Observation of Exciton Formation and Degradation in Quantum Dot Light-Emitting Diodes

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ABSTRACT

Although the performance of quantum-dot (QD) based light-emitting diodes (QLEDs) has been improved so far, mechanisms related to the dynamics of charges and excitons in the QD layer of QLEDs in electrical operation are still unclear. Here we investigated their dynamics based on time-resolved techniques to reveal the specific mechanisms.

1 Introduction

Colloidal quantum dots (QDs) are considered one of the most promising emitter materials, owing to their high photoluminescence (PL) quantum yields, narrow emission spectral bandwidth, and easily tunable peak wavelengths. By utilizing these advantages, a large-sized liquid crystal display based on color conversion of green and red QDs combined with blue light-emitting diodes (LEDs) is now commercially available in the marketplace. As the next step, QD-based electroluminescent (EL) devices, QLEDs, are receiving attention as the next generation display and lighting devices, because they can exhibit high efficiency, high brightness, and high color purity.[1–5] However, operation mechanisms of QLEDs, particularly related to charge injection into QDs, charge transport between QDs, exciton recombination and degradation procedures have not been clearly revealed, because it is difficult to measure the dynamics of charges and excitons of QLEDs in electrical operation. Furthermore, typically-used thin QD emission layer (EML) consisting of 1–3 monolayers, which is regarded as an optimum thickness for high-performance QLEDs, makes it harder to distinctively observe the phenomena occurring sorely in the QD EML.

So far, several kinds of spectroscopic techniques have been utilized to reveal the exciton dynamics, such as transient absorption and transient photoluminescence (TRPL) spectroscopy measurements.[6,7] Based on these techniques, it is revealed that electrons and holes exhibit different injection mechanism into QDs. In other words, an electron charge, which can be easily injected into a QD, charges QDs to a negative state, and then induces a hole charge by Coulomb interaction. However, these results have a limitation that the processes can be different from the electroluminescence (EL) process of QLEDs. Thus, it is required to observe the dynamics of charges and excitons of QLEDs in an electrical operation condition.

Here, we investigated the dynamics of charges and excitons in QLEDs in operation using time-resolved measurement techniques, which are TRPL and transient EL (TREL) spectroscopy techniques. These techniques enable to directly observe the transient behavior of radiative recombination, thereby we can infer the dynamics of charges and excitons. Particularly, with a dual color EML, exciton recombination procedure can be specifically described, which can be used to further improve the QLED performance.

2 Results and Discussion

As mentioned, TREL is a good method to investigate the exciton recombination and dissociation of QLEDs in operation, as shown in Fig. 1. However, we cannot differ that which QD layer in the EML emits light. To clearly observe the dynamics of charges and excitons, it is required to exactly know the position of light emission.

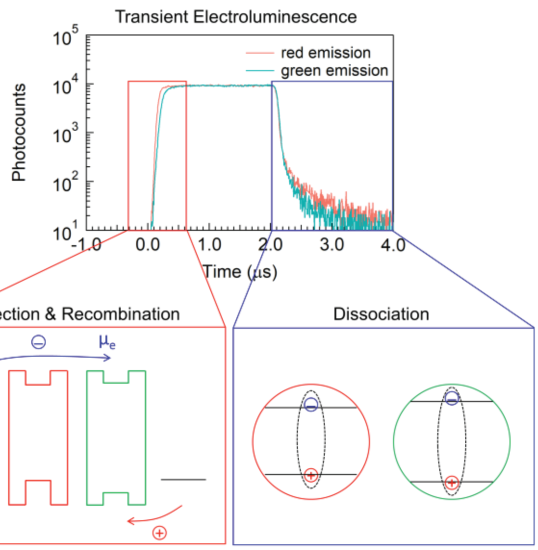

Fig. 1 TREL data of QLEDs. The sequence of charge injection and recombination can be characterized from the rising edge, while exciton dissociation processes can be inferred from the falling edge.

