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The correlation between the shape of the quantum dot emission layer and the device characteristics by mixing the small molecular hole transport material

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ABSTRACT

We found that the efficiency of green QLEDs could be improved through the incorporation of hole transport materials. However, it has been found that mixing more than a certain ratio is disadvantageous because it also blocks the flow of electrons when mixing more than a certain ratio.

1 INTRODUCTION

The ultimate goal of display devices is high-efficiency and long-life self-luminescence, and electroluminescent quantum dot light-emitting diodes (QLEDs) are being extensively studied as one of the candidates for next-generation full-color displays and light sources.[1,2] QD is attracting attention as a next-generation display material and process because it has narrow spectral characteristics compared to organic materials, can mass-produce light-emitting materials, and can manufacture QLEDs by adopting a solution process.[2] The fact that it can be manufactured by applying the solution process can be said to provide a fairly advantageous method because it is possible to produce devices at a relatively low cost compared to other processes.[2] However, the efficiency and lifetime of devices made using only QDs make them unsuitable as display or lighting devices for practical purposes. In recent research, studies to increase efficiency and stability are being conducted to make devices that are actually commercially available. In practice, efforts are being made, such as the use of polymer matrices capable of crosslinking and shell construction utilizing some modified QD or ligand materials to have stabilized films. ZnO and ZnMgO used as an electron transport layer (ETL) are also well known to improve device characteristics. In the hole transport layer (HTL) study, a mixture of a polymer material capable of crosslinking and a polymer material with high mobility was mainly used to improve the hole transport characteristics.[3] Besides, efforts have been made to improve the performance by introducing a small-molecular-type hole transport material mixture into the light emitting layer (EML). In this study, we fabricated a QLED device by utilizing all of these previous studies, and in particular, studied the structural or morphological effects of mixing a small-molecular-type HTL material in the EML.[4]

2 EXPERIMENT

Each layer of QLED was prepared through solution processing. First, indium-tin oxide (ITO)-based glass with an active area of 3 mm x 3 mm was used to install the device. To remove all organic impurities, the substrate was washed with acetone and IPA, and irradiated with UV-O_3 treatment and used to improve the wettability of the substrate. Then, poly(3,4-ethylenedioxythiophene) : poly-(styrenesulfonate) (PEDOT : PSS, Al4083,) was spin-coated on the ITO substrate at 4000 rpm for 60s and annealed at 150°C for 15min. The crosslinkable HTL solution containing [4-(9-phenyl-9*H*-carbazol-4-yl)-phenyl]-bis-(4′-vinyl-biphenyl-4-yl)-amine (PCP-bis-VBPA, PbV,0.4 wt% in toluene) and poly[(9,9-dioctylfluorenyl-2,7-diyl)-co-(4,4′-(*N*-(4-*sec*-butylphenyl)diphenylamine)] (TFB, 0.5 wt% in toluene) was loaded and coated on the PEDOT:PSS at 3000 rpm for 30s and annealed at 220°C for 60 min. The CdSe/ZnS quantum dot containing 4,4′,4″-tris(*N*-carbazolyl)triphenylamine (TCTA) dissolved in toluene was spin-coated at 3000 rpm for 60s and then annealed at 90°C for 15min. The ZnMgO (in ethanol : isopropyl alcohol (IPA) = 2:1) solution was loaded and spin-coated on the top of EML at 3000 rpm for 60s and baked at 90°C for 30min. The aluminum (Al) was deposited at a pressure of ~5 x 10^{-7} Torr.

3 RESULT

In principle, the X-ray scattering experiment has the advantage of maintaining the target concentration as it is, so it was possible to obtain the characteristics of the prepared sample even thought the concentration of the sample is very low. Moreover, X-ray scattering measurements are more reliable for scattering measurements in that they do not change the structure of the sample. So, using this, we found the difference in the quantum dot arrangement. To investigate the difference in morphological properties, we mixed TCTA in the QD emission layer as shown in **Figure 1** to make samples of various proportions.

