

# Controlling Charge Injection Properties of Quantum Dot Light-Emitting Diodes

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## ABSTRACT

Efficient charge carrier injection is one of the most important factors to achieve high performance quantum dot (QD) light-emitting diodes (QLEDs). Here, we investigated the effects of charge carrier injection properties on the QLED performance by modifying the surface ligands of QDs and by adopting an interlayer between the QD layer and the charge transport layer.

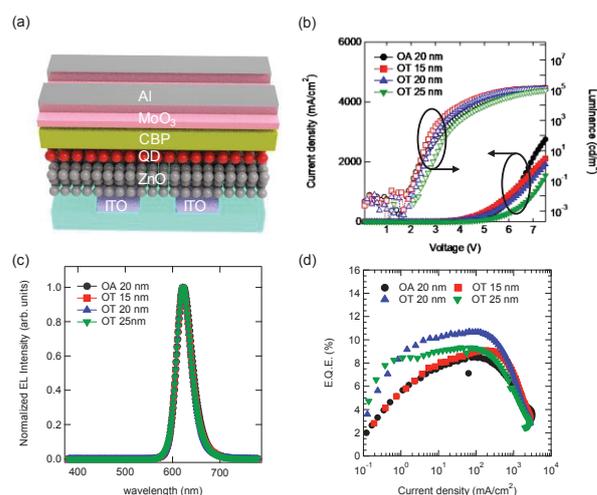
## 1 INTRODUCTION

Colloidal nanocrystal quantum dots (QDs), which have advantages such as the easy color tunability by changing the size of the core, narrow full width at half maximum (FWHM), and high photoluminescence quantum yield (PL QY), is a promising candidate for the emitter of the light-emitting devices and display devices. Thus, for the realization of wide color gamut (WCG) displays, QDs are of interests both in academic and industrial fields.

Among various display technologies using QDs, QD light-emitting diodes (QLEDs) are considered as a prospective technology. However, there are a plenty of issues to be solved for their practical application, such as efficiency and stability of the QLEDs. In particular, if the inter-dot distance between QDs is too short, the non-radiative Förster resonance energy transfer (FRET) between QDs occurs and thus it reduces the performance. There are a few studies trying to reduce this process by modifying the synthetic procedures of QDs, and they remarkably increased the efficiency [1,2]. On the other hand, if one type of carriers (e.g., electrons) outnumbers the other type of carriers (e.g., holes), interactions between carrier–exciton and/or exciton–exciton is highly related to the recombination process. Especially in QDs, Auger recombination (AR) by multicarrier in a single QD is one major reason for efficiency roll-off and reduced performance. In order to reduce these processes and improve the charge carrier balance, so far, inserting an interlayer between the transport layer and the emissive layer [3] and doping at the transport layer [4] have been reported. Chemical engineering-based method is also reported, which is to change/modify the ligands. There have been several studies improving the performance of QLEDs by substituting ligands for QDs. For example, Li et

al. adopted tris(mercaptopmethyl)nonane (TMMN) as the ligands to enhance the surface passivation effect and to reduce their insulating property [5]. Rastogi et al. used various ligands and found that the energy level of QDs and the electrical properties of the QLEDs highly depend on the ligands [6].

Here, we investigated the effects of charge carrier injection properties on the QLED performance by modifying the surface ligands of QDs and by adopting an interlayer between the QD layer and the charge transport layer. First, we exchanged the ligands from oleic acids to shorter thiol-based ligands and increased electrical conductivity. We also demonstrate the use of semiconducting polymers as ligands of QDs to modulate the injection of electrons from the electron transport layer to the emissive layer. Alkylamine ligands were also exchanged onto InP QDs to reduce the trap states. In addition, to improve the charge balance, we adopted an interlayer between QDs and charge transport layers. We systematically investigated the effects of the ligand exchange and inserting an interlayer on the performance of the QLEDs.

