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Improvement of Color Chromaticity and Efficiency in Quantum Dot Light-Emitting Diodes by Using Emitting Layer Composed with Quantum Dot and Carrier Transporting Material

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ABSTRACT

We developed cadmium-free quantum-dot light-emitting diodes (QD-LEDs) whose emitting layers are composed of QDs and an organic electron-transporting material. Wide-area coverage (~80%) of the color reproduction area specified in Recommendation ITU-R BT.2020 was achieved by the fabricated red, green, and blue QD-LEDs.

1 Introduction

Colloidal quantum dots (QDs) consisting of an inorganic nanocrystal semiconductor core and a coating of organic passivating ligands are attractive because their size-dependent optical properties are expected to be useful in optoelectronics devices [1]. The emission spectra of QDs show narrow peaks when the distribution of the core size is narrow. The narrow spectra lead to high color saturation, making QDs suitable for use in wide-color-gamut displays. The wide-color gamut for ultra-high-definition television is specified in Recommendation ITU-R BT.2020 (BT.2020). Red-, green-, and blue-emitting devices compliant with BT.2020 are required. Although QD light-emitting diodes (QD-LEDs) based on cadmium (Cd)-containing QDs [2] have achieved wide coverage of the BT.2020 color space, their potential for widespread use is limited by the toxicity of Cd. Therefore, the development of QD-LEDs with low-toxicity QDs is required.

InP- or ZnSe-based QDs have been widely investigated as promising candidates for Cd-free QDs. A red QD-LED using InP QDs and a blue QD-LED using ZnSe-based QDs showed external quantum efficiencies greater than 20% [3,4]. QDs based on materials other than InP or ZnSe, including those based on chalcopyrites such as $CuInS_2$ and $AgInS_2$, have also been investigated [5,6].

To develop efficient Cd-free QD-LEDs that emit highly saturated color, we have been investigating QD materials and the structure of QD-LEDs. We reported that the external quantum efficiency of QD-LEDs was improved by applying an emitting layer (EML) composed of QDs and an electron-transporting material [7]. Here, we report an improvement of the shape of the electroluminescence (EL) spectrum and an increase in efficiency of QD-LEDs as a result of using an EML composed of QDs and an electron-transporting material.

2 Experiment

Figure 1(a) shows the structures of the fabricated bottom-emitting QD-LEDs. The zinc oxide nanoparticles (ZnO NPs) were synthesized using a previously reported method [8]. QDA-RH001 and QDA-GO001 (Merck) were used as red and green InP QDs, respectively. ZnSeTe QDs as blue QDs [9] and $AgInS_2/GaS_x$ (AIS) core/shell QDs [10] were synthesized using previously reported methods.

The QD-LEDs were fabricated as follows. The electron-injecting layer of ZnO NPs was spin-coated onto an indium-tin oxide (ITO)-coated glass substrate at 2000 rpm under a N_2 atmosphere. Then, as shown in Fig. 1(b), the EML was formed via spin-coating from a mixed solution of QDs and electron-transporting materials. A stacked structure of the QDs and electron-transporting material layers can be formed as a result of phase separation [11]. A hole-transporting layer of tris(4-carbazoyl-9-ylphenyl)amine (TCTA), a

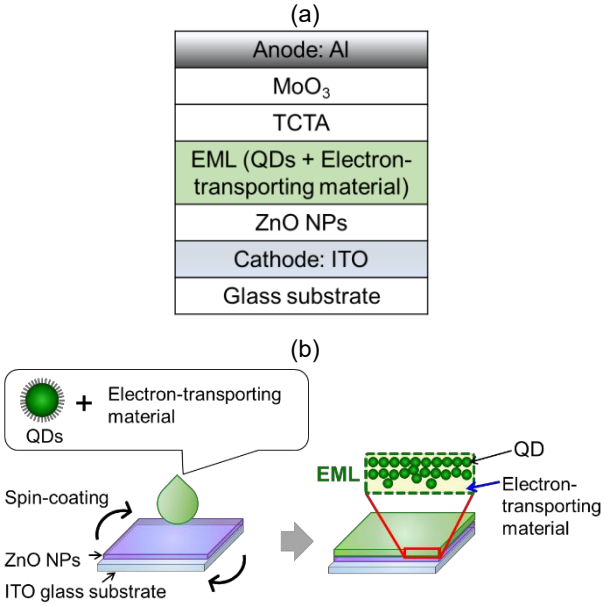

Fig. 1 (a) Device structure of the fabricated QD-LEDs and (b) the formation of an emitting layer (EML) by spin-coating a mixed solution of QDs and an electron-transporting material.

hole-injecting layer of molybdenum oxide (MoO_3), and an anode of Al were then sequentially deposited via vacuum deposition.

