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Invited

The Latest Development in High-Efficiency Heavy-Metal-Free QDEL

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ABSTRACT

Electroluminescent QDEL devices with heavy metal free InP and ZnTeSe quantum dots are one of the most promising future display technologies. Here we report improved efficiency of 19.6%, 17.6%, and 12.7% for red, green, and blue QDEL devices, respectively. The blue QDEL devices exhibit true blue emission with peak wavelength of 453 nm.

1 INTRODUCTION

Electroluminescent devices using semiconductor quantum dots (QD) as emitter material are widely considered as the next generation display technology that combines the benefits of OLED and QDs: wide color gamut, facile color tuning, wide viewing angle, high contrast ratio, and flexible device architecture. The development of heavy metal free QDs is crucial for commercialization of such QDEL devices, because the toxicity and regulation of cadmium and lead compounds will prevent market uptake.

Over the last year, progress in QDEL devices with heavy metal free QDs has accelerated mostly due to the development of better QD structures and synthesis protocols. Green InP QDs were improved by increasing the ZnS shell thickness in an InP/GaP/ZnS QD architecture. A maximum EQE of 6.3% was achieved for particles with an average diameter of 7.2 nm [1]. For red InP QDs, two major milestones in improving QD composition were reported. Controlling the stoichiometry with respect to the indium to phosphorus ratio and avoiding indium incorporation in the ZnSe/ZnS shell resulted in PL QY of 95% and a maximum EQE of 12.2% [2]. Etching of oxide species from the InP core surface as well as improved deposition of a thick and uniform ZnSe/ZnS shell led to a PL QY of 100% and a maximum EQE of 21.4% [3]. For blue QDEL device free of heavy metals a ZnTeSe QD composition was reported with a peak wavelength of 441 nm, FWHM of 32 nm, PL QY of 70%, and maximum EQE of 4.2% [4].

2 RESULTS

2.1 RGB Device Results

Current EL performance data with Nanosys materials is given in Table 1. Significant progress has been made on blue QDs. Previously, we reported 9.0% maximum EQE for blue QDEL device, which were based on ZnSe QDs emitting at 433 nm [5]. We also reported development of a ZnTeSe QD composition as a true-blue emitter with a peak wavelength around 450 nm. In the past year, we significantly improved the synthesis and device structure for this new QD composition. Our best ZnTeSe QDEL device achieved a maximum EQE of 12.7% at a peak wavelength of 453 nm and FWHM of 29 nm. The EL spectrum corresponds to CIE color coordinates (0.147, 0.048), which is very close to the BT.2020 blue primary (0.131, 0.046), as shown in Figure 1. Significant contributions to the increased EQE are better synthetic control of the QDs and optimized device structures towards charge balance.

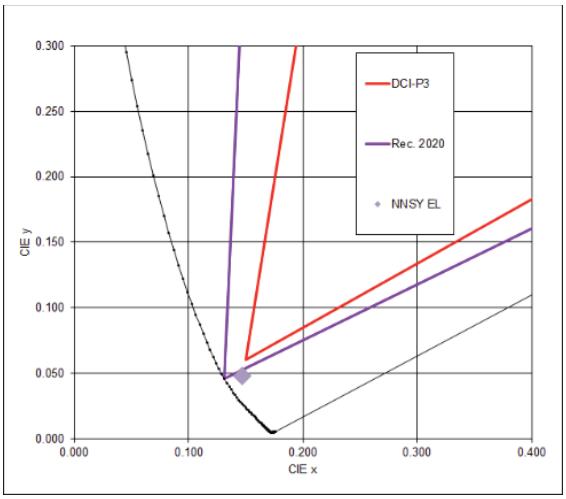

Figure 1. CIE color coordinates of Nanosys true-blue QDEL device.

Table 1. Electroluminescent properties of QDEL devices with heavy metal free QDs as emitter.