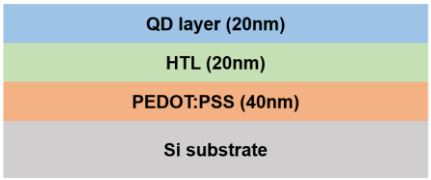


Figure 1. The sample structure for evaluation of morphology

Meanwhile, **Samples A - F** were prepared with the different EML having different composition (e.g. **Sample A** – EML: QD, **Sample B** – EML: QD:TCTA = 10:1, **Sample C** – EML: QD:TCTA = 10:2, **Sample D** – EML: QD:TCTA = 10:3, **Sample E** – EML: QD:TCTA = 10:5, **Sample F** – EML: QD:TCTA = 10:8)

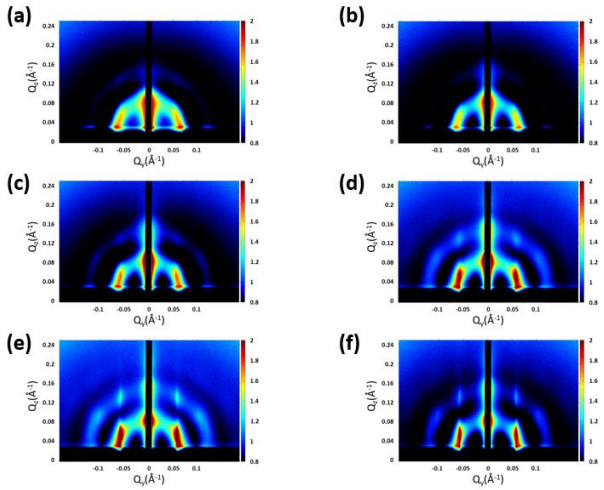


Figure 2. Images of GISAXS measurement at 0.15° incidence angle of **Sample A – F**

In fact, Grazing Incident Small X-ray Scattering (GISAXS) measurement was performed to confirm the change according to the difference in the mixing amount of TCTA added to the QD layer in the EML structure with QD.**Figure 2** shows that the quantum dot layer composed of CdSe/ZnS quantum dot particles with an oleic acid ligand has a faint halo-shaped ring pattern and that QD has a spherical shape. This is because the GISAXS technique can analyze even structural factors. When Q_Z=0.029 Å^{-1}, the line cut result of the plane is shown in the figure above. In all results, GISAXS measurements have been revealed that quantum dot particles form linear packing in in-plane properties (Q_y≃0.06 Å^{-1},0.115 Å^{-1}). Referring to the nearest adjacent short-distance order in the plane of **Figure 2(A)-(C)**, most quantum dot particles exhibit linear packing characteristics in the plane direction, but can be confirmed to add TCTA with stronger vertical reinforcement characteristics, and **Figure 2(D)-(F)** shows that they have 2D hexagonal packaging characteristics and uniform stacking distance. This shows that the Gaussian fit of the peak representing the corresponding characteristics has values such as 0.056 Å^{-1} and 0.066 Å^{-1} in the QD-only state, and the arrangement characteristics of QD are divided. The second peak of the plane is Q_y≃0 corresponding to D=5.5 nm.It's 115 to 1. In addition, △Q with the first in-plane peak is Qy≃0.055 Å^{-1} corresponding to △D = 11.4 nm. When the QD layer is composed of a small amount of TCTA exclusively for QD or mixed with QD, QD particles have linear packing characteristics. Q_y and △Q of the first plane represent the distance between points, which means the nearest neighbor distance. These changes may change the electrical characteristics of the actual device. Six different green QLED devices were prepared according to the solution process to confirm this behavior within the actual device. They were prepared through the following device structure. (Refer to **Figure 3**).