3 Results and Discussion

3.1 QD-LEDs using InP and ZnSeTe QDs

The fabricated QD-LEDs emitted light when a voltage was applied. Figure 2 shows the EL spectra of the blue QD-LEDs with an EML composed of only ZnSeTe QDs or a mixture of ZnSeTe QDs and the electron-transporting material tris(2,4,6-trimethyl-3-(pyridine-3-yl)phenyl)-borane (3TPYMB). In the QD-LEDs without the electron-transporting material, Mg-doped ZnO NPs were used as an electron-injecting layer instead of the ZnO NPs. The EL spectra of the QD-LED fabricated without the electron-transporting material broadened as the luminance decreased. We speculated that electrons were injected into the lower-energy defect state of ZnSeTe QDs at low voltages, causing defect-associated emission in the longer-wavelength range. By contrast, in the case of the QD-LEDs with an electron-transporting material, the EL spectra did not change as the luminance changed. In the QD-LED whose EML was composed of QDs and an electron-transporting material, electrons were injected from the electron-transporting material into the conduction-band energy level of the ZnSeTe QDs, which reduced the emission from defect levels in the EL spectra. An improvement of the EL spectrum by application of the EML composed of QDs and an electron-transporting material was observed also in the case of the InP-based green QD-LED.

Figure 3 shows the composition of the EMLs, the EL spectra, and the chromaticity coordinates for the red, green, and blue QD-LEDs. For the red and green QD-LEDs, a mixture of red InP QDs and 2,4,6-tris(*m*-pyridin-3-yl-phenyl)-triazine (TmPPyTz) and a mixture of green InP QDs and 2,4,6-tris(3′-(pyridine-3-yl)biphenyl-3-yl)-1,3,5-triazine (TmPPPyTz) and TmPPyTz were used as the EML, respectively. Narrow

(a)

	Composition of EML	
	QDs	Electron-transporting material
Red	InP	TmPPyTz
Green	InP	TmPPPyTz + TmPPyTz
Blue	ZnSeTe	3TPYMB

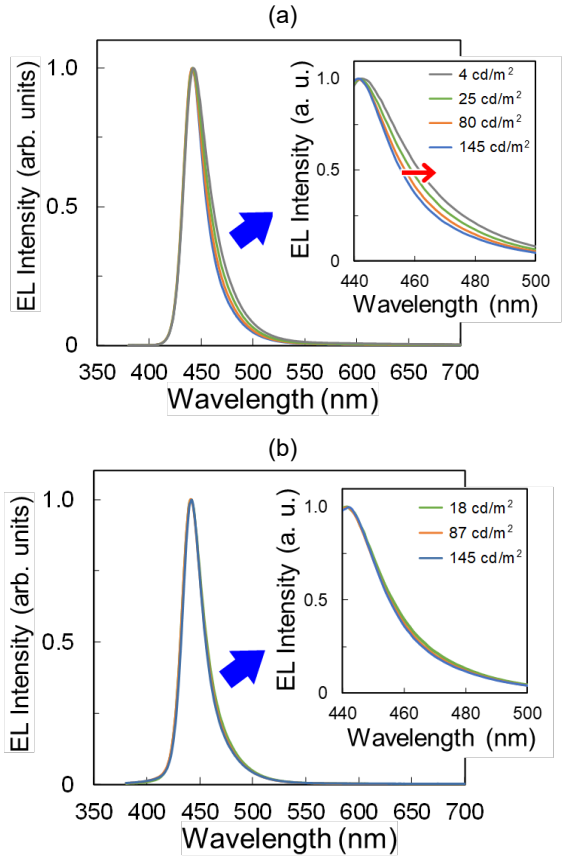

Fig. 2 EL spectra of the QD-LEDs whose EML was composed of (a) only ZnSeTe QDs and (b) the mixture of ZnSeTe QDs and ETM.

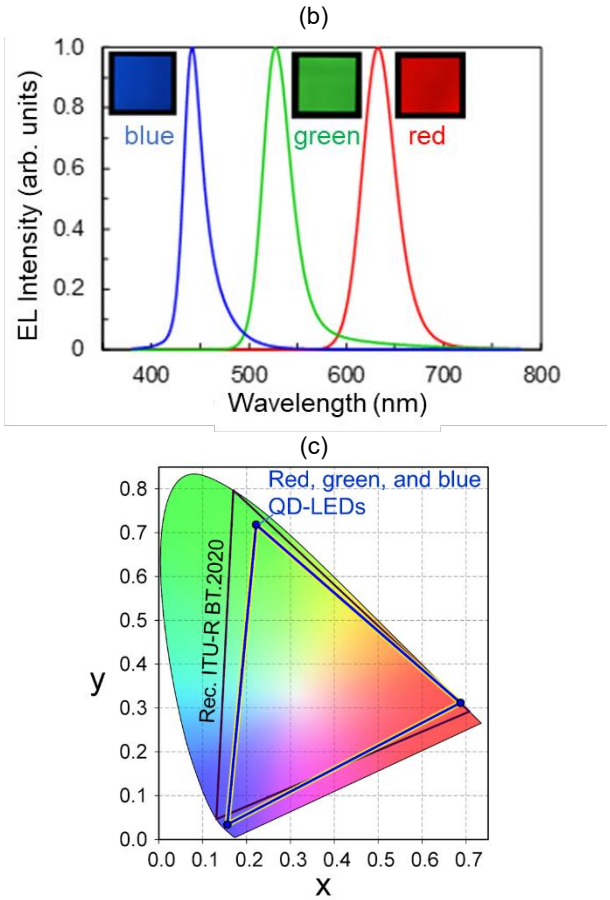

Fig. 3 (a) Composition of the EML, (b) the EL spectra, and (c) the chromaticity coordinates (CIE1931) at a luminance of 100 cd m^{-2} for the fabricated red, green, and blue QD-LEDs.