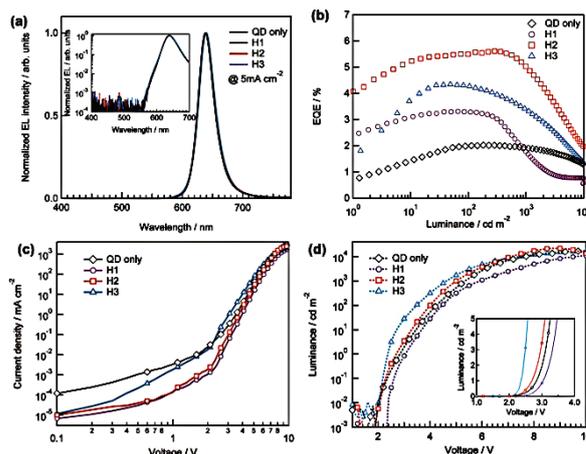


**Figure 1** (a) Device structure of the inverted QLEDs used in this work, (b) and the QLEDs performance using QDs capped with OA and OT ligands. (c) Normalized EL spectra, and (d) the external quantum efficiency of the QLEDs.

## 2 RESULTS AND DISCUSSION

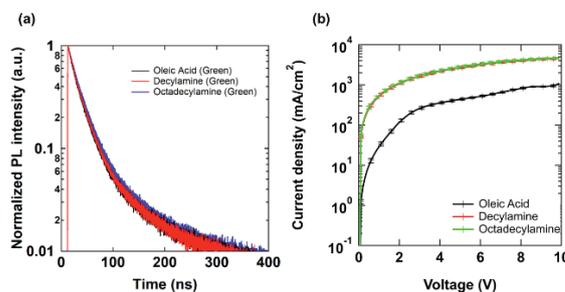
First, we investigated the effect of ligand exchange on the device performance of the QLEDs. Typically, colloidal QDs are capped with bulky acids with long hydrocarbon chains to enhance the dispersibility of QDs in organic solvents. However, these organic ligands have insulating properties which hinder carrier injection and transport. To enhance the electrical properties, we adopted octanethiol (OT)-based ligands by replacing long oleic acid (OA) ligands. We fabricated inverted QLEDs consisting of ITO cathode (150 nm)/ZnO nanoparticle (40 nm)/QDs (1–2 monolayers, 20 nm)/4,4'-bis(*N*-carbazolyl)-1,1'-biphenyl (CBP, 60 nm)/MoO<sub>3</sub> (10 nm)/Al (130 nm) anode. The device structure is depicted in Fig. 1(a). ZnO, CBP, and MoO<sub>3</sub> were used as the electron transport layer (ETL), the hole transport layer (HTL), and the hole injection layer (HIL), respectively. As shown in Fig. 1(b), the device with OT ligands exhibits a higher current density (*J*) and luminance (*L*) than that with OA ligands. At the driving voltage (*V*) of 4.2 V, the maximum luminance of 13200 cd/m<sup>2</sup> was achieved with the OT capped QDs, which is 3.7-fold higher than that with the OA capped QDs. Fig. 1(c) and 1(d) show the enhanced maximum external quantum efficiency (EQE) of 10.6% in the QLEDs with the OT ligands, which is higher than that of 8.4 % in the QLEDs with the OA ligands, without any significant difference in their electroluminescence (EL) spectra with the peak wavelength at 622 nm.

We also tested another types of ligands, which is a conducting polymer with anchoring groups. Because the QD layer was stacked on top of the ZnO layer, excessive electrons can be injected into QDs, as reported before [4]. Thus, resultant charge carrier imbalance in QDs can lead to non-radiative recombination processes, such as Auger recombination. Using the ligand exchange process, we adopted a ligand possessing carbazole-based polymer group with a relatively high lowest unoccupied molecular orbital (LUMO) energy level. The polymeric ligands formed a large electron injection barrier between ZnO and QDs, so that excessive electrons injection into QDs can be suppressed. We fabricated the QLEDs, H1, H2, and H3, which have different QD:polymer ratios as 1:0.5, 1:0.375 and 1:0.25, respectively. As shown in Fig. 2(a), there was no contribution to EL emission from the ligands. The current density of the devices H1–H3 decreased as the polymer content increased, and the leakage current was also decreased when we adopted the polymer ligands, as displayed in Fig. 2(c). As a result, we could achieve the peak EQE of 5.6% in the ligand exchanged device, which is over 2 times higher than that of the pristine QD device. It means that the carbazole-based polymer can effectively control electron injection into the QDs. We are currently investigating more in detail on the optimization of the device performance and operational lifetime of the QLEDs using the polymeric ligands.

