Enhanced Operational Stability of Quantum Dot based Light-Emitting Diodes by Improving Charge Injection Balance

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ABSTRACT

Charge injection balance is the key factor for high efficiency and lifetime of quantum dot light-emitting diodes (QLEDs). However, it is unidentified how the operational conditions affect lifetime of QLEDs. Herein, grounded on the quantitative assessment, the impact of electrical parameters to QLEDs performance and operational stability is identified.

1 INTRODUCTION

Colloidal quantum dot light-emitting diodes (QLEDs) are p-i-n junction diodes exhibiting excellence in color gamut, brightness and flexible form factors, promising their use in next-generation displays.[1-4] Within the last few decades, QLEDs have demonstrated great progress in efficiency and brightness that are comparable to the performance of commercialized organic light-emitting diodes (OLEDs) are reported.

To enhance performance of QLEDs, lots of attempts have been made on QD and QLED, such as modifying core/shell composition and structure, surface ligand modification, and optimization QLEDs device architectures.[5-7] Through these methods, tremendous improvement in terms of photoluminescence quantum yields (PL QY) of QDs and external quantum efficiency (EQE) of QLEDs have been accomplished. However stability of QLEDs is still miles behind. There have been studies related to enhancement of QLEDs lifetime by insertion of blocking layer to prevent acidity of HTL or improving electron-hole balance by modifying device structure, but the mechanism of optical and electrical deterioration is still insufficient.

For the practical use of QLED, it is prerequisite to identify the relation between device operation conditions (Applied current density, voltage, and charge balance factors) and QLED lifetime. However lifetime analysis of the QLEDs, which have different structures (QDs or charge transport layer), leads unreliable comparison results due to the different operating conditions.

In this study, we demonstrated improved QLEDs lifetime and performance with enhanced hole transport property by insertion of thin fullerene (C_{60}) as hole injection interlayer between CBP HTL and MoO_3 layer. Insertion of buffer layer which has high highest occupied molecular orbital (HOMO) level such as C_{60} can eliminate pinning effect between CBP and MoO_3 layer. This eventually increase hole transport property in QLEDs and enhance balance of electron and hole transport rate to QD emissive layer. To clarify the relation between operational condition and lifetime of QLED, we quantitatively conduct the comparison between electrical properties of QLEDs and photophysical properties of the QD emissive layer within the devices under various operation condition. As these analytic researches are

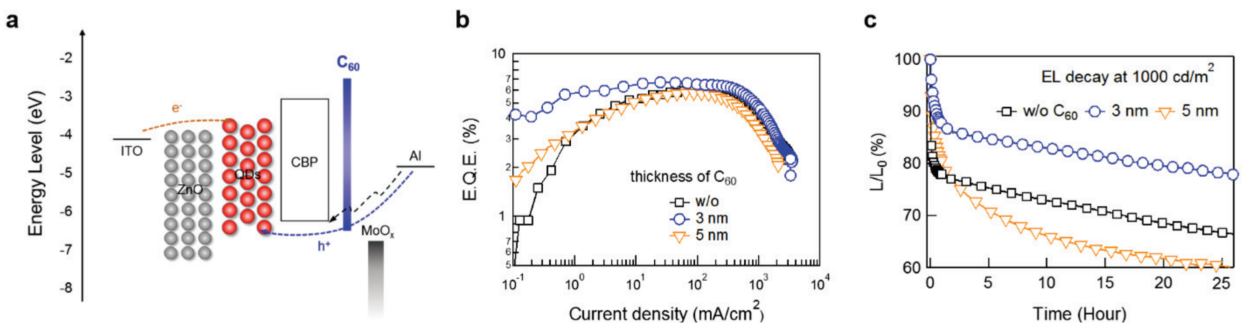

Figure 1 Energy band diagram of QLED inserting C_{60} hole injection interlayer. (b) Current density dependent device external quantum efficiency (EQE) and (c) lifetime of QLED with varying C_{60} thickness.

taken in the QLEDs which have nearly identical structure, the result shows intuitive understanding on the effect of operational condition in QLEDs.

