

Green Electroluminescence Generated by Band-edge Transition in Ag–In–Ga–S/GaS_x Core/shell Quantum Dots

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ABSTRACT

Quantum dot (QD) light-emitting diodes (LEDs) that exhibit vivid green emission were fabricated using Ag–In–Ga–S/GaS_x core/shell QDs. For these QD-LEDs, the broad defect emission in electroluminescence was larger than that in photoluminescence. The addition of an electron transporting material to the emitting layer effectively suppressed the defect emission.

1 INTRODUCTION

Ultra-high-definition television systems have been researched and developed to realize television services that provide realistic visuals. Their wide color gamut, which can express a wider range of colors than a conventional high-definition television, requires red, green, and blue primary colors with extremely high color purity.¹ Quantum dots (QDs), which emit luminescence with high color purity, have thus attracted attention. Their narrow spectra are suitable for use in displays with a wide color gamut. Therefore, the application of QDs to electroluminescence (EL) devices has been studied.² QD light-emitting diodes (LEDs) with a QD film as an emitting layer (EML) enable the fabrication of thin, lightweight, and flexible displays with a wide color gamut and high image quality.

Advances in device structure and QD materials have led to improvements in QD-LEDs. Although Cd-based QD-LEDs have excellent EL properties, the toxicity of Cd remains a problem. Attempts have thus been made to fabricate QD-LEDs with low-toxicity QDs.³ Unfortunately, the luminous efficiency and color purity of low-toxicity QD-LEDs are inferior to those of Cd-based ones.

Chalcopyrite-type QDs composed of I–III–VI₂-group elements have been investigated. These QDs are promising luminescent materials because they are direct-transition semiconductors and are composed of low-toxicity elements. The solid-solution nanoparticles (NPs) of AgInS₂–ZnS⁴ and AgInS₂–AgGaS₂⁵ have tunable bandgaps that depend on the particle size as well

as Zn or Ga content. In addition, their photoluminescence quantum yield (PLQY) is high enough for use in LEDs. QD-LEDs with AgInS₂-based NPs have been reported.⁶ However, their emission spectra are much broader than those of II–VI and III–V semiconductor QDs due to emission originating at lattice defect sites.

Recently, I–III–VI-based QDs have been reported to generate intense, spectrally narrow photoluminescence (PL) from a band-edge transition.⁷ Although AgInS₂ QDs exhibit a broad PL peak, AgInS₂/GaS_x core/shell QDs exhibit an intense narrow PL peak.

Furthermore, it has been reported that Ag–In–Ga–S/GaS_x (AIGS) core/shell QDs, which include solid-solution NPs of AgInS₂ and AgGaS₂ with a GaS_x shell, exhibit band-edge emission, the wavelength of which is tunable in the visible-light wavelength region.⁸ These findings indicate that AIGS core/shell QDs are a promising candidate material for QD-LEDs.

In the present study, we fabricated QD-LEDs using AIGS core/shell QDs that exhibit vivid green emission and investigated their EL properties. The fabricated QD-LEDs exhibited broad defect emission and sharp band-edge emission. The defect emission was effectively suppressed by the addition of an electron transporting material (ETM) in the EML, resulting in enhanced color purity of the EL emission.

2 EXPERIMENTS

2.1 Synthesis of AIGS QDs

AIGS core/shell QDs were synthesized using the following method.⁸ Elemental sulfur powder (0.23 mmol), as an S²⁻ precursor, and a mixture of silver acetate (0.083 mmol), gallium acetylacetonate (0.075 mmol), and indium acetylacetonate (0.05 mmol), as a metal ion precursor, were put into a test tube. After the addition of a mixture of oleylamine (2.75 mL) and 1-dodecanethiol (0.25 mL), the solution was heated at 300 °C for 10 min with vigorous stirring under a N₂ atmosphere. Large

particles were removed by centrifugation, and AIGS QDs were precipitated by the addition of excess methanol. 10 nmol (in terms of NPs) of AIGS core NPs were dispersed in chloroform and mixed with a gallium acetylacetonate (0.053 mmol) and thiourea (0.053 mmol) suspension in oleylamine (3.0 mL). The reaction mixture was heated to 300 °C for 15 min. The AIGS core/shell QDs were washed several times with methanol and ethanol and uniformly dissolved in chloroform.

