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Realizing High Performance Quantum Dots Light Emitting Diodes (QLEDs) through the Novel Device Structure and Transporting Materials

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ABSTRACT

The lifetime problem of blue QLEDs is the most challenging issue in QLED, and the performance of green QLEDs also need to be improved to meet the requirement of commercialization. In this work, great progress of green/blue QLEDs has been implemented by using top emitting structure and modifying transporting materials.

1 Introduction

Quantum dots light emitting diode（QLED）, has been widely recognized as the next-generation display technology, due to its capacity of reaching 100% Rec. 2020 color gamut, high luminescence efficiency, and low cost of manufacturing[1-3]. Due to its compatibility of all-solution-processing, QLED development has been ranked with high priority by a great number of display companies and research institutes, with lots of efforts already been put on. Over the past 20 years, the efficiency of QLED devices has been rapidly increased. In 1994, the first QLED device only had a EQE around 0.001%[4]. By the year of 2014, the efficiency of red QLED has been pushed to more than 20%[5], very close to the theoretical limit. At current stage, researchers were able to develop QLED devices with efficiency above 20% for all colors, including green and blue[6-7]. However, with the rapid enhancement in devices' efficiencies over the past two decades, QLEDs still face critical lifetime challenges towards commercialization. Based on previous reports, the T95 lifetime of a red QLED @1000nits has well exceeded 2000 hours[8], which has been the only QLED device with lifetime being able to meet mass production requirement. The green QLED devices have relatively less lifetime performance, with a T95 lifetime@1000nits close to 1000 hours[7]. Given the fact that the industry requirement for green QLED, including both efficiency and lifetime, is much higher than the other two colors, the further improvement of green QLED performance also need to be paid attention to. Meanwhile, the blue QLED, especially, has a lifetime far below the requirement of commercialization, which is facing severe degradation issue with a lifetime (T95@1000nits) at only 10 hours[7].

To solve the lifetime issue of green/blue QLED, one of the strategies is to investigate in novel device structure, such as top emitting (TE) structure. This kind of device structure emits light through the top semitransparent electrodes and would not suffer from loss due to blockage of driving circuit as in bottom emission devices. It has several advantages towards the use in display devices, such as high aperture ratios, efficient light outcoupling, as well as the easy control of microcavity phenomena[9], so could be a potential method to enhance the lifetime of QLEDs.

On the other hand, the degradation mechanism of QLED device has to be focused on, and the energy level mismatch in QLED device is believed to be one of the major reasons for the inefficient lifetime. The general QLED device structure is consisted of four functional layers with a pair of electrodes. Currently, QLEDs with best lifetime performance is reported using TFB as hole transporting layer (HTL) and zinc oxide as electron transporting layer (ETL). Since the highest occupied molecular orbitals (HOMOs) of TFB are unable to match the deep-lying valence-band maximum (VBM) of QDs, the hole injection barrier issue exist in all three color QLED devices. But in a blue QLED, more problems emerge besides the hole injection barrier issue. The severe electron injection barrier between ZnO and QDs should also be paid attention to as the emissive layer materials turns from red QDs to blue QDs, which could be the main reason for the inefficient lifetime of blue QLED device[10].

Therefore, to increase the lifetime performance of green/blue QLED, it is of great importance to apply the top emitting structure in QLED device and optimize the energy level of functional layers for a minimal energy level mismatch. Here in this paper, we reported our recent progress on the top emitting structure of green QLED and our effort on minimizing the energy level mismatch between ETL layer and QDs of blue QLED.

2 Method and Experiment

2.1 Materials Synthesis

The quantum dots used in this work were prepared according to the methods previously reported in the related literatures with appropriate modifications[8]. For a typical synthesis of CdSe/Cd1-xZnxSe/ZnSe QDs, 0.4

mmol of CdO, 6 mmol of zinc acetate and 7 ml of oleic acid (OA) were placed in a 50 ml flask and heated to 170 °C in flowing high-purity argon for 30 min. Then 15 ml of 1-octadecene (ODE) was added to the flask and the temperature was elevated to 300 °C. A stock solution containing 0.9 mmol of selenium (Se) dissolved in 2 ml of trioctylphosphine (TOP) was quickly injected into the flask. The reaction temperature was kept for 10 min. Then 0.1 mmol Se dissolved in 1 ml TOP were injected into the flask at the elevated temperature of 300 °C and reacted for 10 min. Finally, the reaction mixture was cooled to room temperature. Then washed and dispersed in octane with a concentration of 30 mg/mL.

