White light-emitting diode based on Multi-core/shell CdSe/ZnS quantum dots

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Received December 10, 2010; accepted January 13, 2011; posted online June 29, 2011

Core/shell CdSe/ZnS quantum dots (QDs) are synthesized by thermal deposition using cadmium oxide and selenium as precursors for a hot lauric acid and hexadecylamine trioctylphosphine oxide hybrid. The CdSe/ZnS QDs show high photoluminescence efficiency, with a quantum yield greater than 48% and size-tunable emission wavelengths ranging from 500 to 620 nm. A diode that emits white light with color coordinates of (0.311, 0.321) and luminous efficiency of 46.7 lm/W at 20 mA, as standardized by the Commission Internationale de L'Eclairage or International Commission on Illumination, is fabricated by combining a blue indium-gallium nitride (InGaN) chip with multi-CdSe/ZnS QDs.

OCIS codes: 230.3670, 230.5590.
doi: 10.3788/COL201109.S10703.

White light-emitting diodes (WLEDs) have the potential to replace traditional incandescent and fluorescent lamps for their special characteristics, namely, long lifetimes, savings of energy, and environmental protection[1−3]. WLED based on a blue LED plus yellow phosphor (YAG) is widely used and commercially available. However, this kind of WLED has several disadvantages of blue/yellow color separation and poor color rendering index (CRI) property caused by lack of red component in the spectrum. Recently, quantum dots (QDs) of II-VI semiconductor have drawn significant attention over the past decade[4−8]. Semiconductor QDs, which have a broad absorption band, can be effectively excited by ultraviolet (UV) or visible light basically. In particular, CdSe QDs have been regarded as promising materials for white LEDs due to their size-dependent emission tunability and high quantum yield. The CdSe cores can be chemically synthesized with a surrounding shell of a wider band-gap semiconductor that passivates the surface states of the nanocrystal, with a consequent increase in the QD photoluminescence quantum efficiency. In this letter, QD LEDs are fabricated by using a monolayer of colloidal CdSe/ZnS nanocrystals as the light-emitting layer.

The CdSe/ZnS QDs were synthesized by the following steps. The Cd-precursor was prepared by dissolving 5 mmol of cadmium acetate in a mixture of 25 mmol of lauric acid and 8 mmol of hexadecylamine at 300 °C under argon flow. The Se-precursor was prepared by dissolving 5 mmol of Se-powder in 6.5 mmol of trioctylphosphine. After the Se-precursor was injected into the hot Cd-precursor, CdSe nuclei were formed. Next, the solution of CdSe was cooled to approximately 60 °C. Reduction of temperature stopped conglobation but allowed the nuclei to continue growing. The size of the CdSe nanocrystal was controlled by the growth time. The products were washed using hot methanol and collected by a size-selective method. For the *in situ* ZnS overcoating process, zinc acetate and sodium sulfide ($9H_2O$) were injected directly into the CdSe nanocrystal solution alternately, maintaining the mixture's backflow rate at 100 ml/min at a temperature close to 40 °C. CdSe/ZnS nanocrystals were then obtained. By appropriately collocating multi-different kind size of QDs on the indium-gallium nitride (InGaN) chip, a WLED, containing a blue InGaN chip, along with green-, yellow-, orange-, and red-emitting QDs, was fabricated.

Figure 1 shows the transmission electron micrograph (TEM) of a typical sample containing CdSe/ZnS QDs. The average size of the CdSe/ZnS QD sample is 5.5 nm, and the QD has a spherical shape.

To increase the stability of the CdSe QDs, shells such as CdS, ZnS or shell/shell CdS/ZnS were used. Figure 2 shows the absorption spectra of the CdSe QDs before and after coating with different shells. The CdSe QDs can absorb light efficiently from the near-ultraviolet to the blue (400−520 nm) regions of the spectrum. For the QDs of CdSe, CdSe/CdS, and CdSe/ZnS, the absorption peaks are found at 450, 445, and 444 nm, respectively. It can be seen that the excitation wavelength of the CdSe/CdS is close to the emission wavelength (460 nm) of the InGaN LED chip. However, considering the environmental protection, we used the ZnS as the shell of the CdSe QDs, though it's excitation intensity is slightly lower than that of the CdSe/CdS. Figure 3 shows the PL spectra of the CdSe/ZnS QDs.

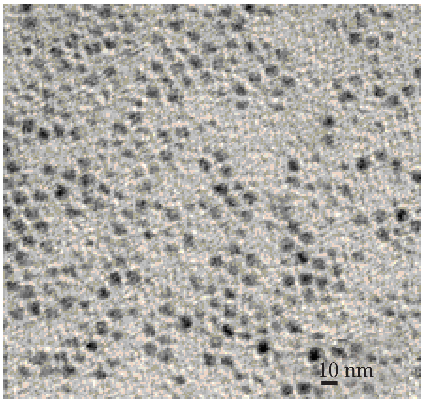

Fig. 1. TEM image of CdSe/ZnS QDs.