full-widths at half-maxima of 40 nm, 34 nm, and 23 nm were obtained for the red, green, and blue QD-LEDs, respectively. The calculated coverage of the color gamut (CIE1931) by the red, green, and blue QD-LEDs for BT.2020 standards was as high as 80% [12].

The EML composed of QDs and an electron-transporting material demonstrated an advantage from the viewpoint of efficiency. The external quantum efficiency of the red and green InP QD-LEDs with the EML composed of QDs and the electron-transporting material was 7%, whereas that of the red and green InP QD-LEDs with the EML composed of only QDs was as low as 4% and 0.1%, respectively.

3.2 QD-LEDs with chalcopyrite-type AIS QDs

In most cases, photoluminescence (PL) spectra of chalcopyrite-type QDs are much broader than those of II–VI and III–V semiconductor QDs because their emission originates from lattice defect sites. By contrast, $AgInS_2/GaS_x$ (AIS) core/shell QDs have been reported to exhibit an intense narrow PL peak from a band edge transition [10]. This indicates that AIS core/shell QDs are potential low-toxicity QDs.

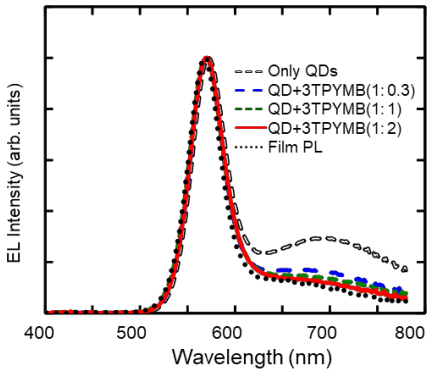

Fig. 4 The EL spectra of the QD-LEDs fabricated using AIS core/shell QDs, and the PL spectrum of the QD film.

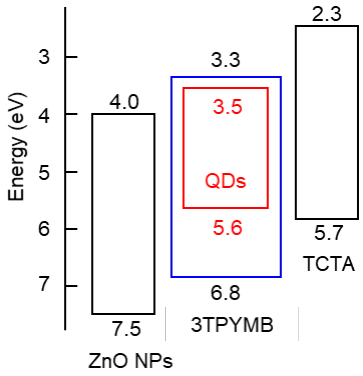

Fig. 5 Energy levels of the materials used in the QD-LEDs fabricated using AIS core/shell QDs.

We fabricated QD-LEDs with an EML composed of yellow AIS core/shell QDs and 3TPYMB as the electron-transporting material [6]. Figure 4 shows the EL spectra of the QD-LEDs. The EL spectra of the QD-LEDs whose EML was composed of only QDs included a large defect-based emission component in the wavelength range from 600 to 800 nm. The intensity of the defect emission in the EL spectra was higher than that in the PL spectrum of the QD film. The difference between the EL and PL spectra suggests the existence of specific defect sites between the AIS core and the GaS_x shell. The defect emission in the EL spectra was found to be suppressed with increasing amount of 3TPYMB in the EML. For the QD-LED without 3TPYMB, there is an electron-injection barrier of 0.5 eV at the interface between the ZnO NPs and AIS core/shell QDs, as shown in Fig. 5. The electrons that could not cross the injection barrier were more likely to be injected into the defect levels of the QDs. By contrast, for the QD-LEDs with an EML composed of QDs and 3TPYMB, the number of electrons injected into the defect level of the QDs decreased because the direct injection route for the electrons was blocked, which led to suppression of the defect emission. The improvement of the EL spectra by incorporating an EML composed of QDs and an electron-transporting material was also confirmed in the QD-LED prepared using green Ag–In–Ga–S/GaS_x core/shell QDs [13].

4 Conclusions

We demonstrated an improvement of the EL spectrum shape and the efficiency of QD-LEDs prepared using an EML composed of QDs and an electron-transporting material. Wide-area coverage (~80%) of the color reproduction area specified in Recommendation ITU-R BT.2020 was achieved by the fabricated red, green, and blue QD-LEDs whose EML were InP and ZnSeTe QDs and electron-transporting materials. The EL spectrum of the QD-LED fabricated using chalcopyrite-type AIS core/shell QDs was also improved by incorporating an EML composed of QDs and an electron-transporting material.

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