InGaN–CdSe–ZnSe Quantum Dots White LEDs

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***Abstract*—White light-emitting diodes (WLEDs) were fabricated by combining blue InGaN chips with luminescent colloidal core-shell CdSe–ZnSe quantum dots (QDs). The core-shell CdSe–ZnSe QDs synthesized by thermal deposition approach exhibited high photoluminescence efficiency with a quantum yield more than $\sim$40%, and size-tunable emission wavelengths from 510 to 620 nm. Three-band red–green–blue WLED was successfully assembled by blue InGaN chips and green-emitting and red-emitting CdSe–ZnSe QDs. Based on QDs with flexibly selected color, the WLEDs exhibited white light with a CIE-1931 coordinate of (0.33, 0.33) and color rendering index R_a of 91.**

***Index Terms*—Light-emitting diodes (LEDs), phosphors, quantum dots (QDs).**

WHITE light-emitting diodes (WLEDs), also known as solid-state devices, have been intensively investigated recently. The major advantages of the WLEDs are low-power consumption, long lifetime, and rugged construction. Therefore, they have great potential for lighting, signal, and display applications. Three types of WLEDs have been reported—multichips WLEDs, ZnSe-based WLEDs, and single-chip InGaN WLEDs. Multichips WLEDs, constructed by a red-, a green-, and a blue-emitting chip, show three emission bands and possess a good color rendering. However, they are expensive and need a relatively complex external detector and feedback system because each chip degrades at a different rate [1]. ZnSe-based WLEDs emit white light by blending blue light from a ZnSe active layer with yellow light from a ZnSe substrate [2]. They have a lower emission efficiency and a shorter lifetime than InGaN WLEDs, so they are less considered in the present case.

Single-chip WLEDs will be used as general lighting in the future due to low cost and high luminescence efficiency. This WLED comprises only a blue InGaN chip and a yellow-emitting yttrium aluminum garnet (YAG) phosphor, so white light is produced by mixing yellow emission from YAG excited by some of the InGaN blue emission, with the remaining InGaN blue light.

Typical YAG doped with cerium is most widely used in single-chip WLEDs, however, such source lack red component giving lower color rendering than that of multichips WLEDs [3]. Consequently, some novel phosphors, for example, organic phosphors with flexibly selected emission color and high efficiency have been reported [4], [5]. Nevertheless, the instability and long-term reliability of organic materials are doubtful.

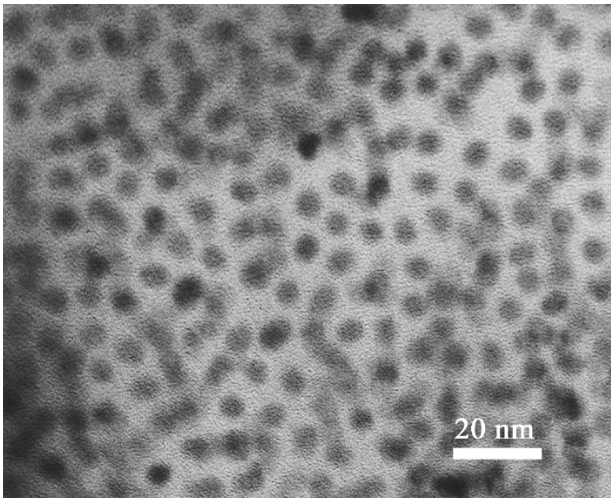

Fig. 1. TEM image of the core-shell CdSe–ZnSe QDs.