Recently, we have reported a way to make it possible, by designing dichromatic inverted QLEDs comprising of two monolayers of CdSe/CdZnS QD EMLs of which each individual monolayer emits different colors in two different sequence—red/green or green/red QD monolayers.[8] Using the dichromatic QLEDs, the position of the entire processes related to charge injection, transport, and exciton recombination could be clearly observed with the TREL analysis. To pile up two QD layers, it is required to use orthogonal solvents for QD deposition. Using hexane and chlorobenzene, two monolayers of QDs could be stacked successively. As expected, dichromatic devices emit two primary colors. For comparison, monochromatic QLEDs (i.e., red or green) with the same thickness of the EML consisting of red/red or green/green QD monolayers. From the rising edge of the TREL data, the emission sequence and delay time (i.e., the time interval from the voltage bias to the rise of light signal) could be presented. In both dichromatic devices, interestingly, the QD layer adjacent to the ZnO electron transport layer (ETL) emitted light earlier than the other QD layer. For instance, the red/green device exhibited red emission prior to green emission. However, the intensity of EL from the QD layer close to the hole transport layer (HTL) was much stronger than the other QD layer, meaning that radiative exciton recombination occurs dominantly in the QD/HTL interface.

The TREL results obtained from the dichromatic QLEDs provide several information on the dynamics of charges and excitons in an electrical operation condition. First, electron is dominant within the QD EML, which can be attributed to the higher electron mobility (μ_e) of the ZnO ETL than the HTL. Also, inorganic II-VI QDs are known to have higher electron mobility than hole mobility. Second, the delay of EL emission between two different colors enabled to estimate a lower-bound electron mobility of the QD layer of QLEDs in operation. The mobility of both red and green QDs was calculated to be ~10^{-5} cm^2/Vs, which are similar to the mobility of the QDs measured by the space-charge-limited current method.

The falling edge of the TREL signal is related to exciton dissociation/annihilation processes. Considering that main exciton recombination occurs in the QD layer adjacent to the HTL, the charges accumulated at the QD/HTL interface are likely to affect exciton quenching processes. In the work, owing to the use of two different color of QDs, the effects of Förster resonant energy transfer (FRET) between two different QDs can be characterized based on the FRET efficiency calculation.[9] The analysis showed that the FRET efficiency was approximately 2–6% in all devices, indicating that FRET between QDs is not a level of significance in electrical operation. Combined with the TRPL measurement under a bias voltage, charge-induced quenching was directly quantified. It is thought that these analyses contributed to quantitively understand the dynamics of charges and excitons in QLED operation.

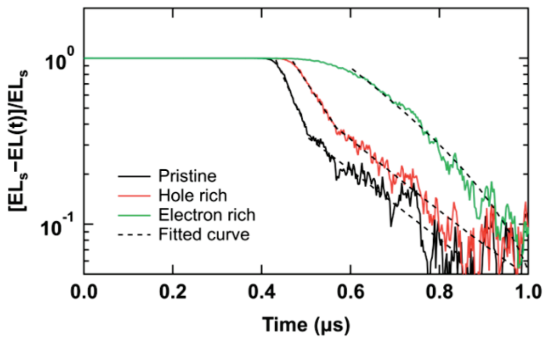

Fig. 2 Saturation signals of TREL signal of QLEDs in charge-balanced, hole- or electron-rich devices.

The TREL analysis is also helpful to understand the device characteristics depending on the majority carriers, which are the charge-balanced, hole- or electron-rich QLEDs. Fig. 2 plots the TREL difference of rising curves between the saturation value of signal EL_s and the time-dependent signa $EL(t)$ normalized by EL_s. It shows that the pristine (balanced) device has two slopes, steep and delayed which are related to the electron injection and consecutive hole injection, as explained previously. In the hole-rich device, the shape of the curve is same but delayed due to the reduced electron injection. On the other hand, the electron-rich device exhibits only a gentle slope, meaning that the emission is determined mainly by late hole injection. The shape of TREL, therefore, can be practically utilized to know the in-situ charge balance of the devices.

3 Conclusion

In this paper, we focused on the transient analysis of QLED operation to further advance understandings on the dynamics of charges and excitons. By using a double EML structure, charge injection, exciton recombination, and exciton quenching processes can be characterized. Also, charge balance of QLEDs can be directly observed using the TREL measurement. The analysis and findings investigated in this paper would be helpful for the future research to achieve high-performance QLEDs.

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