Interfacial engineering toward improved characteristics of printed light-emitting diodes based on green emissive InP/ZnSe/ZnS quantum dots

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Keywords: quantum dots, light-emitting devices, InP, green emission.

ABSTRACT

A controlled green electroluminescent (EL) spectrum was obtained owing to improved emission recombination into InP/ZnSe/ZnS quantum dot (QD) modified both the ligands and ZnSe intermediate shell. Green emissive InP/ZnSe/ZnS QD light-emitting diode using self-assembly monolayer-treated NiOₓ hole-injection layer exhibits a narrower EL spectrum and almost the same EL intensity at low current density, compared to yellow-green emissive polymer light-emitting diode based poly(9,9-dioctylfluorenyl-alt-benzothiadiazole).

1 Introduction

Organic light-emitting diodes (OLEDs) with a long lifetime and excellent durability for flat-panel display applications have been realized. There are some requirements for OLEDs when they are used not only in display applications but also as various lighting sources. Microlight sources with high color purity are also useful for virtual reality and augmented reality displays and sensor applications for developing the Internet of Things (IoT).

Quantum dots (QDs) have been widely noticed due to their unique optoelectronic properties of size-tunable emission wavelengths, narrow emission linewidths, high photoluminescence (PL) quantum yield, and inherent photophysical stability. Although the application of hybrid OLEDs containing QDs as an emissive layer (QD-OLED) is promising, widely studied cadmium-based QDs with excellent luminescence properties [1] are toxic to the environment and living organisms. Recently, high efficient red QD-OLEDs containing InP-based QDs have been realized. [2] The development of green and blue InP-based QDs is essential for realizing high-performance full-color QD-OLEDs displays.

The key to obtaining a high luminance is to improve the carrier injection into InP cores. QDs with core/shell structures and ligands have various interfaces themselves. From the viewpoints of interfacial engineering, such as organic/inorganic and inorganic/inorganic interfaces, the research and development of fabrication in QD-OLEDs are essential for obtaining high device performance.

In this study, we investigated the optical properties of green emissive InP/ZnSe/ZnS QDs with different ligands and ZnSe thicknesses and their application to the hybrid light-emitting diodes using solution-processed inorganic wide-bandgap oxides as the carrier transporting layers.

2 Experiment

All layers except for indium-tin-oxide (ITO) anode and Ag cathode were fabricated on the glass substrate by spin coating. A substrate was degreased with solvents and cleaned in a UV ozone chamber.

Zinc oxide and Ni oxide layers were fabricated by the sol-gel and combustion methods, respectively. InP QDs synthesized were described in detail elsewhere.[3]

The current density-voltage-luminance (J–V–L) characteristics of devices were obtained using a digital sourcemeter (Keithley2400), and a luminance meter (Minolta LS-100). The electroluminescent (EL) spectra were measured using a photonic multichannel spectral analyzer (Hamamatsu Photonics, PMA-11). The PL spectra, and absolute PL quantum yields (PLQYs) were measured using an absolute PL quantum yield measurement system (Hamamatsu Photonics Quantaurus-QY).

3 Results and Discussion

The QDs are modified by organic ligands, to be specific oleic acid, to become solution processable. To figure out the effect of ligands on device characteristics, we adopted two kinds of InP/ZnSe/Zn QDs (QD1, QD2) as a light-emitting layer (QD-OLED) is promising, widely studied cadmium-based QDs with excellent luminescence properties [1] are toxic to the environment and living organisms. Recently, high efficient red QD-OLEDs containing InP-based QDs have been realized. [2] The development of green and blue InP-based QDs is essential for realizing high-performance full-color QD-OLEDs displays.

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layer) / poly[(9,9-di(3,3’-N,N’-trimethylammonium) propylfluorenyl-2,7-diyl)-alt-co-(9,9-dioctylfluorenyl-2,7-diyl)] diiodide salt, PFN (interlayer) / QDs / tris(4-carbazoyl-9-ylphenyl)amine, TCTA (hole transport layer) / MoOx / Ag (anode).