2.2 Fabrication of QD-LEDs

Glass substrates, onto which a 100-nm-thick indium tin oxide (ITO) cathode was patterned, were degreased by sequential sonication in a detergent solution and ethanol, followed by further treatment using an ultraviolet (UV)–ozone cleaner. A 40-nm-thick layer of ZnO NPs, as the electron injection layer (EIL), was formed by spin-coating a 1-butanol dispersion prepared in accordance with a previously reported method.⁹ The AIGS core/shell QD concentration was fixed at 2.3 mg mL⁻¹ in chloroform, and tris(2,4,6-trimethyl-3-(pyridin-3-yl)phenyl)borane (3TPYMB), as an ETM, was added to the dispersions to yield QD:3TPYMB = 1:1.3 by weight. The QD dispersions for EMLs were spin-coated onto the EIL. The substrates were then loaded into a vacuum deposition chamber, and a 40-nm-thick hole transport layer (HTL), consisting of tris(4-carbazoyl-9-ylphenyl) amine (TCTA), a 10-nm-thick hole injection layer (HIL) made of MoO₃, and an 80-nm-thick anode made of Al, was deposited. The devices were encapsulated with a glass cap under a N₂ atmosphere.

3 RESULTS AND DISCUSSION

3.1 PL characteristics of AIGS core/shell QDs

Fig. 1 shows the PL spectra of the synthesized AIGS core/shell QDs dispersed in chloroform and those embedded in a spin-coated film. The spectra are normalized with respect to the band-edge emission peak intensity. The QD dispersion exhibited green PL with an intense sharp peak at approximately 539 nm and a broad shoulder at wavelengths longer than 600 nm. The appearance of a sharp peak derived from a band-edge transition implies the effective suppression of surface defects by the GaS_x shell. The full-width at half maximum value was 36 and 39 nm for the dispersion and film, respectively. The PLQY of the dispersion was 10.1%.

3.2 EL spectra from AIGS core/shell QDs

Fig. 2(a) shows the structure of the QD-LED fabricated in this study with an EML consisting of only the AIGS core/shell QDs. Fig. 2(b) shows the corresponding spectra recorded under two luminance conditions; the intensity was normalized with respect to the peak wavelength of the sharp band-edge emission. The inset photograph of the

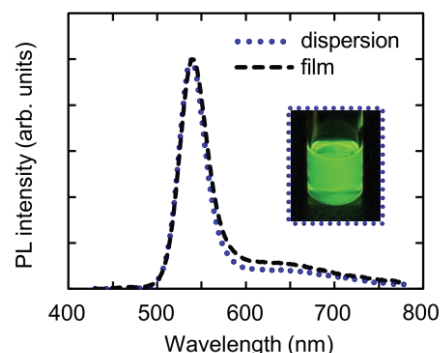


Fig. 1 PL spectra of synthesized AIGS core/shell QDs dispersed in chloroform and an AIGS core/shell QD film. Inset shows a photograph of an AIGS core/shell QD dispersion under UV light.

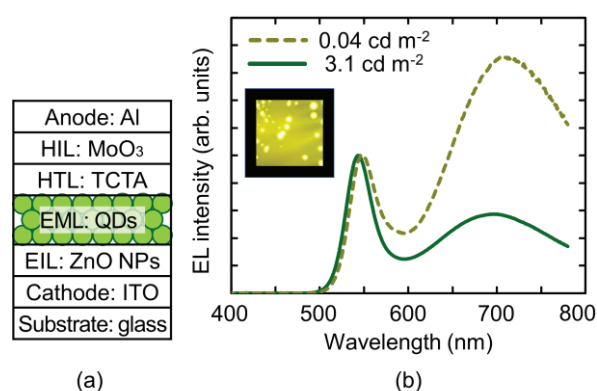


Fig. 2 (a) Structure of a QD-LED with an EML consisting of only AIGS core/shell QDs. (b) EL spectra of the QD-LED for two values of luminance. Inset shows a photograph of EL from the QD-LED at approximately 1 cd m⁻².

AIGS QD-LEDs at approximately 1 cd m⁻² shows yellow EL with some bright spots due to the non-uniformity of the QD layer. Of note, the EL peaks derived from defect sites for both luminance conditions are more distinct compared to those in the corresponding PL spectrum of the QD film (see Fig. 1).

