in diameter from $t = 60$ to $t = 2760$ min (46 h). This small change in diameter is accompanied by a relatively large change in the Zn to Cd ratio as well as a relatively large shift of the first absorption peak to the red. This situation suggests that at $t = 7$ min the structure is most likely a (ZnSe)CdSe core–shell structure and that for $t > 7$ min the structure becomes a $Cd_xZn_{1-x}Se$ alloy, as a result of the migration of cations in the material.[3] It is of note that a decrease in particle diameter is initially observed following the introduction of neat hexadecylamine ZnSe growth solution (2.6 ± 0.5 nm in diameter) into TOPO/phosphonic acid solution at 160 °C after about 2/3 of the Cd and Se precursors have been added (7 min aliquot, 1.9 ± 0.3 nm in diameter). This particle etching is plausible based on the large excess of acid present in the solution.

Table 1: Experimental data and the results of effective-mass-approximation calculations of the first transition energy of alloyed ($Cd_xZn_{1-x}Se$) versus core–shell (ZnSe)CdSe NCs.

Growth time [min][a]	Outer diameter [nm][b]	Zn/Cd[c]	Absorption wavelength [nm][d]	Calculated alloy wavelength [nm]	Calculated core–shell wavelength [nm]	Inner diameter [nm][e]
0	2.6 ± 0.5		350			
7	1.9 ± 0.3	0.33	413	324	416	0.65
60	3.1 ± 0.5	0.18	438	477	509	1.64
2760	3.2 ± 0.5	0.08	470	505	534	1.35

[a] Time from when the Cd and Se precursors were introduced into the flask containing the ZnSe NCs to when the aliquot was removed from the flask (complete addition of the Cd and Se precursors occurred at 9.5 min). [b] Measured from TEM. [c] Measured from WDS. [d] First absorption feature from absorption spectra shown in Figure 1 a. [e] Calculated from the Zn/Cd ratio and the known outer NC diameter from TEM measurements. This parameter is relevant only for the core–shell calculations, while the alloy results depend only on the outer diameter.

To help confirm our analysis of the NC morphology ($Cd_xZn_{1-x}Se$ alloy versus (ZnSe)CdSe core–shell) we performed calculations whose results are summarized in Table 1. The energies of an electron and hole within an alloyed or a core–shell semiconductor NC were calculated using the effective-mass approximation.[22,23] These calculations used electron and hole effective masses and band gaps optimized to match reported experimental results for both pure CdSe and ZnSe NCs.[24–26] We performed two sets of calculations using these optimized parameters to represent an alloyed material or a strict core–shell structure. To model an alloyed NC we adjusted the optimized band gap and electron/hole effective masses by a linear interpolation of the parameters for the pure materials based upon the experimentally determined stoichiometry (i.e., Zn to Cd ratio determined by WDS, shown in Table 1). To model a core–shell structure, we used the measured stoichiometry to determine the core radius and calculated the lowest electron and hole energies of a material with a ZnSe core, CdSe shell, and organic capping layer which has a high band offset (5 eV) for the electron and hole. The lowest transition energy is then determined by adding the electron and hole energies to the optimized band gap[26] along with the Coulombic binding energy of the electron and hole as determined from perturbation theory.[27] It can be seen that the calculated first transition energy for a core–shell structure is a good match for the NC material after the initial (7 min aliquot) exposure to the Cd and Se precursors. After prolonged (>1 h) exposure, the trends in our calculations suggest that an alloyed structure better matches the experimental results, while a core–shell material has a first absorption that is too low in energy. These results suggest that an alloy better represents the electronic structure of our materials.

The ($Cd_xZn_{1-x}Se$)$Cd_yZn_{1-y}S$ core–shell NCs were isolated by precipitation out of solution twice with a miscible non-solvent and then filtered through a 0.2 μm syringe filter before use in device fabrication. QD-LED fabrication consisted of first thermally evaporating 4,4′-*N*,*N*′-dicarbazolyl-biphenyl (CBP) (hole transport layer (HTL)) onto an indium tin oxide (ITO) coated glass substrate at $< 5\times10^{-6}$ torr. The QD monolayer, under air-free conditions, was then deposited onto the organic thin film of CBP using micro-contact printing. The substrate was then transported back into the thermal evaporator without exposure to air, where the hole blocking layer (HBL), 3-(4-biphenylyl)-4-phenyl-5-*tert*-butylphenyl-1,2,4-triazole (TAZ), and then the electron transporting layer (ETL), tris(8-hydroxyquinoline)aluminum (Alq_3), were deposited. Finally the metal cathode (50 nm thick Mg:Ag, 50:1 by weight, 50 nm Ag cap) was thermally evaporated through a shadow mask to define devices of 1 mm in diameter (see Figure 2a for a diagram of the assembled device structure).