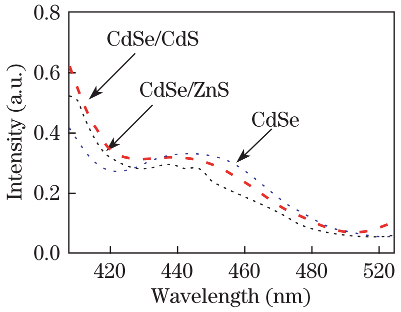

Fig. 2. Excitation spectra of CdSe QDs. before and after coating with different shells.

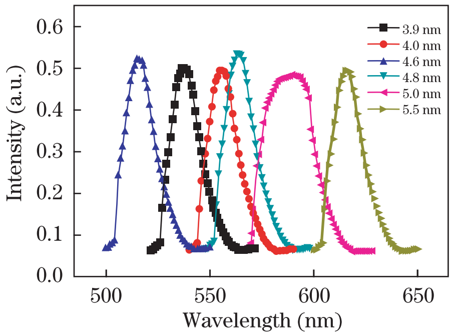

Fig. 3. PL spectra of CdSe/ZnS QDs of various sizes.

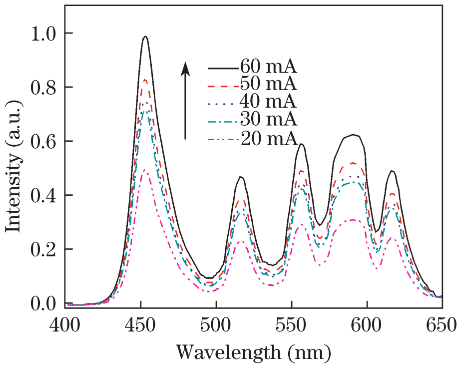

Fig. 4. Electroluminescence spectra of a combination of green (λ_{PL} = 520 nm), yellow (λ_{PL} = 558 nm), orange (λ_{PL} = 590 nm), and red (λ_{PL} = 620 nm) QDs with blue LED (λ_{EL} = 450 nm) at various currents at room temperature.

The peak energies of CdSe/ZnS QDs exceed those of the bulk CdSe and depend on the particle size. In our experiments, a series of core/shell CdSe/ZnS QDs of different sizes showed emission wavelengths ranged from 500 to 620 nm. In addition, the quantum yield was found to be ~48%.

Hybridizing a combination of green, yellow, orange, and red CdSe/ZnS QDs (λ_{PL} = 520, 558, 590, and 620 nm, respectively) on 450 nm blue InGaN LED, we obtain the electroluminescence spectra presented in Fig. 4. In this design, we carefully choose the combination of green, yellow, orange, and red QDs with the right hybridization parameters to satisfy the white light condition and place these QDs films one after the other in the order of longer to shorter PL wavelength to prevent the re-absorption of emitted photons from each QDs layer going through the subsequent QDs layers. It can be seen that the green, yellow, orange, and red QDs are stable with the increasing of the forward bias from 20 to 60 mA. And this WLED showed a luminous efficiency of 46.7 lm/W under the forward bias of 20 mA.

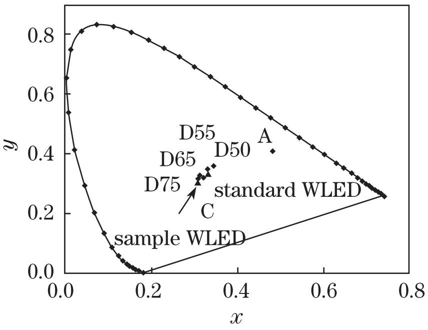

Fig. 5. Color coordinates of QDs WLED and standard illuminants A, C, D50, D55, D65, and D75 in the CIE 1931 chromaticity diagram.

Figure 5 shows the color coordinates of InGaN/QDs WLED, measured under a forward bias of 20 mA. Compared with the six standard illuminants A, C, D50, D55, D65, and D75, the Commission Internationale de L'Eclairage (CIE) color coordinates of the light emitted by the InGaN-based QD-containing WLEDs were (0.311, 0.321) and the CRI was 89, which is larger than the CRI of YAG:Ce WLEDs. And this WLED showed a luminous efficiency of 46.7 lm/W under the forward bias of 20 mA.

In conclusion, CdSe/ZnS QDs, with a quantum yield of approximately 48% and size-tunable emission wavelengths ranging from 500 to 620 nm, are fabricated within a novel WLED. The WLED (a blue InGaN chip, with green-, yellow-, orange-, and red-emitting CdSe/ZnS QDs) yields emits white light with CIE coordinates of (0.311, 0.321) and CRI of 89.

This work was supported by the Zhejiang Provincial Natural Science Foundation of China (No. Y1100792) and the Science and Technology Department of Zhejiang Province (No. 2011C31G2080032).

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