The high luminescence efficiency and size-tunable bandgap of colloidal CdSe quantum dots (QDs) have attracted considerable interest from scientists in the past decade. Based on the quantum confinement effect (QCE), the band structure of QDs can be altered by varying the diameter so the emission and absorption characteristics can be determined [6]. Passivated with a thin overcoat of high-bandgap ZnS (or ZnSe), core-shell CdSe–ZnS QDs exhibit high-emission efficiency (quantum yield >50%) in the visible range [7]. The emission peak of CdSe ($E_{g,\mathrm{bulk}} \sim 1.72$ eV, $\lambda_{\mathrm{em,bulk}} \sim 720$ nm) can be shifted from red to blue ($\lambda_{\mathrm{em,QDs}}$: $640 \sim 480$ nm) by reducing particle size. In general, semiconductor QDs with a broad absorption band can be effectively excited by ultraviolet (UV) or visible light. Hence, colloidal QDs seem to be suitable as a phosphor in WLEDs. The author recently demonstrated novel UV WLEDs, using white-emitting organic-capped ZnSe QDs as phosphors [8]. This letter reports WLEDs based on blue InGaN chips and core-shell CdSe–ZnSe QDs. A two-band WLED (blue InGaN chip and yellow-emitting CdSe–ZnSe QDs) and a three-band red–green–blue (RGB) WLED (a blue InGaN chip, green- and red-emitting CdSe–ZnSe QDs) were assembled.

CdSe QDs were synthesized by thermal deposition using cadmium oxide and selenium as precursors in a hot stearic acid–trioctylphosphine oxide–hexadecylamine hybrid [9]. ZnSe shells were grown by *in situ* overcoating [10]. The QDs naturally adsorbed the trioctylphosphine oxide (TOPO) molecules, making them soluble in organic matrixes or solvents such as toluene.

The TEM image in Fig. 1 indicates that the spherical CdSe–ZnSe QDs are smaller than 5 nm. Fig. 2 shows the photoluminescence (PL) spectra of CdSe QDs with various sizes. The peak energies of CdSe QDs exceed E_g of the bulk CdSe

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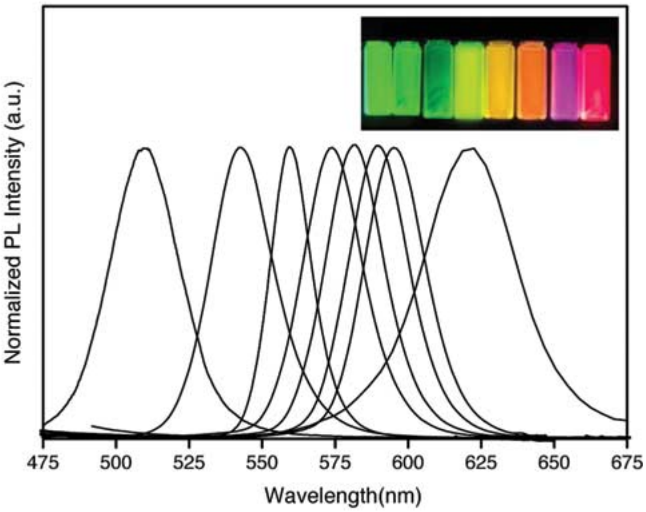

Fig. 2. PL spectra of the CdSe–ZnSe QDs with various sizes (from left to right, the particle sizes are 2.2, 2.7, 3.2, 3.4, 3.7, 3.8, 4.0, and 4.8 nm).

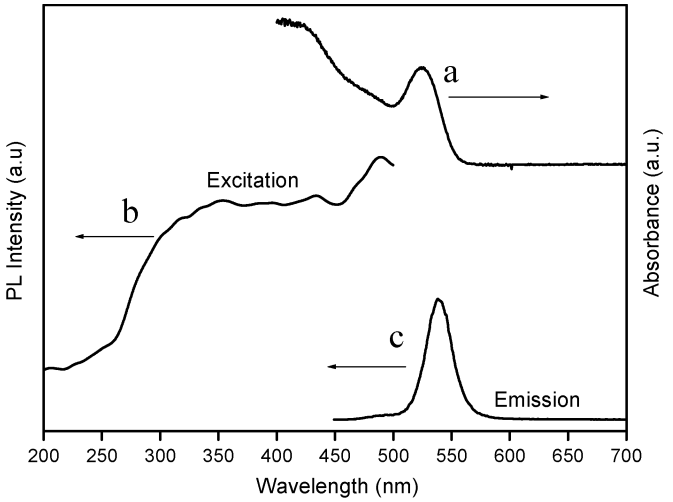

Fig. 3. (a) Optical absorption spectrum, (b) PL excitation spectrum (emission: 540 nm), and (c) PL spectrum (excitation: 432 nm). The CdSe–ZnSe QDs were dispersed in hexane.