Figure 2a shows the EL spectrum of a typical green-emitting QD-LED. The small peak in the EL spectrum at $\lambda = 380$ nm is CBP emission, which is only 2.6% of the total emission from the device, the rest being QD emission. When the EL spectrum shown in Figure 2a is transformed into its corresponding CIE chromaticity diagram color coordinates ($CIE_x = 0.21$ and $CIE_y = 0.70$) we see that it lies far outside of the standard NTSC color triangle (Figure 2b). This shows that using these saturated green-emitting QD-LEDs for a display would provide a significantly larger color triangle on the CIE chromaticity diagram. Figure 3 shows a plot of the external quantum efficiency (EQE) for the device versus current density (*J*) as well as the current–voltage plot. These devices show low operating voltages (<10 V) and peak EQEs of 0.5%.

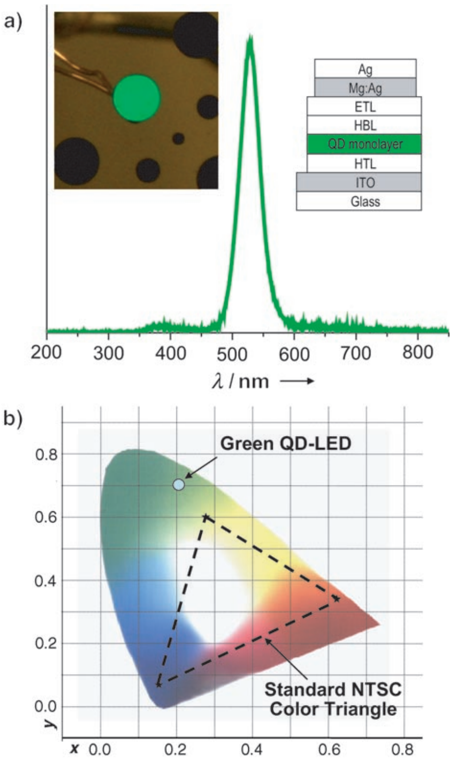

Figure 2. a) The electroluminescence (EL) spectrum for the device: ITO/HTL/($Cd_xZn_{1-x}Se$)$Cd_yZn_{1-y}S$ QD monolayer/HBL/ETL/Mg:Ag/Ag (assembled device structure is shown in the inset on the right; see text for details). The emission of the QD-LED peaks at 527 nm with a FWHM of 35 nm. The inset on the left is a photograph of the working green QD-LED. b) The EL spectrum shown in (a), transformed into its CIE chromaticity diagram color coordinates. The standard NTSC color triangle is shown for comparison.

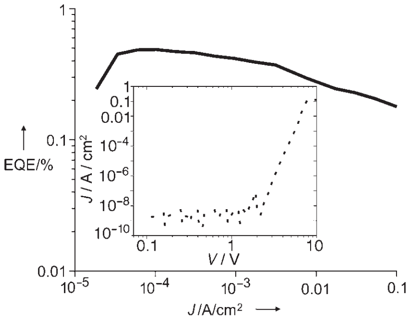

Figure 3. External quantum efficiency (EQE) versus current density (*J*) for the device (assembled device structure is shown in the inset on the right of Figure 2a). The inset shows the current–voltage curve.

In summary, we have synthesized $Cd_xZn_{1-x}Se$ alloy core nanocrystals and overcoated these nanocrystals with $Cd_yZn_{1-y}S$ to create core–shell nanocrystals with the ideal wavelength of emission for QD-LED displays. We have used these $(Cd_xZn_{1-x}Se)Cd_yZn_{1-y}S$ core–shell nanocrystals to fabricate color-saturated green-emitting QD-LEDs, suitable for display applications.

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