ZnO nanoparticles were synthesized by a solution-precipitation process reported in the literature[8]. For a typical synthesis, a solution of zinc acetate in dimethyl sulfoxide (DMSO) (0.5 M) and 30 ml of a solution of tetramethylammonium hydroxide (TMAH) in ethanol (0.55 M) were mixed and stirred for 1 h in ambient conditions, then washed and dispersed in ethanol with a concentration of 30 mg/mL. 5%Mg doped ZnO nanoparticles, denoted as ZMO, were synthesized by the similar method with a mix solution of 5% molar ratio of magnesium acetate and 95% molar ratio of zinc acetate as salt precursor. Additionally, for the PEI treated zinc oxide nanoparticles, denoted as PEI-ZnO, 0.1 weight% PEI were added to the 30 mg/mL ZnO nanoparticles solution to get the PEI-ZnO nanoparticles.

2.2 Device Fabrication

QLED devices were fabricated by consecutively deposited each functional layer on glass substrates pre-coated with an indium-tin oxide anode (ITO, sheet resistance is about 50 Ω). For a typical device structure, A 25 nm thick PEDOT:PSS layer was first deposited onto the cleaned substrates, then annealed at 190 °C in air to remove residual water. A 40 nm thick TFB (American Dye Source) layer was then deposited in a N2 glove-box, followed by a thermal anneal at 200 °C for 30 min. After that, a QD layer and a ZnO nanoparticle layer were sequentially deposited in the glove-box, respectively, then annealed in the same environment at 120 °C to remove the residual solvents. The optimal thicknesses for QD layers and ZnO layers were 20 nm and 40 nm, respectively. After the fabrication of the solution-processed layers, all samples were transferred to a vacuum deposition chamber with chamber pressure less than 10^{-6} torr (P< 10^{-6}torr) for Ag cathode (100 nm thick) deposition, followed by the final encapsulation with a UV-curable epoxy and cover glasses in the N2 glove-box.

2.3 Characterizations

Electroluminescence spectra were obtained using an Ocean Optics USB 2000+ spectrometer with the devices driven at a constant current with a Keithley 2400 source meter. The J-L-V characteristics of the devices were taken under ambient conditions with a Keithley 2400 source meter measuring the sweeping voltages and currents and a Keithley 6485 Picoammeter together with a calibrated silicon detector (Edmund) measuring light intensities. The current efficiency (as photons per electron) was calculated by converting the photo current to emitted photons and the device current to electrons simultaneously. Luminance was calibrated using a photometer (Spectra Scan PR655) with the assumption of Lambertian emission pattern of all devices. The lifetime test was conducted under ambient conditions using a commercialized lifetime test system (Guangzhou New Vison Opto-electronic Technology Co. Ltd.).

3 Results and Discussion

3.1 The Application of Top Emitting Structures in Green QLEDs.

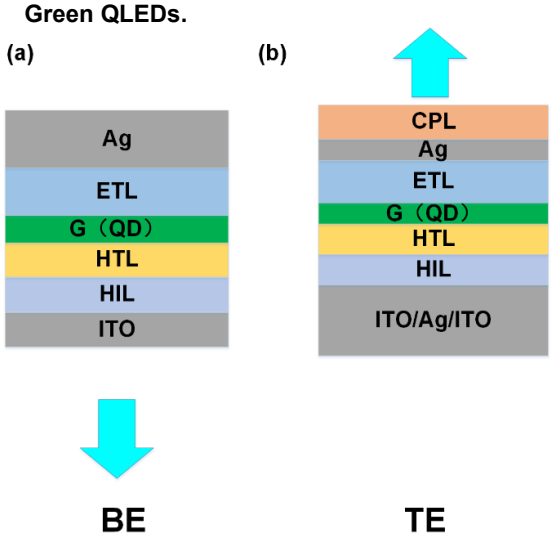

Figure 1. Device structures of green QLEDs. (a) bottom emitting device structures, (b) top emitting device structures.

to increase the lifetime performance of green QLED, the top emitting structure has been applied in our green QLED device. As shown in figure 1, Top emission QLEDs (TE-QLED) were prepared with the same HIL, HTL, QDs and ETL material of bottom emission devices. The charge injection layer, transporting layers and QD layer were sandwiched between an Ag bottom reflective mirror and a thin Ag top semitransparent mirror. Moreover, a capping layer (CPL) over top electrode was also prepared to control light output efficiency. TE-QLEDs were then optimized by tuning the thickness of functional layers between two metal electrodes[9].

