High Color Gamut Blue Quantum Dot Light Emitting Diodes: Material&Device Optimizations

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Keywords: QLED, High Color Gamut, Blue Quantum Dots, High Performance

ABSTRACT

A high performing blue quantum dot light emitting diode (QLED) device has been developed synergizing high color gamut (y_{CIE}<0.06) colloidal blue quantum dots and device optimization with balanced charge carriers. To realize high color gamut blue QLEDs, a novel blue quantum dot structure has been designed with enlarged particle dimension. Such improvement could raise the valance band for 0.2 eV, which significantly lowered the hole injection barrier. With further tuning of electron injection, the optimized device could reach a maximum EQE of 15.2% with life time of T_{95}@1000nits up to 68 hours.

1. Introduction

As one of the most promising candidates towards next-generation display technology, QLED has attracted lots of attention both in academia and industry, owing to many distinctive advantages, such as high color purity/gamut, economic production method via solution processing, and scalable manufacturing by ink-jet printing, etc[1]. In the past three decades, significant improvement of QLED has been reported, especially the optimization of the colloidal quantum dots core-shell structure design[2], charge transport layer development[3,4], as well as the in depth research of the degradation mechanism[5]. Peng group has reported a red QLED device with EQE exceeding 20% and T_{50}@100nits above 100,000 hours with the incorporation of PMMA interfacial layer for enhancement in charge carrier balance[6]. In 2018, Qian et al. has discovered the hole barrier of ZnSe and TFB to be much lower than that of ZnS and TFB. Utilizing a shell structure of ZnSe could significantly balance charge carrier. QLED devices with such improved quantum dots can achieve a life time of T_{50}@100nits above 2,000,000 hours[7]. Further improvement has been reported by Shen Group in 2019 utilizing a synthesis strategy with Se element incorporated throughout the entire quantum dot core-shell structure in order to raise the hole injection efficiency. Such green QLED device was able to reach EQE over 21% with T_{50}@100nits over 1,600,000h[8].

The up-to-date reported red and green QLED performance is comparable to that of organic light emitting diodes (OLEDs). However, for mass-production of QLED displays, blue QLED remains the bottle neck issue. Although numerous work has been done to improve the efficiency and life performance via materials and device optimization, the lack of color gamut consideration further impedes the commercialization of QLED[9]. Through our research, we found that the low device performance of blue QLED can be attributed to two main reasons. First of all, blue quantum dots have much deep lying valance band resulting in a large hole barrier. At the same time, the high electron mobility of ZnO based electron transport layer (ETL) is one to two magnitudes higher than that of hole transport layer (HTL). Such huge offset in electron and hole injection/transport lead to the severely unbalanced charge carriers. Moreover, the excess electron injection causes quantum dots to be negatively charge and can result in expedited degradation of hole transport materials. Secondly, as the core of the radiative recombination zone, quantum dots synthesized with high quality is of great importance. The blue dots usually have smaller diameters, as compared with red and green dots. The huge surface to volume ratio usually leaves higher surface trap states that directly causes exciton trenching. The commonly reported work of blue QLED optimization includes device structure tuning [10], ETL materials modifications [11], ligand exchange[12,13], etc. These works were successful in bringing up the current efficiency. However, the life time progress has rarely been reported.

In this work, we were able to integrate quantum dots development via core-shell material structure design, as well as ETL optimization for enhancement in charge carrier balance. The fine-tuning of blue dots band alignment for a lowered hole injection barrier could effectively facilitate hole injection. At the same time, the electron injection and transport is lowered for better carrier balance. Furthermore, the lower surface to volume ratio with larger colloidal quantum dot diameter significantly reduces surface trap sites, which eventually decreases non-radiative recombination loss. We were able to achieve a blue QLED device with wide color gamut and a life time performance of T_{95}@1000nits over 68 h.

2. Method and Experiment

The synthesis of CdZnSe/ZnSe/ZnS core/shell nanocrystal was followed by a synthesis procedure of mxing 0.2 mmol CdO, 5 mmol $Zn(Ac)_2$, 5 mL of OA and 15 mL of ODE in a 100 mL round flask. Such mixture was heated to 150 ºC and degassed for 20mins with further heating to 300 ºC to form clear solution of $Cd(OA)_2$ and $Zn(OA)_2$. Then 2 mL of Se solution and 0.5 mL DPP were quickly injected into the reaction flask. The samples were extracted to monitor their PL spectra. The growth of the shell was initiated right after the core formation for 25 mins. The ZnSe shell growth determines the nanoparticle diameter via growth temperature tuning between 300-330 ºC. The peripheral shell of ZnS was formed by dropwise addition of precursor with a syringe pump with further annealing at 310 ºC for 30 mins. Then the solution was purified using acetone followed by additional centrifuge purifications. The purified QDs were re-dispensed in hexane solvent for processing and characterizations.