	Red InP	Green InP	Blue ZnTeSe
EQE (%)	19.6	17.6	12.7
PWL (nm)	632	532	453
FWHM(nm)	40	39	29

2.2 True-Blue QD Synthesis

Blue QDs are synthesized in a core/shell architecture based on zinc chalcogenide materials. Zinc selenide has a bulk band gap of 2.7 eV, and ZnSe quantum dots often emit at wavelengths shorter than 440 nm. By incorporating a small amount of tellurium in the zinc selenide core, the emission wavelength can be shifted to the desired range for true blue emission. Table 2 shows examples of different QDs covering the blue emission range and their optical properties. The corresponding PL spectra are shown in Figure 2. High QY is ensured by a high-quality shell consisting of a ZnSe buffer and ZnS outer shell. The quality of that shell is evident from the TEM image in Figure 3 which shows uniform particles with spherical morphology.

Table 2. Optical properties of different blue QD batches covering the true-blue wavelength range.

#	PWL / nm	FWHM/ nm	QY / %
1	445	24	79
2	449	28	80
3	454	28	87
4	461	30	74

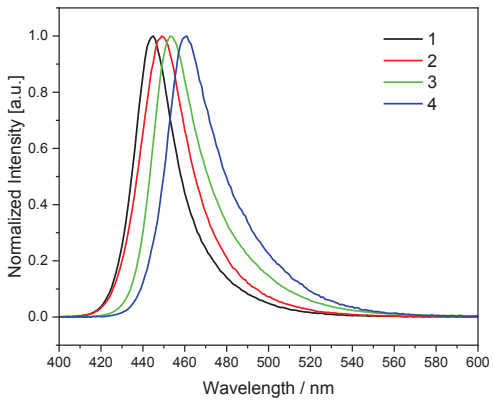

Figure2. Photoluminescence spectra of different blue QDs with different peak emission wavelengths.

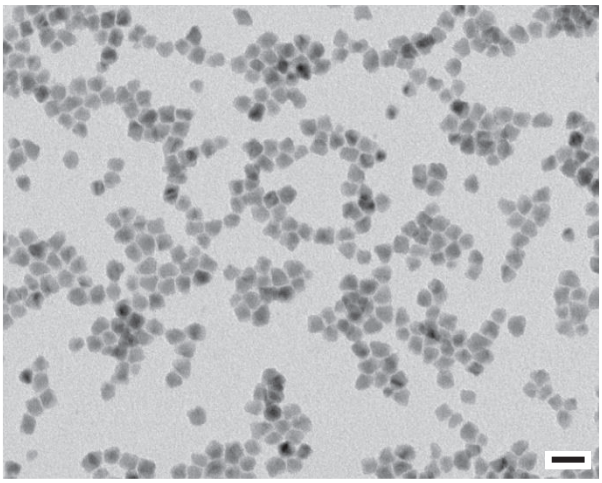

Figure 3. TEM image of true-blue QDs (scale bar 20 nm).

2.3 True-Blue QDEL Development

Device Fabrication:

The blue QDEL devices structure is shown in Figure 4. QDEL devices were prepared by a combination of spin coating and thermal evaporation processes. Firstly, the hole injection material was spin coated onto a UV-ozone treated indium tin oxide (ITO) substrate and baked for 15 minutes at 200°C. The devices were transferred to an inert atmosphere and the hole transport material was deposited by spin coating. A solution of QD was deposited by spin coating, followed by spin coating of the electron transport material. An Al cathode was then deposited by thermal evaporation followed by encapsulation of the device using a cap-glass, getter, and epoxy resin.

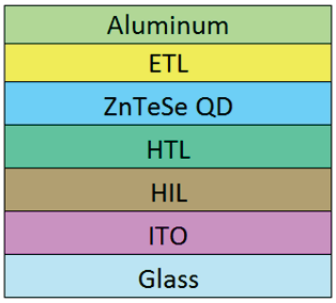

Figure 4. Device structure of blue QDEL device.

Device Performance:

One of the major advantages of QDEL devices is the low drive voltage when compared with OLEDs. The key reason for this special property is that the EML layer in QD has only emitters and no host materials. In this case, holes and electrons are not forced to be injected into the HOMO and LUMO levels of host materials which have larger bandgap than the emitters. A comparison of drive voltage at 500 cd/m2 for QDEL devices and phosphorescent OLED is shown in Table 3. The data for OLED are taken from literature and data for QDEL devices come from measurement of Nanosys QDEL devices. Table 3 clearly demonstrates that the QDEL devices have significantly lower drive voltages

comparing to OLEDs at the same luminance.

