Efficient InP-based Quantum Dot Light-emitting Diodes Using an Emitting Layer Combined with Organic Electron-transporting Materials

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ABSTRACT

We report quantum dot light-emitting diodes (QD-LEDs) whose emitting layers are composed of InP-based QDs and an organic electron-transporting material (ETM). We demonstrated green QD-LEDs with a high maximum external quantum efficiency of 10% and a low driving voltage. In addition, the origin of the high performance was investigated.

1 INTRODUCTION

Colloidal quantum dots (QDs) have been attracting much interest because of their unique characteristics, which include narrow photoluminescence (PL) spectra and a tunable emission wavelength.[1] QDs with saturated color emissions are suitable for use in wide-color-gamut displays. The wide-color gamut with RGB primaries positioned on the spectral locus is specified in Recommendation ITU-R BT.2020 for ultra-high-definition television (UHDTV).[2] Therefore, the color purity of RGB devices must be improved to realize UHDTV displays that are compliant with BT.2020.

QD light-emitting diodes (QD-LEDs) are one of the promising candidates to meet BT.2020. Although high efficiency and high color purity have been achieved with QD-LEDs fabricated using Cd-based QDs,[3,4] their potential for widespread use is limited by the toxicity of Cd. QD-LEDs with low-toxicity QDs such as InP-based QDs have been investigated as alternatives. However, the electroluminescence (EL) characteristics of InP-based QD-LEDs such as color purity and luminous efficiency are generally inferior to those of Cd-based QD-LEDs.[5] Although attempts to improve EL characteristics are continuing, further improvement is required.

To improve EL characteristics, advances in InP-based QDs and improvements in the device structures and peripheral materials of QD-LEDs have been attempted. One of the approaches is to insert an organic layer between ZnO nanoparticle (NP) and QD layers. Improving charge balance and suppressing exciton quenching may improve the EL characteristics of QD-LEDs. We reported QD-LEDs whose emitting layers (EMLs) are composed of QDs with a ZnInP core and the organic electron-transporting material (ETM) tris(2,4,6-trimethyl-3-(pyridin-3-yl)phenyl) borane (3TPYMB).[6] The EML was formed by a single spin coating process from a mixed solution of QDs and organic ETMs. Because a stacked structure of the QDs and organic ETM layers can be formed as a result of phase separation,[7] an organic ETM can be easily deposited between ZnO NPs and QDs. However, the conditions for improving the EL characteristics of QDs with organic materials are complicated and have not been sufficiently clarified.

In this study, to investigate the effect of organic ETMs combined with QDs on the EL characteristics of QD-LEDs, we evaluated the characteristics of QD-LEDs whose EMLs were composed of green InP-based QDs and various organic ETMs. By using a suitable organic ETM, the external quantum efficiency (EQE) and driving voltage were found to be markedly improved. We demonstrated QD-LEDs with a high maximum EQE of 10.0% and a low turn-on voltage of 2.4 V, and the turn-on voltage is the same as that of the QD-LEDs without ETMs. Furthermore, the origin of the high performance was investigated. Our results suggested that the difference in EQE was due to the suppression of hole current leakage from the QD layer to the ETM.[8]

2 EXPERIMENT

2.1 Fabrication of QD-LEDs

Fig. 1(a) shows the device structure of the fabricated green QD-LEDs: indium tin oxide (ITO) (100 nm)/ZnO NPs (40 nm)/ETM:QDs (25 nm)/tris(4-carbazoyl-9-ylphenyl)amine (TCTA) (40 nm)/MoO_3 (10 nm)/Al (50 nm). The ZnO NPs in a 1-butanol dispersion were synthesized by a previously reported method.[9] Fig. 1(b) shows the molecular structures of the four organic ETMs used in this study—1,3,5-tri[(3-pyridyl)-phenyl-3-yl] benzene (TmPyPB), 1,3,5-tris(6-(3-(pyridin-3-yl)phenyl)pyridin-2-yl)benzene (TmPyPPyB), 3TPYMB, and 2,4,6-tris(3′-(pyridin-3-yl)biphenyl-3-yl)-1,3,5-triazine (TmPPPyTz). QDA524-100 (Merck) was used as green InP-based QDs. A toluene dispersion of the QDs demonstrated a PL peak wavelength of 525 nm, a full width at half maximum (FWHM) of 40 nm, and a PLQY of 81%. Glass substrates with patterned ITO were cleaned with ultrapurified water, detergent solution, and