As a result, the QLEDs with C_{60} interlayer showed 10% reduced initial rapid luminance drop compared to non- C_{60} interlayer QLEDs which leads to 5 times increase in operational lifetime at 1000 nit. (75% lifetime (LT_{75}) ~ 5.6 hours @ 1000 cd/m^2 for non-C_{60} interlayer QLEDs and (LT_{75}) ~ 36.5 hours @ 1000 cd/m^2 for C_{60} interlayer QLEDs).

2 RESULT AND DISCUSSION

2.1 Device Characteristics

Currently, QLED is composed of several functional layers and each layer possess possibility of degradation. To clarify degradation mechanism we chose device structure with well-known degradation and operation mechanism. Inverted QLED consists of ITO cathode (150nm)//ZnO nanoparticle (40nm) ETL//QDs (1-2 monolayers, 20nm) emitting layer//4,4'-bis(9-carbazolyl)-1,1'-biphenyl (CBP, 60 nm) HTL//Fullerene (C_{60}, 1-5nm) interlayer// MoO_3 (10nm) HIL//Al anode (130nm) (Figure 1a). This device structure shows turn on voltage as low and optical band gap (2.2 eV) of QDs and peak external quantum efficiency of 6.7 %. In this device structure electron injection into QD is easier than hole injection. So we insert fullerene (C_{60}, IE = 6.4 eV) layers of varying thicknesses (i.e., 0, 3 and 5 nm) at the interface between HTL and MoO_X hole injection layer (HIL) to enhance hole transport and alleviate the imbalance of hole and electron injection into QDs in inverted QLED.[8] We used CdSe (core radius (r) = 2.0 nm)/$Zn_xCd_{1-x}S$ (shell thickness in radius (l) = 3.5nm) core/shell type-I heterostrucutred red QDs (PL QYs ~ 80%) with oleic acid ligands as a light emitting material.[9]

QLEDs with C_{60} interlayer showed enhanced performance than QLEDs without C_{60} interlayer. Although the peak EQE remained similar (EQE 6.7 % for C_{60} interlayer QLEDs and EQE 6.2 % for non-C_{60} interlayer QLEDs), in a low current region showed clear EQE enhancement in the devices with C_{60} interlayer (Figure 1b).

Device lifetime experiment was conducted at initial luminance of 1000 cd/m^2 at room temperature with encapsulated condition. The 1000 cd/m^2 luminance operation current was 22.83 mA/cm^2 for non-C_{60} interlayer device, and 19.15 mA/cm^2 for 3 nm C_{60} interlayer device. (Figure 1c) The $LT_{75\%}$ of device with 3nm C_{60} interlayer shows prolonged lifetime compared to pristine devices. The notable factor that makes lifetime difference was initial rapid luminance drop. Initial luminance drop in non-C_{60} interlayer device reached to 78% within 30 minutes. However device with C_{60} interlayer device showed reduction of initial luminance drop (Reached 86% within 30mins). We surmised that the increase in electron-hole balance reduces initial luminance drop of QLEDs due to the reduction of accumulated extra charge carriers in QD emissive layer.