3. Results and Discussion

In order to suppress quenching caused by surface traps, we have optimized our blue light quantum dots to increase the dot diameter with reduced surface to volume ratio. Such large

quantum dot (B-QD) has an average core diameter of 7.38 nm, whereas the standard dot (S-QD) has a core diameter of 4.79 nm. In order to achieve further surface passivation, a shell layer with ZnSe/ZnS was grown on both B-QD and S-QD. The size distribution and corresponding TEM images of B-QD and S-QD were illustrated in Fig.(1).

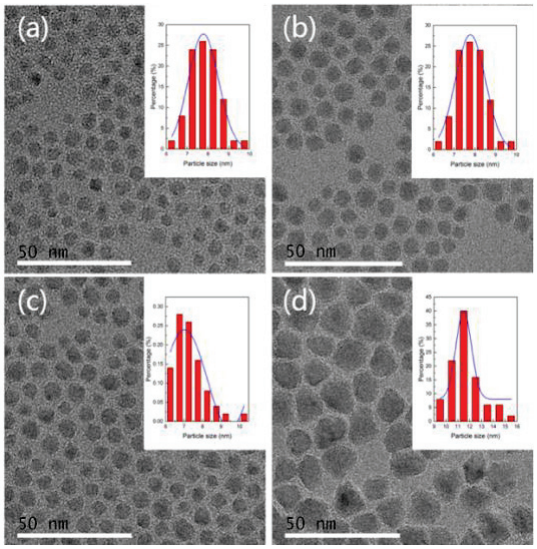


Fig. (1). Size distributions and TEM images of S-QD core (a), core-shell (b), B-QD core (c) and core-shell (d).

Knowing that the Auger-recombination rate is directly related to the surface trapping sites. As a result, an effective strategy is to increase the particle sizes in order to reduce the surface to volume ratio. In our work, we were able to design and synthesize quantum dots that effectively lower trap sites and alleviate Auger-recombination rates. As shown in Fig.(2), the photoluminescence quantum yield (PLQY) of S-QD was measured to be 75%, whereas the that of B-QD was increased to 85%.

The energy band edge has been measured by UPS and derived by the equation of VBM=excitation energy-(E_{cutoff}-E_{oneset}). The calculated VBM of S-QD is about 0.2 eV deeper than that of B-QD. We also evaluated how the shallower valance band edge of B-QD could facilitate the hole injection in blue QLED devices by evaluation the electrical behaviors of electron and hole only devices. The hole only device (HOD) was prepared using a structure of ITO/PEDOT:PSS/TFB/QD/MoO3/Ag, and the electron only device(EOD) was based on the structure of ITO/ZnMgO/QD/ZnMgO/Ag. It was shown in Fig.(4) that the current density of single charge carrier devices of B-QD were significantly higher than that of S-QD, especially for the HODs. Such behavior was also seen in literature indicating a better hole injection capability of B-QD than S-QD[14].

The electroluminescent performance of S-QD and B-QD was compared in bottom emission devices shown in Fig.5(b-c) with band alignment shown in Fig.5(a). The external quantum efficiency(EQE) of B-QD was increased to 15.2%, whereas that of S-QD remains below 10%. Such improvement could be attributed to the rise of charge carrier injection.

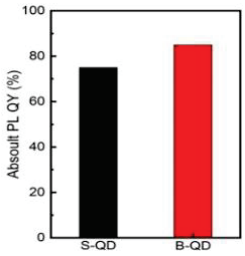


Fig.(2) PLQY of quantum dots in octane solution.