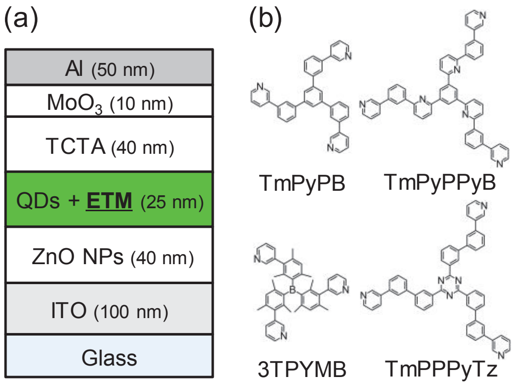

Fig. 1 (a) Device structure of QD-LEDs, (b) molecular structures of the organic ETMs.

organic solvents, and then treated with UV–ozone under ambient conditions. The electron-injecting layer of ZnO NPs was spin-coated from the 1-butanol dispersion (20 mg mL^{-1}) at 2000 rpm under N_2 atmosphere and baked at 130 °C for 30 min. The EML was formed by spin coating from a mixed solution of InP-based QDs (4 mg mL^{-1}) and each organic ETM (4 mg mL^{-1}) at 2000 rpm under N_2 atmosphere, and baked at 100 °C for 30 min. The substrates were then loaded into a vacuum deposition chamber. A hole-transporting layer of TCTA, a hole-injecting layer of MoO_3, and an anode of Al were sequentially deposited without breaking the vacuum at a pressure of approximately 10^{-4} Pa. The QD-LEDs were encapsulated using a UV-epoxy resin and a glass cover under N_2 atmosphere.

2.2 Fabrication of hole- and electron-only devices

Hole-only devices with a structure of ITO (100 nm)/ poly(3,4-ethylenedioxythiophene):polystyrenesulfonate (PEDOT:PSS) (30 nm)/ETM:QDs (25 nm)/TCTA (40 nm)/MoO_3 (10 nm)/Al (50 nm) were fabricated to investigate the charge transport properties. PEDOT:PSS (Heraeus CH8000) and the EML were prepared by spin coating from a dispersion. Other layers were deposited by vacuum deposition in the same way as the green QD-LEDs. Electron-only devices with a structure of ITO (100 nm)/ZnO NPs (40 nm)/ETM:QDs (25 nm)/LiF (1 nm)/Al (50 nm) were also fabricated. LiF was deposited by vacuum deposition.

3 RESULTS AND DISCUSSION

3.1 Device characteristics of green QD-LEDs

Fig. 2(a) shows a cross-sectional scanning transmission electron microscopy (STEM) image of the QD-LED with TmPPPyTz. The QDs and ETM (TmPPPyTz) are roughly separated and stacked in two layers by phase separation. Fig. 2(b) shows the normalized EL spectra of the fabricated QD-LEDs and the normalized PL spectrum of the QD film. Pure-green

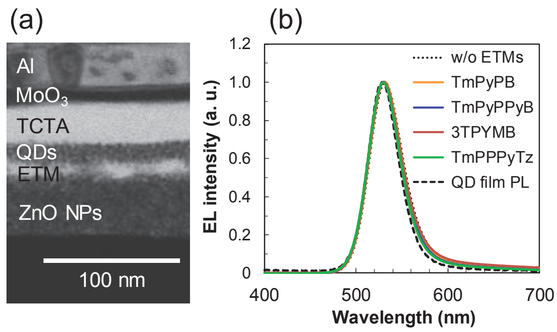

Fig. 2 (a) Cross-sectional STEM image of the QD-LED with TmPPPyTz, (b) EL spectra of the QD-LEDs and PL spectrum of the QD film.

emissions were observed in all QD-LEDs and the EL spectra are almost the same. Upon comparing the EL spectra with the PL spectrum of the QD film, we found that the EL was solely generated from the QDs, and no parasitic emission from the neighboring layers was observed. The QD-LEDs exhibited EL emission, where the peak wavelength, FWHM, and Commission Internationale de l'Eclairage (CIE) 1931 chromaticity coordinates of the QD-LEDs were 530 nm, 42 nm, and (0.25, 0.69), respectively.