The normalized EL spectra of two devices with different QDs and normalized PL spectra of QD films are shown in Fig. 1. The shape of EL spectrum of QD2 was good agreement with that of PL spectrum. QD1 and QD2 devices emitted yellow-green light at peak wavelengths of approximately 560 nm. For the QD2 device, the blue emission from the TCTA layer below 500 nm was suppressed by the exchange ligand, pointing out that the emission recombination within QDs was improved. The ligand of QD was partially changed from oleic acid to Cl, which further improved the color purity. The narrowing of the EL spectrum with a full width at half maximum of approximately 50 nm was achieved from all-solution processed QD-OLED except for electrodes.

![Normalized EL spectra of inverted devices and normalized PL spectra of QD films.](image)

The multilayer structure is useful for achieving effective carrier injection and transport and improving emission efficiency. It is important to develop various interlayers to achieve all-solution-processed devices. A wide-bandgap p-type inorganic semiconductor, NiOx is widely used in organic and organic-inorganic hybrid devices. Using NiOx is expected to enhance carrier confinement to the emission layer due to the high conduction band energy of NiOx. To suppress the surface defects of printed NiOx film on the printed light-emitting diodes, the improvement of hole injection properties was confirmed by applying a self-assembly monolayer (SAM) to printed NiOx. By using poly[N,N'-bis(4-butylphenyl)-N,N’-bis(phenyl)-benzidine], poly-TPD as the hole transport layer, poly(vinyl carbazole), PVCz as the electron-blocking layer, QD as the emission layer, and ZnOx as the electron injection layer, a sharper EL spectrum can be obtained, which is expected to be applied to QD-OLED devices. The hole injection properties of the NiOx thin film treated with 1H,1H,2H,2H-perfluoro-n-octyl phosphonic acid (FOPA), were significantly improved. Green emissive InP/ZnSe/ZnS QD-OLED using SAM-treated NiOx hole-injection layer exhibited a narrower EL spectrum and almost the same EL intensity at low current density of 10

![Fig. 2 (a) Photographs of typical QD solutions under UV illuminated light (λ=365 nm) and normalized PL spectra of QDs in solution with different ZnSe thicknesses.](image)
mA/cm², compared to yellow-green emissive polymer light-emitting diode based poly(9,9-dioctylfluorenyl-alt-benzothiadiazole), F8BT, as shown in Fig. 3. NiOx functioned as an electron-blocking layer and could be effective in confining electrons to the luminescent layer. The difference between the EL and PL spectra suggests the presence of defects.

**Fig. 3 Typical EL spectra of ITO/NiOx (25 nm)/poly-TPD (20 nm)/PVCz (5-10 nm)/QD/ZnOx (50 nm)/PFN (< 5nm)/Ag and ITO/NiOx/poly-TPD/F8BT/PFN/Ag at low current densities of 10 mA/cm², and PL spectrum of QD.**

Although the QDs usually exhibited excellent PLQYs in the solution state, their PLQYs in the closely packed thin film become markedly reduced as a result of the efficient nonradiative Förster resonance energy transfer (FRET). Increased ZnSe thickness suppresses the nonradiative FRET. Partial Cl ligand exchange leads to improved carrier injection and recombination into QDs. PLQY of QD with increased ZnSe thickness (ZnSe*3) and partial Cl ligand exchange was estimated to be approximately 20-30 %. The device with QD utilizing only oleic acid ligand hardly emitted. The thin QD layer thickness leads to improved carrier injection from transporting layers. For QD with increased ZnSe thickness (ZnSe*3) and partial Cl ligand exchange, the typical device with FOPA-treated NiOx (20 nm) exhibited a maximum luminance of 4000 cd/m², as shown in Fig.4. The thin QD layer thickness also results in the improved J-V characteristic.

**4 Conclusions**

Modified ligands and ZnSe intermediate shell and SAM-treated NiOx layer result in improved EL emission. This work is anticipated to be useful for the development of solution-processed QD-OLED.

**References**