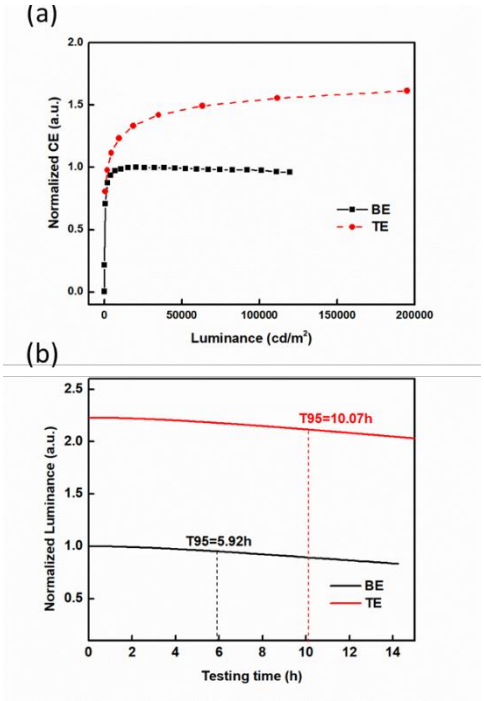

Figure 2. The comparison of green QLED performance between TE and BE device structure. (a) relative current efficiency of TE and BE green QLED; (b) relative operational lifetime of TE and BE green QLED;

The performances of top emission and bottom emission QLEDs were compared in figure 2. Due to the same electrode structures and functional material, the energy level and charge mobility of TE-QLED are in accordance with the same BE-QLED. However, the thinner functional layers of TE-QLEDs are advantageous for carrier transport and recombination. Based on the Fabry-Perot optical harmonic resonator theory, opposed to the bottom emission devices, the emission light intensity of TE-QLED is significantly enhanced. Such result can be attributed to the constructive interference occurs between the initial and reflected light waves at optimal thickness of electrode and charge functional layers. In addition, in the top emission structure, light does not pass through the ITO and the glass substrate with quite high refractive indices. The waveguide mode loss and substrate mode loss, which usually lead to the lowering of the outcoupling efficiency to as much as 40%, can be remarkably reduced due to the elimination of the glass substrate and the ITO electrode in the direction of emission. Therefore, the green TE-QLEDs exhibit remarkably higher current efficiency than that of the BE-QLEDs, as shown in figure 2(a), owing to their optical and electrical improvement. Besides the current efficiency improvement, we have demonstrated a much stable top emitting green QLED device with microcavity enhanced luminance and enlarged operational lifetime. The lifetime measurement result of this green TE-QLED has been shown in figure 2(b), comparing with the lifetime results of green BE-QLED. It can be seen that under the same driving current density, the initial luminance of the green TE-QLED is about 2.2 times higher than that of the green BE-QLED. Moreover, the practical lifetimes of the green TE-QLED were augmented 1.7 times comparing to the green BE-QLED. Therefore, due to the higher luminance and longer practical lifetime, the T95 lifetime@1000nits of the green top emission devices could be almost 4 times longer than that of the green BE-QLED, revealing that the top emitting device structure could an effective method to enhance the performance of QLED, especially for current efficiency and operational lifetime.

3.2 The modification of ETL Layers in Blue QLEDs

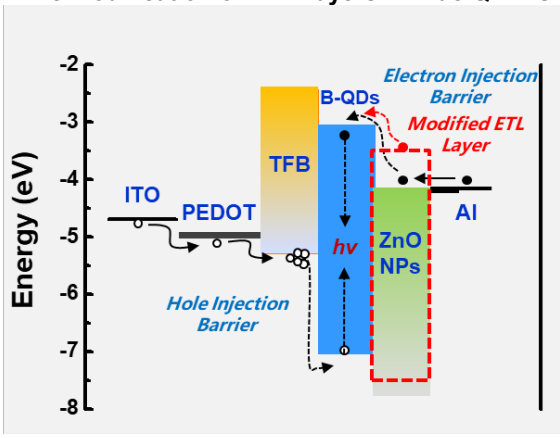

Figure 3. Schematic energy level diagrams of the standard blue QLED device with ZnO nanoparticles as electron transporting layer and the electron injection improved blue QLED device with modified ETL layer.