Fig. 3 shows the luminance–voltage characteristics of the fabricated QD-LEDs. The driving voltage strongly depends on the organic ETM combined with the QDs. The QD-LED with TmPPPyTz exhibited a low turn-on voltage of 2.4 V, which is the same as that of the QD-LED without ETMs. In contrast, the QD-LEDs with other ETMs exhibited a high turn-on voltage of 3.6 V. The QD-LEDs with TmPPPyTz demonstrated the lowest driving voltage of 3.6 V at 100 cd m^{-2} in all QD-LEDs. The triazine moiety of TmPPPyTz is considered to be associated with a low driving voltage. Fig. 4 shows the EQE–current density characteristics of the QD-LEDs. The QD-LEDs using an EML combined with ETMs showed a higher EQE than the QD-LED without ETMs. One of the reasons for the increase in EQE upon inserting an ETM between the QDs and the ZnO NPs is

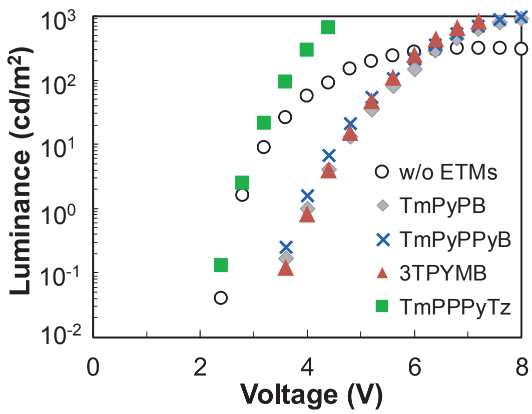

Fig. 3 Luminance–voltage characteristics of the QD-LEDs.

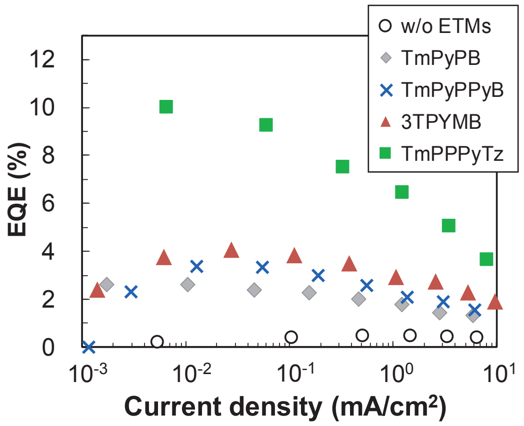

Fig. 4 EQE–current density characteristics of the QD-LEDs.

considered to be the suppression of exciton quenching. Among the QD-LEDs with an ETM, the QD-LED with TmPPPyTz exhibited a high maximum EQE of 10.0%, whereas the QD-LEDs with other ETMs exhibited maximum EQEs of 2–4%. Furthermore, we evaluated the concentration dependence of the EQEs of the QD-LEDs in which 3TPYMB or TmPPPyTz was mixed with the QDs. The QD concentration was fixed and the ETM concentration was varied. Table 1 shows the maximum EQEs with ETM concentrations of 2.0, 4.0, and 5.2 mg mL^{-1}. Both QD-LEDs exhibited the highest EQE values at 4.0 mg mL^{-1}. The results of STEM images of the QD-LEDs and atomic force microscopy evaluations of the EML films suggest that the high performance in the QD-LEDs with TmPPPyTz was not caused by the difference in the morphology of the EML.