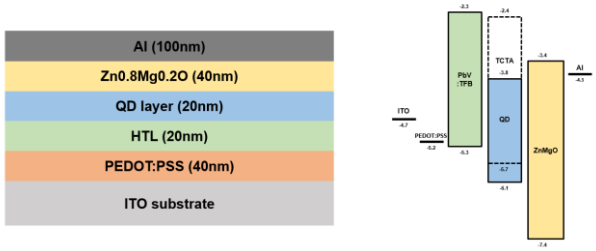
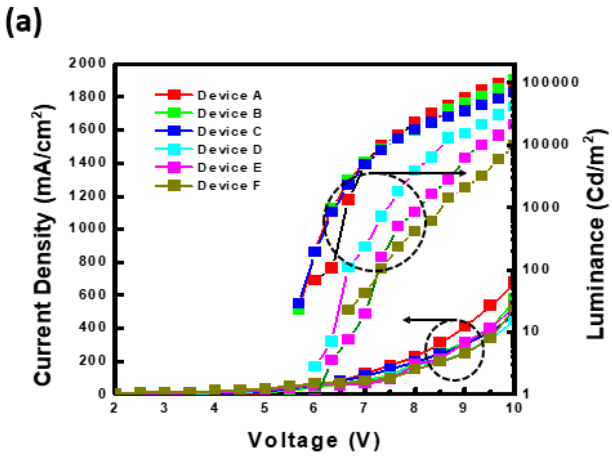


Figure 3. The Device structure for Actual electrical characteristics.

Meanwhile, **Device A - F** were prepared with the different EML having different composition (e.g. **Device A** – EML: QD, **Device B** – EML: QD:TCTA = 10:1, **Device C** – EML: QD:TCTA = 10:2, **Device D** – EML: QD:TCTA = 10:3, **Device E** – EML: QD:TCTA = 10:5, **Device F** – EML: QD:TCTA = 10:8)



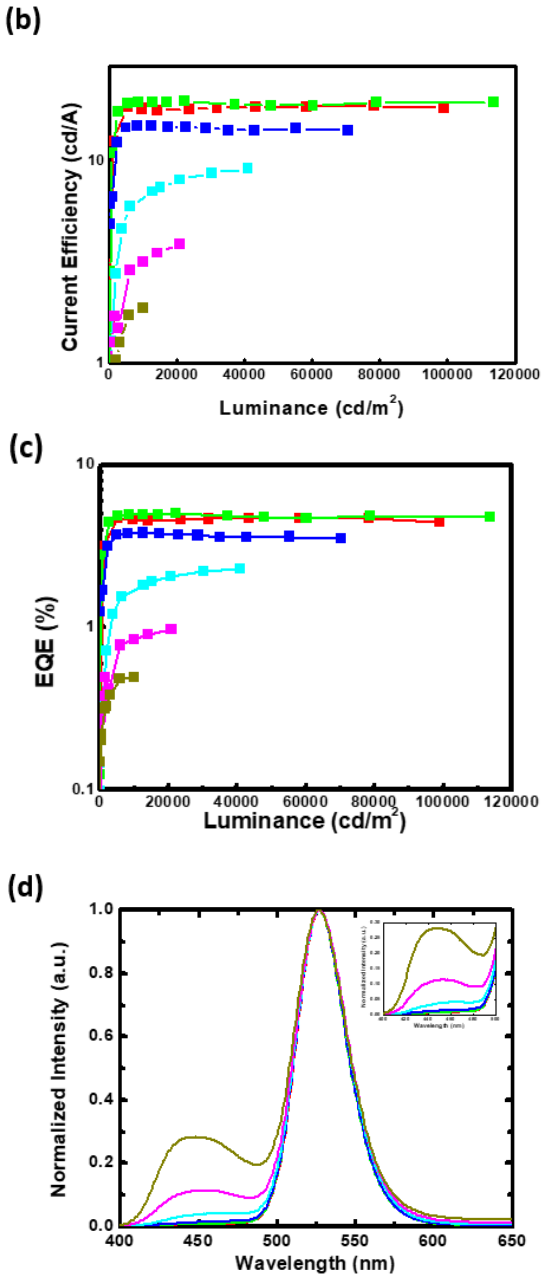


Figure 4. (a) Current density – voltage - luminance (*J-V-L*) characteristics, (b) Current efficiency – luminance, (c) external quantum efficiency (EQE) - luminance and (d) EL spectra of green emitting QD-only device and TCTA doped QD devices.