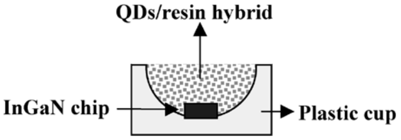

Fig. 4. SMD InGaN/QDs WLED structure. The device consists of a InGaN LED (chip size: 0.33×0.33 mm^2 and the cup size: L3.5 × W2.8 × H1.8 mm^3) and CdSe QDs/silicone resin hybrid.

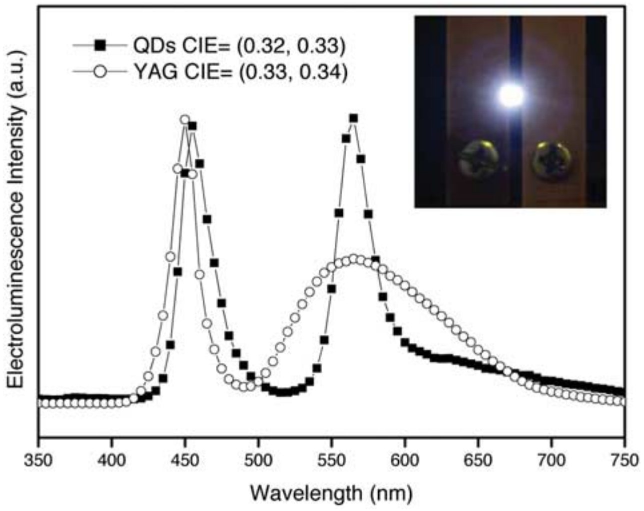

Fig. 5. Emission spectra of hybrid InGaN–CdSe–ZnSe QDs and conventional InGaN/YAG WLEDs. The inset is the WLED driven at 3.0 V/20 mA.

and depend on the particle size. This size-dependence has been attributed to the QCE. The quantum yields of QDs in toluene estimated relative to Rhodamine 6G in methanol of the same optical absorbance (~0.01) under 525-nm excitation were 59% (2.2 nm), 55% (2.7 nm), 53% (3.4 nm), 52% (3.7 nm), 50% (3.8 nm), 48% (4.0 nm), and 40% (4.8 nm).

The optical absorption spectrum of the CdSe–ZnSe QDs is shown in Fig. 3(a). The first exciton peak clearly appears in the spectrum, indicating that the size distribution of the QDs is quite narrow. Conventional phosphors such as YAG are ineffectively if the excitation wavelength is not around 460 nm. The excitation band of CdSe–ZnSe is so broad that they can absorb light efficiently in the UV or blue range, as shown in Fig. 3(b). In making a WLED, a surface mounted device (SMD) blue InGaN LED (Light-House Inc., $\lambda_{\rm em} = 455$ nm) was utilized as an excitation source, and yellow-emitting CdSe–ZnSe QDs ($\lambda_{\rm em} = 560$ nm, $d = 3.3$ nm) were used as a phosphor. The QDs were coated onto the chip following mixing with silicone resin. Fig. 4 shows the structure of the WLED. The TOPO-adsorbed CdSe QDs are soluble in toluene so they are well dispersed in the silicone matrix. The high dispersivity of phosphors in the resin not only increases the efficiency of the WLEDs but also improves the uniformity of their color.