Table 3. Drive voltages of phosphorescent OLEDs and QDEL devices at 500 cd/m^2

	OLED	QDEL
Red	2.9 [6]	2.1
Green	3.9 [7]	2.5
Blue	5.5 [8]	3.7

The current density and luminance as a function of drive voltage of the blue QDEL device is shown in Figure 5. The device has a sub-bandgap turn on voltage of 2.5 V, and reaches 7,000 cd/m2 at a low voltage of 7 V. The drive voltage for 500 cd/m2 is 3.7 V, which is significantly lower than that of a phosphorescent OLED [8].

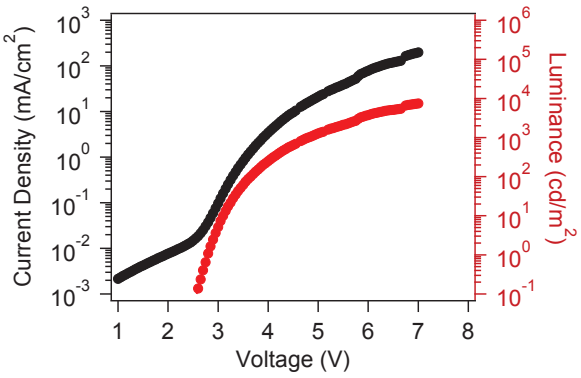

Figure 5. Current density (left axis; black curve) and Luminance (right axis; red curve) as a function of voltage of the blue QDEL device.

The device EQE and current efficiency as a function of luminance level is shown in Figure 6. The device has >10% EQE for luminance levels up to 6,000 cd/m2, and a peak EQE of 12.7%. To our best knowledge, this is the highest EQE reported for a heavy metal free QDEL device with an emission peak wavelength at about 450nm. This efficiency performance has already surpassed that of commercial blue fluorescent OLEDs.

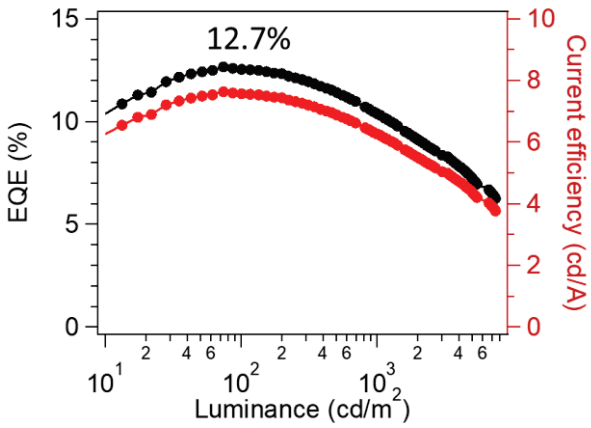

Figure 6. EQE (left axis; black curve) and Current efficiency (right axis; red curve) as a function of Luminance of the blue QDEL device.

Figure 7 shows the picture of Nanosys QDEL demo with seven QDEL devices having a rainbow of colors. All these devices were made with Cd-free QDs.

Figure 7. Nanosys QDEL demo with seven QDEL devices having a rainbow of colors.

3. Conclusion

New developments in structure and synthesis of heavy metal free QDs have resulted in significant improvement of the efficiency of electroluminescent QDEL devices with such QDs. Efficiencies of red and green InP QDEL devices are 19.6% and 17.6% and thus close to the theoretical maximum of 20%. For blue QDEL device, we moved to a new QD composition based on ZnTeSe which emits at a true-blue wavelength over 450 nm with a narrow linewidth of 29 nm. We significantly improved the efficiency of QDEL device using this new QD composition to 12.7% EQE, which is higher than fluorescent OLED efficiency.

4. Impact

QDEL devices will be the next generation display technology because they combine benefits of QD and OLED. Our report of high efficiency for all three colors using heavy metal free QDs, in particular a true-blue emitting QD, is a major milestone towards the commercialization of QDEL devices.

5. References

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