The ratio of defect emission to band-edge emission in the EL spectra at 3.1 cd m⁻² was lower than that at 0.04 cd m⁻². The difference in the intensity ratio of defect emission to band-edge emission between EL and PL suggests the existence of specific defect sites between the GaS_x shell and AIGS core. If such defect sites can more easily accept externally injected electrons and/or holes than their photogenerated counterparts, it would explain the higher ratio of defect emission in the EL spectra. Even if such defect sites exist, electrons or holes, which overflow at defect sites due to an increase in the injection rate, flow to the conduction or valence bands, respectively. This might explain why the intensity ratio of

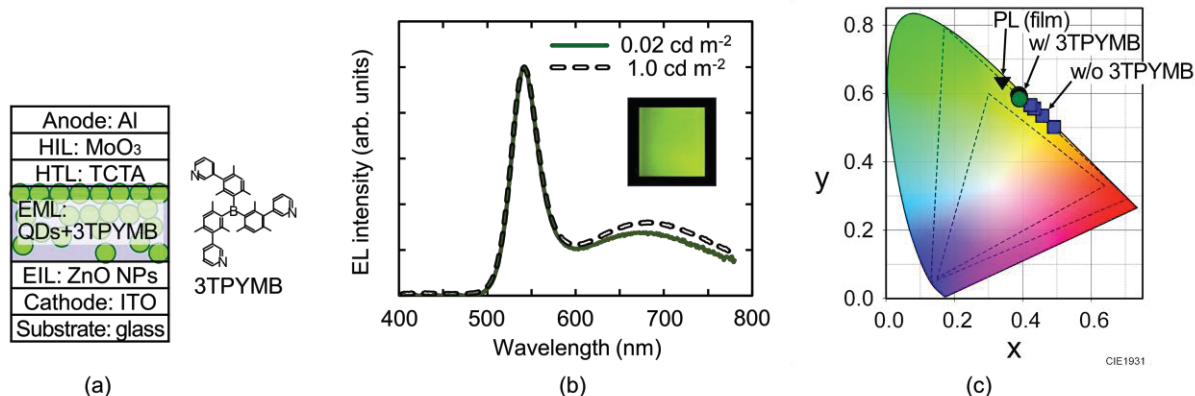


Fig. 3 (a) Structure of a QD-LED with an EML containing QDs mixed with 3TPYMB. (b) EL spectra of the QD-LED with 3TPYMB for two values of luminance. Inset shows a photograph of EL from the QD-LED at approximately 1 cd m⁻². (c) Chromaticity variation according to the luminance of QD-LEDs without and with 3TPYMB in the CIE 1931 color space.

defect emission to band-edge emission at 3.1 cd m⁻² was lower than that at 0.04 cd m⁻².

3.3 Suppression of defect emission by mixing ETM into QDs

To improve the purity of band-edge emission, we added 3TPYMB as an ETM into the QD film, as schematically shown in Fig. 3(a). The EML was spin-coated from chloroform solutions containing QDs and 3TPYMB with a mixing ratio of 1:1.3 by weight. It was found that the ETM effectively suppressed defect emission, as shown in Fig. 3(b), which shows EL spectra recorded under two luminance conditions. The inset photograph shows the EL from the QD-LEDs at approximately 1 cd m⁻²; it is greener than that shown in Fig. 2(b) and uniform.

The existence of specific defect sites that preferentially accept externally injected electrons or holes was suggested above to explain the difference between PL and EL spectra. Because the addition of ETM suppressed defect emission, we speculate that specific defect sites exist in the electron passes around the conduction band edge of the AIGS core.

Fig. 3(c) shows the chromaticity variation according to the luminance of QD-LEDs with and without 3TPYMB in the International Commission on Illumination (CIE) 1931 color space. The QD-LED without 3TPYMB exhibited a large change in chromaticity, from (0.491, 0.502) to (0.422, 0.566), whereas that with 3TPYMB exhibited only a slight change in chromaticity, from (0.388, 0.596) to (0.390, 0.584). Although the chromaticity of the QD-LED with 3TPYMB was not as good as that of the PL from the QD film, namely (0.340, 0.635), it was greatly improved compared to that of the QD-LED without 3TPYMB.