The overlap of the absorption band with the PL band of QDs shown in Fig. 3, causes the larger QDs to absorb light emitted by the smaller ones in the resin, so reducing the color rendering and the efficiency of the WLED. Accordingly, the QDs/resin hybrid was placed on a flat surface for about 1 h to cause the heavier particles to drop downward. Another approach for solving this problem is to coat the smaller QDs hybrid onto the chip following the larger QDs hybrid.

Fig. 5 shows the luminescence spectra and Commission Internationale de l'Eclairage (CIE) chromaticity coordinates of conventional InGaN/YAG and InGaN/QDs WLEDs. The CIE-1931 coordinate of the InGaN/QDs WLED is (0.32, 0.33), which is close to that of the InGaN/YAG WLED, indicating the luminescent QDs could be used as a phosphor of WLEDs.

Nevertheless, the QDs have a narrow spectral band so the color rendering of this binary complementary color WLED was low (color rendering index $R_a = 50$). Since the emission color of the QDs can be tuned by varying the size, a three-band RGB WLED, containing a blue SMD InGaN chip, green-emitting QDs, and red-emitting QDs was fabricated. Fig. 6 shows that this WLED exhibited white light and had an efficiency of 7.2 lm/W at 20 mA with a CIE-1931 coordinate of (0.33, 0.33). The efficiency is still low in comparison with that of commercial WLEDs (15–30 lm/W). Since the device was prepared in a simple process it could be enhanced by optimizing conditions

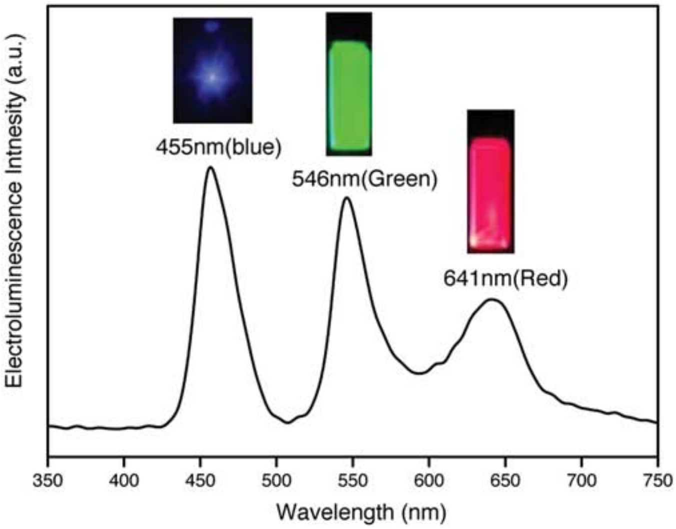

Fig. 6. Three-band RGB WLED combined a blue InGaN chip, green-emitting CdSe–ZnSe QDs, and red-emitting CdSe–ZnSe QDs.

such as dispersion and coating of the QDs in further study. The R_a of this device was 91, which is higher than that of conventional YAG-based WLEDs. Its spectrum covered the visible range, except for a little part around 510 nm. However, it could be improved by appropriately collocating the QDs.

Although using luminescent QDs rather than YAG in single-ship WLEDs is promising, however, some problems remain to be solved. One is the decay in the luminescence of QDs during the curing stage of the silicone resin. This is attributed to the production of water molecules from silicone after the curing stage, which poisons the QDs. Another is the environment-unfriendliness of Cd compounds. A possible solution is to isolate the QDs by polymer encapsulation, or recycling of WLEDs (Their plastic materials in which they are packaged also affect the environment.) A detailed discussion of the problems and possible solutions will be reported elsewhere.

In summary, novel WLEDs, composed of CdSe–ZnSe QDs and InGaN chips, are reported. The binary complementary color WLED (a blue InGaN chip and yellow-emitting CdSe–ZnSe QDs) provides white light with a CIE-1931 coordinate of (0.32, 0.33) and color rendering index R_a of 50. The three-band RGB WLED (a blue InGaN chip, with green-emitting, and red-emitting CdSe–ZnSe QDs) gives white light with a CIE-1931 coordinate of (0.33, 0.33) and R_a of 91.

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