3.2 Device characteristics of single-carrier devices

To clarify the origin of the difference in EQE among the QD-LEDs, we investigated the current of single-carrier devices. Fig. 5 shows the current density–voltage characteristics of the hole-only devices. The current density of the hole-only devices was decreased by inserting an organic ETM between the QDs and the ZnO NPs. The hole-only device with TmPPPyTz exhibited a considerably lower current density than the others. Fig. 6

Table 1 Concentration dependence of the maximum EQEs of the QD-LEDs with 3TPYMB and TmPPPyTz (2.0, 4.0, and 5.2 mg mL^{-1}).

Organic ETM concentration (mg mL^{-1})	Maximum EQE (%)	
	3TPYMB	TmPPPyTz
2.0	2.2	3.4
4.0	4.1	10.0
5.2	2.3	6.9

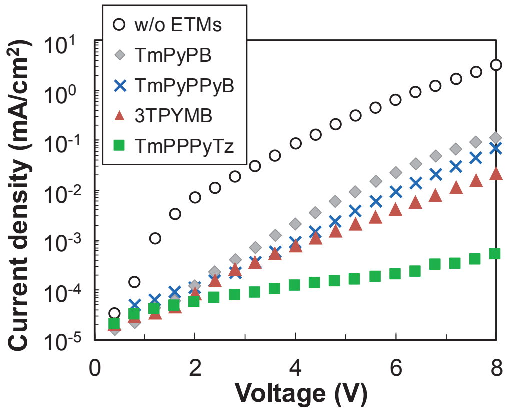

Fig. 5 Current density–voltage characteristics of the hole-only devices: ITO/PEDOT:PSS/ETM:QDs/TCTA/MoO_3/Al.

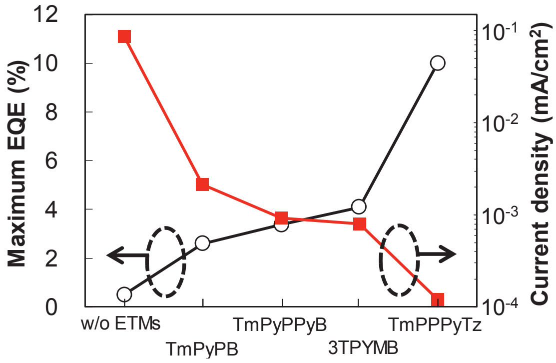

Fig. 6 Relationship between the maximum EQE and the current density of the hole-only devices at 4 V.

shows the relationship between the EQE of the QD-LEDs and the current density of the hole-only devices at 4 V. The lower the current density of the hole-only devices, the higher the EQE of the QD-LEDs. The low current density of the hole-only devices may be attribute to the suppression of hole current leakage from the QD layer. Because the QD-LEDs with TmPPPyTz demonstrated the highest EQE among all QD-LEDs, the hole suppressing ability of the organic ETMs from the QD layer is considered to be correlated with the EQE of the QD-LEDs. The current density of the electron-only devices was also evaluated. Unlike the hole transporting properties, the electron transporting properties were confirmed to be uncorrelated with the EQE.

3.3 Device characteristics of red QD-LEDs

To investigate the effect of TmPPPyTz in other colored QD-LEDs, we fabricated the QD-LEDs whose emitting layers were composed of red InP-based QDs and TmPPPyTz. The red QD-LED with TmPPPyTz exhibited an EQE of 5%, whereas the QD-LED without ETMs exhibited a substantially low EQE under 1%.

4 CONCLUSIONS

We fabricated red and green InP-based QD-LEDs using an EML combined with various organic ETMs. The EQEs and driving voltages were markedly improved by using suitable organic ETMs. By using TmPPPyTz as an ETM, we demonstrated green QD-LEDs with a high maximum EQE of 10.0% and a low driving voltage. To investigate the origin of the high EQE of the QD-LEDs with TmPPPyTz, we evaluated single-carrier devices. Our results suggest that the high EQE of the QD-LEDs with TmPPPyTz may be attributed to the suppression of hole current leakage from the QD layer.

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