As mentioned in the introduction part, a typical blue QLED has severe electron injection problem between ZnO and QDs. The constantly imbalanced state of charge injection in blue QLEDs could push the excitons to the interface between QD emissive layer and charge transporting layer, causing them to be quenched by the accumulated charges at the interface. This could be the main reason to cause the large reduction of the operational lifetime in blue QLED device.

To solve the electron injection issue, the effective way is to change the conduction band minimum of ZnO by ETL layer modification, as shown in figure 3, such as ionic doping. Dopants with similar ionic radius and larger energy band gaps were usually chosen, such as Mg^{2+} cations[11]. After doped with Mg^{2+} cations, the conduction band minimum of ZnO is shifted upwards, leading to better electron injection condition. Figure 4 compares the relative current efficiency and lifetime results of the Mg doped ZnO (ZMO) device with that of the ZnO device. From the results we can see that, the ZMO device showed enhanced current efficiency and luminance, which is about 70% higher than that of the ZnO device, confirmed the better electron injection condition. However probably due to the negative effect of Mg

doping on the surface properties and the electron mobility, the practical lifetime of the ZMO device is only one third of that of the typical blue device, leading to a worse operational lifetime. Therefore, ionic doping approach for ZnO ETL layer is not an ideal method to optimize ETL layer and to improve the operational lifetime of the blue QLED.

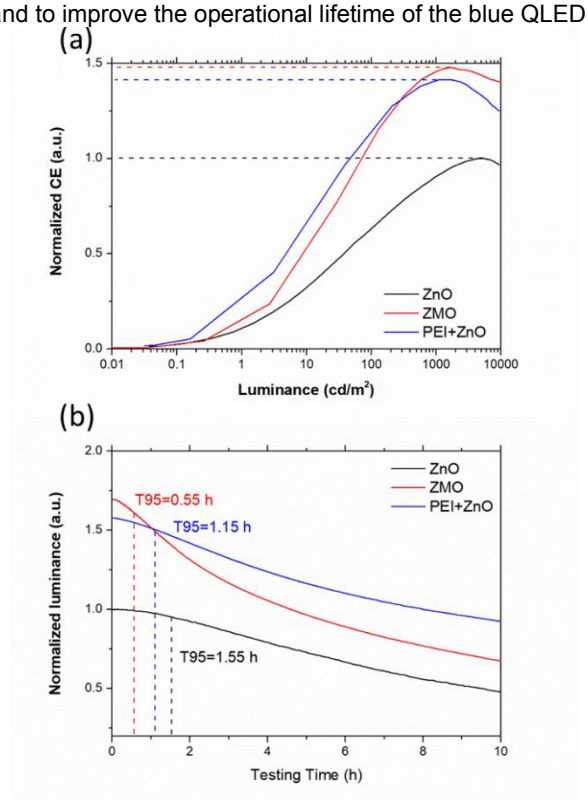

Figure 4. The comparison of blue QLED performance between different ETL layer modification device. (a) relative current efficiency of different ETL layer modification device; (b) relative operational lifetime of different ETL layer modification device;

An alternative way to optimize ETL layer is using surface dipole ligands, such as PEI, to change the conduction band minimum of ZnO[12]. This kind of PEI ligands would weakly bind to the ZnO nanoparticle surface, without dramatically changing the surface properties, and move the conduction band minimum of ZnO upwards to improve the electron injection. From the results in figure 4 we can see that, PEI modified ZnO layer could greatly increase the current efficiency and luminance while maintaining relatively good practical lifetime, leading to an operational lifetime (T95@1000nits) about 1.7 times higher than that of the typical blue QLED, and confirming that surface dipole ligands modified ETL layer could be an effective method to improve the performance of blue QLEDs, especially for operational lifetime.

4 Conclusions

In this work, we have demonstrated high performance green and blue QLED devices to meet the requirement of commercialization. In order to achieve such excellent performance, top emitting structure has been applied in green QLED device, and PEI modified ETL layer has been fabricated in blue QLED device. Significant enhancement of device performance, including both current efficiency and operational lifetime, were demonstrated for both optimized green/blue QLEDs. We hereby conclude effective methods to realize high performance green and blue QLEDs.

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