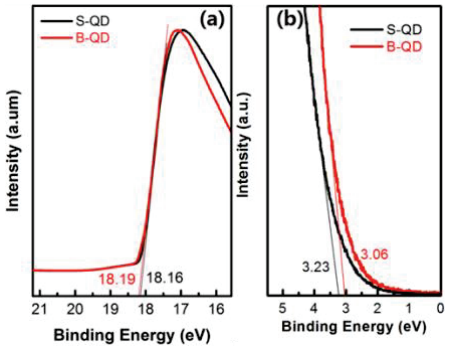


Fig.(3) UPS spectra of (a) the high-binding energy secondary electron cut-off regions and (b) the valance band edge regions of S-QD and B-QD.

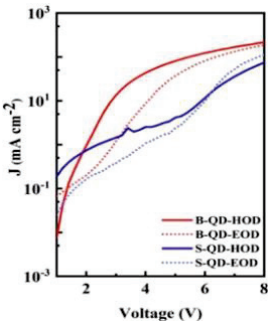
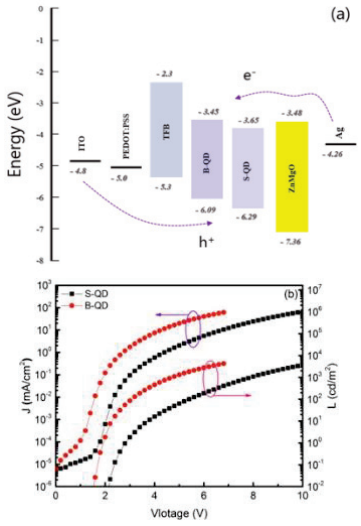


Fig. (4) Current density-voltage (J-V) characteristics of electron-only(solid line)and hole only devices (dash-line) for S-QD and B-QD.



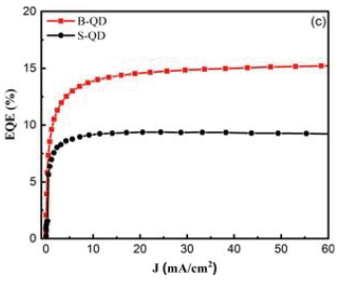


Fig (5) QLED device based on S-QD and B-QD: (a) energy band diagram, (b) J-V-L curves, and (c) EQE-J curves.

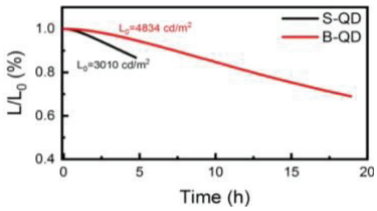


Fig.(6) The life time test result of blue QLED devices based on S-QD and B-QD

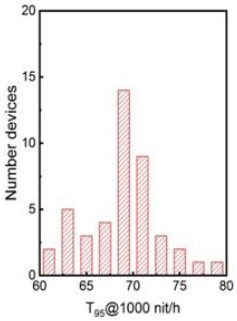


Fig.(7) Life time distribution of bottom emission blue QLED devices based on B-QD.

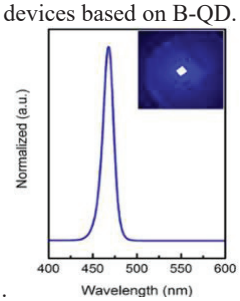


Fig.(8) EL spectrum and image of a QLED device

The life time performance was evaluated and derived by L_o^n x T95=constant, where L_o and n were initial luminance and acceleration constant, respectively. Here the acceleration constant was calibrated to be 1.7. As demonstrated in Fig (6), the T95@1000nits of B-QD is about 68 hours, whereas that of S-QD at 14 hours. The histogram of the bottom emission devices were shown in Fig.(7) with a sample size of 50. To our knowledge, it is highest reported blue QLED lifetime performance fulfilling the high color gamut requirement with yCIE=0.06.

The electroluminescent spectrum was shown in Fig.(8) with an EL peak at 468 nm and FWHM at 14 nm. The corresponding color coordinate was measured to be (0.13, 0.06), which was wider than the standard blue light color coordinate at (0.11, 0.08). This exhibits the novel design of B-QD presents wide color gamut with high performance towards display applications.

4. Conclusion

In this paper, we have presented a high performance QLED device with wide color gamut by novel design of blue quantum dots. The effective rise of valance band edge could effectively lower the hole injection barrier which result in better balanced charge carriers. We were able to confirm such higher charge injection states via single carrier devices. With further enhancement in electron transport layer and device structure, we were able to achieve a maximum EQE of 15.2% and T_{95}@1000nits at 68 h. This work gives insights for future blue quantum dots optimization.

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