2.2 Operational Stability Analysis

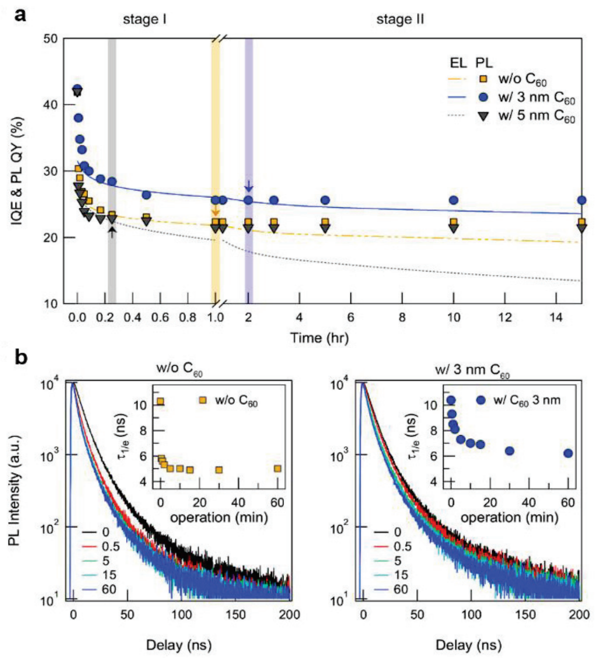

Figure 2 Operation test of pristine QLED and QLED with 3, 5 nm of C_{60}. (a) Operation time dependent-traces of internal quantum efficiency (IQE) of QLED without C_{60} and with 3, 5 nm of C_{60} under a current density of 30 mA/cm^2 and the photoluminescence quantum yield (PL QY) of QD emissive layer within device. (b) Normalized PL decay curves of the QD emissive layer after operation for 0, 0.5, 5, 15, and 60 min (insets: Calculated average lifetime of PL decay curves).

The previous lifetime comparison showed enhanced operational stability when it was compared at same luminance. However the operating condition (Applied current density and applied voltage) differs from each devices. The QLEDs with 3 nm C_{60} interlayer require smallest operating condition factors which will affect the least deterioration to the operating devices. Therefore we fixed applied current density for all the devices to compare in the least changeable conditions.

To clarify the effect of operational conditions on the stability of QLED, we compared internal quantum efficiencies (IQEs) and photoluminescence quantum yields (PL QYs) decay of QLEDs under the same 30 mA/cm^2 constant current density bias. QLEDs with three different C_{60} interlayer thickness (0 nm, 3 nm, and 5 nm) were measured for comparison of different hole injection properties. Initial IQEs are calculated from EQE at the current density 30 mA/cm^2 with the out-coupling efficiency estimated as 0.2.

Initial PL QY of the QD emissive film is 42%. From

Table 1 Characteristics of operational condition on the QLEDs with varying thicknesses of C_{60} interlayer at current densities of 30, 100 and 200 mA/cm^2.

	EQE* (%)	Voltage* (V)	$(J_{e0}-J_h)/J_{e0}$ ($\times 10^{-9}$)	K_I (hr^{-1})	K_{II} (hr^{-1})
			30 mA/cm^2		
w/o C_{60}	*5.7*	*4.1*	*6.5*	*15.7*	*1.1*
3 nm C_{60}	*6.7*	*3.7*	*5.5*	*12.6*	*0.2*
5 nm C_{60}	*5.5*	*6.4*	*6.8*	*15.8*	*4.9*
			100 mA/cm^2		
w/o C_{60}	*6.1*	*4.6*	*6.0*	*47.5*	*15.9*
3 nm C_{60}	*6.5*	*3.9*	*5.4*	*55.3*	*4.8*
5 nm C_{60}	*5.8*	*7.1*	*7.1*	*69.6*	*23.8*
			200 mA/cm^2		
w/o C_{60}	*6.3*	*5.1*	*5.8*	*63.7*	*28.6*
3 nm C_{60}	*6.4*	*4.2*	*5.7*	*67.0*	*25.6*
5 nm C_{60}	*5.5*	*7.6*	*7.2*	*137.4*	*47.6*

* Device characteristics at the initial operation (t=0)

Figure 2a we can see the solid line IQE decay graph matches well with PL QY decay points. Interestingly, QLEDs with 3 nm C_{60} interlayer which has higher hole injection properties saturated at high intensity both in IQE and PL QY compared to 0 nm or 5 nm C_{60} interlayer devices. As the previous report presented the initial rapid deterioration (Stage I) originates from the charge accumulation in the QD emissive layer due to electron hole injection imbalance, we surmise that 3 nm C_{60} interlayer enhances electron-hole balance resulting reduced deterioration in initial stage I lifetime decay.[10] Meanwhile 5 nm C_{60} interlayer QLEDs showed increased initial drop compared to 3 nm C_{60} interlayer QLEDs, indicating electron-hole imbalance increased. It is attributed to insulating properties of C_{60} happening when high HOMO interlayer stacked thicker than certain thickness (3 nm).