The suppression of defect emission was achieved by injecting electrons from the 3TPYMB into the QDs. It is necessary for electrons to exceed the injection barrier from the EIL to the QDs under the applied voltage; electrons are more likely to be injected into the defect sites

of QDs at a low applied voltage. However, when the QDs were embedded in 3TPYMB and the direct injection route for the electrons was blocked, the number of electrons trapped at the EIL–QD interface likely decreased. Therefore, the electrons were less likely to be trapped at the defect sites, which led to the suppression of defect emission.

4 CONCLUSIONS

We demonstrated the EL characteristics of QD-LEDs fabricated using AIGS core/shell QDs with green band-edge emission. EL emission mainly composed of band-edge emission was observed for the AIGS-based QD-LEDs. However, the EL spectra of the QD-LEDs were found to include a large defect emission component compared with the PL spectra of the QD film. This defect emission was attributed to the electrons injected into the EML being easily trapped at the defect sites in the QDs. Mixing 3TPYMB as an ETM into the EML effectively suppressed the defect emission, and thus enhanced the EL characteristics.

REFERENCES

- [1] K. Masaoka, Y. Nishida, and M. Sugawara, "Designing display primaries with currently available light sources for UHDTV wide-gamut system colorimetry," *Opt. Express* **22**, 19069 (2014).
- [2] Y. Shirasaki, G. J. Supran, M. G. Bawendi, and V. Bulovic, "Emergence of colloidal quantum-dot light-emitting technologies," *Nat. Photonics* **7**, 13 (2013).
- [3] C. Ippen, W. Guo, D. Zehnder, D. Kim, J. Manders, D. Barrera, B. Newmeyer, D. Hamilton, C. Wang, C. Hotz, R. Ma, J. K. Bin, B. Kim, K. Kim, K. Jang, J. Park, T. Lee, W. Y. Kim, and J. Lee, "High efficiency heavy metal free QD - LEDs for next generation

displays,” *J. Soc. Inf. Disp.* **27**, 338 (2019).

- [4] T. Kameyama, T. Takahashi, T. Machida, Y. Kamiya, T. Yamamoto, S. Kuwabata, and T. Torimoto, “Controlling the Electronic Energy Structure of ZnS–AgInS₂ Solid Solution Nanocrystals for Photoluminescence and Photocatalytic Hydrogen Evolution,” *J. Phys. Chem. C* **119**, 24740 (2015).
- [5] T. Uematsu, T. Doi, T. Torimoto, and S. Kuwabata, “Preparation of Luminescent AgInS₂–AgGaS₂ Solid Solution Nanoparticles and Their Optical Properties,” *J. Phys. Chem. Lett.* **1**, 3283 (2010).
- [6] G. Motomura, K. Ogura, T. Kameyama, T. Torimoto, T. Uematsu, S. Kuwabata, and T. Tsuzuki, “Efficient quantum-dot light-emitting diodes using ZnS–AgInS₂ solid-solution quantum dots in combination with organic charge-transport materials,” *Appl. Phys. Lett.* **116**, 093302 (2020).
- [7] T. Uematsu, K. Wajima, D. K. Sharma, S. Hirata, T. Yamamoto, T. Kameyama, M. Vacha, T. Torimoto, and S. Kuwabata, “Narrow band-edge photoluminescence from AgInS₂ semiconductor nanoparticles by the formation of amorphous III–VI semiconductor shells,” *NPG Asia Mater.* **10**, 713 (2018).
- [8] T. Kameyama, M. Kishi, C. Miyamae, D. K. Sharma, S. Hirata, T. Yamamoto, T. Uematsu, M. Vacha, S. Kuwabata, and T. Torimoto, “Wavelength-Tunable Band-Edge Photoluminescence of Nonstoichiometric Ag–In–S Nanoparticles via Ga³⁺ Doping,” *ACS Appl. Mater. Interfaces* **10**, 42844 (2018).
- [9] J. Kwak, W. K. Bae, D. Lee, I. Park, J. Lim, M. Park, H. Cho, H. Woo, D. Y. Yoon, K. Char, S. Lee, and C. Lee, “Bright and Efficient Full-Color Colloidal Quantum Dot Light-Emitting Diodes Using an Inverted Device Structure,” *Nano Lett.* **12**, 2362 (2012).