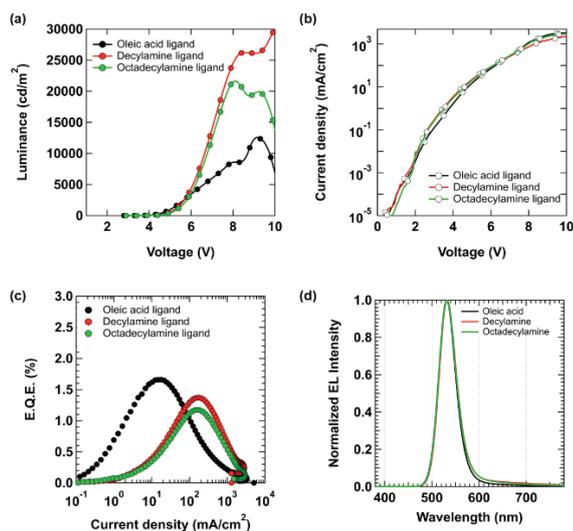


**Figure 2** Device performance of the QLEDs (H1–H3) adopting the polymeric ligands: (a) Normalized EL spectra (inset: normalized EL spectra in a log scale), (b) EQE–luminance, (c) current density–voltage, and (d) luminance–voltage (inset: magnified graph near the turn-on voltage).

We also exchanged the OA ligands with alkylamine ligands for InP/ZnS QDs. Previous researches on interaction between alkylamine ligands and II-VI compound nanocrystals have indicated that alkylamine ligands enhance the PL QY of the QDs [7,8]. Through the ligand exchange, contact between QDs and the carrier transport layers can be improved because of the decreased ligand density on the QD surface, and the reduced defects which were generated during the synthesis and purification process. Fig. 3 (a) shows that the ligand-exchanged QD films have the increased PL lifetime compared to the as-prepared QD films with OA. At first, we anticipated the FRET might be increased due to the short length of the decylamine ligands; however, the PL lifetime was not changed. We also fabricated the electron-only devices (EODs) to compare the electron injection properties. As shown in Fig. 4(b), all of the EODs with alkylamine ligands exhibit much higher current density than the EODs with oleic acid ligands. The results indicate that electron injection was facilitated for InP-based QDs.



**Figure 3** (a) Time-resolved PL measurement and (b) the electron-only device characteristics of the ZnO/QDs films with oleic acid, decylamine, and octadecylamine as the ligands.



**Figure 4** QLED performance with changing the ligands.

The devices with the alkylamine ligands showed higher brightness compared with the device with OA ligands, as shown in Fig. 4. We attribute the enhanced luminance to the improved charge carrier imbalance. Within the devices. Nevertheless, the efficiency was slightly decreased when we used the alkylamine ligands. To solve the problem, the device structure should be optimized. We, therefore, need to introduce an interlayer adjacent to QDs to reduce the quenching phenomena and to improve the charge carrier balance, especially for InP-based QLEDs.

### 3 CONCLUSIONS

We systematically investigated the effect of ligands on the performance of QLEDs. Charge carrier balance is important to achieve high performance in QLEDs. But due to the mismatches between inorganic QDs and organic charge transport layers, it is not easy to achieve electron-hole balance in the QLEDs. From our investigation, we could conclude that modification of the QD surface can be a good approach to tailor the charge injection conditions. The findings will be applicable for further researches for high-performance QLEDs.

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