Figure 4(a)-(d) show J-V-L characteristics of QLED devices prepared with EML having different composition as commented previously. Very interestingly, the current density varied according to the change of EML composition. In principle, the electrons may flow along the lowest unoccupied molecular orbital (LUMO) of QD while holes may move along the highest occupied molecular orbital (HOMO) of TCTA . So, we expected that the hole current may be increased if we increase the amount of TCTA in EML. However, we found that the LUMO level of TCTA is too shallow compared to QD, so electrons can be severely scattered by TCTA. Therefore, Figure 4(a) shows that the current density decreases when the amount of TCTA increases over the condition that the mixing ratio of TCTA, which is judged to be a uniformly mixed state of QD and TCTA, is about 20%. However, since the degree of TCTA blocking electrons does not change from this uniformly mixed condition (~20%), the hole current can be greatly increased when the amount of TCTA is increased over this amount. That is, as the condition changed from **Device A** (0%) to **C** (20%), current densities were measured to 52.6, 50.0 and 29.7 mA/cm^2 (at 6.0V). However, when the amount of TCTA increased by more than 30%, the current density suddenly increased again. In fact, the **Device D-F** observed current densities of 55.2, 56.0, and 61.8 mA/cm^2, respectively. Meanwhile, for **Device A-F**, the maximum luminous intensity values were obtained as 99,066, 113,748, 85,100, 43,148, 20,904 and 10,887cd/m^2, respectively. Thus, the maximum current efficiency was recorded to 19.1 cd/A, 20.0 cd/A, 15.8 cd/A, 9.2 cd/A, 3.9 cd/A, and 1.9 cd/A for **Device A-F**. The corresponding maximum external quantum efficiency (EQE) values from **Device A-F** were 4.7%, 5.0%, 3.8%, 2.3%, 1.0%, and 0.5%, respectively. As shown in the figure above, when TCTA is mixed with 10%, the efficiency of the hole injection into the QD increases, thereby improving the efficiency of the entire device, but at 20% or more, the efficiency decreases. As can be seen, it was confirmed that not only the luminescence phenomenon of TCTA occurs, but also the holes leak laterally, so that the efficiency is rapidly reduced under the 30-80% mixing condition of TCTA. This kind of phenomenon was confirmed from GISAXS study. The detailed device performances were also summarized in Table 1.

Table 1. Changes in device performance of electroluminescent QD-LEDs according to blending changes

Device	V_{on}[a]/V_{op}[b] [v]	CE[c]/PE[d]/EQE[e] [cdA^{-1}/ lmW^{-1}/%]		
		Maximum	at 1,000 cd m^{-2}	at 10,000 cd m^{-2}
Device A	3.2 / 4.7	19.1 / 10.7 / 4.7	12.7 / 8.0 / 3.2	18.4 / 9.6 / 4.6
Device B	2.9 / 4.6	20.0 / 11.2 / 5.0	15.1 / 10.6 / 3.8	19.7 / 10.3 / 4.9
Device C	3.0 / 4.7	15.8 / 8.5 / 3.8	6.8 / 4.7 / 1.7	15.6 / 7.9 / 3.8
Device D	3.4 / 5.8	9.2 / 2.9 / 2.3	2.0 / 1.0 / 0.5	6.8 / 2.7 / 1.7
Device E	4.0 / 6.4	3.9 / 1.2 / 1.0	1.3 / 0.6 / 0.4	3.2 / 1.1 / 0.8
Device F	4.5 / 7.6	1.9 / 0.6 / 0.5	0.7 / 0.3 / 0.3	1.9 / 0.6 / 0.5

[a] V_{on}: turn-on voltage, measured at 1 cd m^{-2} [b] V_{op}: operating voltage, measured at 1000 cd m^{-2} [c] CE: current efficiency [d] PE: power efficiency [e] EQE: external quantum efficiency, The EQE was obtained from the calculation based on the assumption of a Lambertian distribution [f] CIE: Commission International de L'Eclairage.

4 CONCLUSIONS

In conclusion, the addition of a hole transport material to

a thin film composed of QDs is closely related not only to electrical properties but also to morphological properties. However, if more than a certain percentage (20%) of the hole transport material is added, the electrical efficiency drops sharply, which shows that the quantum dot arrangement does not help to improve the efficiency. That is, it was confirmed that the addition of the hole transport material to the QD thin film has a positive effect, but when added in a certain ratio or more, the vertical arrangement of the QDs increases and negatively affects the device characteristics.

5 Acknowledgment

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