We measured Time-correlated single photo counting (TCSPC) measurement on the QD emissive layer with 3 nm C_{60} interlayer device and without C_{60} interlayer device. Similar to previous report, we observed arise of fast decay from PL decay following PL QY decrease. Compared to non-C_{60} QLEDs, QLEDs with 3 nm C_{60} interlayer showed slower PL decay and saturated after longer operation (2 hrs). This implies reduction of non-radiative recombination at 3 nm C_{60} interlayer QLEDs during the early operation stage and enhancement of electron-hole injection rate balance after the saturation point.

The initial device efficiency (EQE (0)) is inversely proportional to the initial charge injection imbalance ($(J_{e0}-J_h)/J_{e0}$) in chosen variation of C_{60} interlayer thickness, implying that the device efficiency enhancement by the presence of C_{60} interlayer is an outcome of the mitigated charge injection imbalance into the QD emissive layer which rises the need of comparison at the current density which has same EQE.

As charge imbalance factor and EQE of QLEDs showed inverse proportional trends, we conduct the device operational stability tests under operation at 100 mA/cm^2 and 200 mA/cm^2, where the device efficiency barley changes upon the variation in C_{60} interlayer thickness (Figure 1) and summarize the relationships between the device operation stability and the device characteristics (Table 1). The result shows that device degradation rates at both Stage I (K_I) and Stage II (K_{II}) highly influenced by the charge carrier injection imbalance into QDs ($J_{e0}-J_h$). This is consistent with the disparity of charge carrier injection rate which is the primary reason for the device degradation at both Stage I and Stage II. The charge injection imbalance provokes the probability of non-radiative Auger recombination processes, leading to the device luminance drop at Stage I. The leakage of extra charge carriers accumulated in the QD emissive layer toward HTL causes structural deformation of HTL (here, CBP) that becomes charge deep traps and reduces the device efficiency at Stage II.[11,12]

The device efficiency at Stage I shows disregard tendency of the applied voltage. By contrast, the device degradation rate at Stage II is majorly influenced by the charge injection imbalance and also followed by the operated voltage. We surmise the origin of device degradation at stage II comes from the irreversible HTL degradation. In the present case, exocyclic C-N bond in CBP is known as a weak bond and easy to become structural deformation that creates additional deep trap sites. The higher operated voltage escalates Joule heating to the devices and consequently the HTL degradation. As the insertion of 3 nm thick C_{60} interlayer reduces the applied voltage in all operating condition (30, 100 and 200 mA/cm^2). As a combined result of enhanced charge balance and the lowered operated voltage, QLED with 3 nm C_{60} interlayer shows enhancement in the device stability at Stage II.

3 CONCLUSION

We fabricated novel QLED structures employing hybrid charge transport layers with enhanced charge injection balance and characterized the device performance of QLEDs. Insertion of a thin C_{60} interlayer enhances charge balance in the QD emissive layer within working devices and reduces operation voltage resulting significantly improved device efficiency and operation stability.

Quantitative analysis and optoelectronic characterization on working devices under varying operation conditions enable us to understand the key factors that are responsible for the QLEDs degradation. The device efficiency drop at Stage I is attributed solely to the charge injection imbalance into QDs. The device efficiency loss at Stage II is also attributed mainly to the charge injection imbalance, and further exacerbated by the increase in the operation voltage.

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