Electrical and optical properties of blue organic light-emitting devices fabricated utilizing color conversion CdSe and CdSe/ZnS quantum dots embedded in a poly(N-vibyl carbazole) hole transport layer

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Abstract: Blue organic light-emitting devices (OLEDs) with color conversion quantum dots (QDs) embedded in a poly(N-vinyl carbazole) (PVK) hole transport layer (HTL) were fabricated. The absorbance and the photoluminescence spectra for the CdSe and the CdSe/ZnS QDs showed dominant exciton peaks. Current densities as functions of the voltage showed enhanced hole trapping and a decreased hole current in the OLEDs containing CdSe and CdSe/ZnS QDs embedded in a HTL. The phenomena were intensified due to the existence of the ZnS shell. The luminance-voltage curve and the electroluminescence spectra showed that the brightness of the blue OLEDs fabricated utilizing the HTL based on CdSe and CdSe/ZnS QDs embedded in a PVK layer reached over 3,000 cd/m^2 and that the dominant exciton peak was shifted to longer wavelength.

OCIS codes: (230.0230) Optical devices; (230.5170) Photodiodes; (230.5590) Quantum-well, -wire and -dot devices.

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1. Introduction

Rapid advancements in the growth technology for organic layers have made possible the fabrication of high-efficiency organic light-emitting devices (OLEDs) for applications in full color displays [1–3]. OLEDs have emerged as excellent candidates for potential applications in mobile displays, flat panel displays and lighting sources with excellent advantages of low-power consumption, fast response time, thin layer, high contrast ratio and low-cost production. Because, however, organic materials with low durability in the presence of moisture and oxidation are used in the fabrication of OLEDs, the stability of the OLEDs is low due to their degradation [4,5]. Blue OLEDs still have inherent problems of low efficiency, poor color purity and short lifetime in comparison with red or green OLEDs [6]. Alternative fabrication technologies for fabricating OLEDs utilizing quantum dots (QDs) have been suggested to achieve high efficiency, high stability, high durability and low cost [7–9], but the efficiencies of OLEDs fabricated utilizing QDs with low dispersion and low carrier injection due to band-gap alignment with a supporting layer are still low. Even though some studies on the fabrication and the device characteristics of blue OLEDs utilizing QDs embedded in a supporting layer have been performed [10–12], very few studies concerning the electrical and the optical properties of OLEDs with color conversion QDs embedded in an organic layer have been reported.

This paper reports data for the electrical and the optical properties of blue OLEDs fabricated utilizing color conversion CdSe and CdSe/ZnS QDs embedded in a poly(N-vinyl carbazole) (PVK) HTL. Current density-voltage-luminance and electroluminescence (EL) measurements were performed to investigate electrical and optical properties of the blue OLEDs with color conversion CdSe and CdSe/ZnS QDs embedded in a PVK HTL.

2. Experimental details

The blue OLEDs with color conversion CdSe and CdSe/ZnS QDs embedded in a PVK HTL used in this study were fabricated on indium-tin-oxide (ITO) layers coated on glass substrates. The sheet resistivity and the thickness of the ITO layer coated on the glass substrates used in this study were 15 ohm/square and 100 nm, respectively. The ITO substrates were cleaned in trichloroethylene, acetone, and methanol at 60°C for 15 min by using an ultrasonic cleaner and were rinsed in de-ionized water thoroughly. After the chemically cleaned ITO substrates had been dried by using N_2 gas with a purity of 99.9999%, the surfaces of the ITO substrates were treated with an ultraviolet-ozone cleaner for 10 min at room temperature and a system

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pressure of 1 atm. After the prepared ITO substrates had been introduced into the evaporation chamber through a glove box in a high-purity N_2 atmosphere, the organic layers and the metal layer were deposited on the ITO substrates at a substrate temperature of 27°C and a system pressure of 9.5×10^{-7} Torr. The deposition rates of the organic layers and the metal layer were approximately 1 and 1.5 Å/s, respectively, which were controlled by using a quartz crystal deposition rate/thickness monitor (Inficon, SQM-160). The poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) purchased from Sigma-Aldrich was spin-coated on the ITO-coated glass substrates and then annealed at 150°C for 10 min. The solutions of CdSe and CdSeZnS were synthesized in toluene at concentrations of 10 and 15 mg/ml, respectively. The QD solution and PVK solution blended with 0.7 wt% chlorobenzene were stirred at a 2:1 ratio for 12 h. The compound solutions were spin-coated on the PEDOT:PSS layer and then annealed at 150°C for 10 min. The solution process was performed in a glove box under a nitrogen atmosphere.

The two kind of OLEDs with color conversion QDs embedded in the PVK HTL used in this study were deposited on ITO substrates and consisted of the following structures from the top: an Al cathode electrode (200 nm)/a lithium quinolate (Liq) electron injection layer (EIL) (0.5 nm)/a 4,7-diphenyl-1,10-phenanthroline (BPhen) electron transport layer (30 nm)/a 1,4-bis(2,2-diphenylvinyl) biphenyl (DPVBi) (30 nm) emitting layer (EML)/a N,N′-diphenyl-N,N′-bis(1-naphthyl)-1,1′-biphenyl-4,4″-diamine (NPB) (15 nm) spacer layer/color conversion CdSe or CdSe/ZnS QDs embedded a PVK HTL/a PEDOT:PSS hole injection layer (HIL) (40 nm)/an ITO anode (150 nm)/a glass substrate. The NPB spacer layer was used to enhance radiative energy transfer from the blue EML to the color conversion QDs [13,14]. The OLEDs with HTLs containing CdSe and CdSe/ZnS QDs are denoted by devices I and II, respectively.

Schematic diagrams of the OLED structures and their corresponding energy bands are shown in Figs. 1(a) and 1(b), respectively [15–17]. A desiccant material was used to absorb the residual moisture and oxygen in the encapsulated device. The blue OLEDs were encapsulated by using a covering glass and an adhesive epoxy sealant. The current-voltage characteristics were measured on a programmable electrometer with built-in current and voltage measurement units (M6100, McScience). The brightness was measured by using a brightness meter, and the EL spectrum was measured by using a luminescence spectrometer (CS-1000, Minolta).

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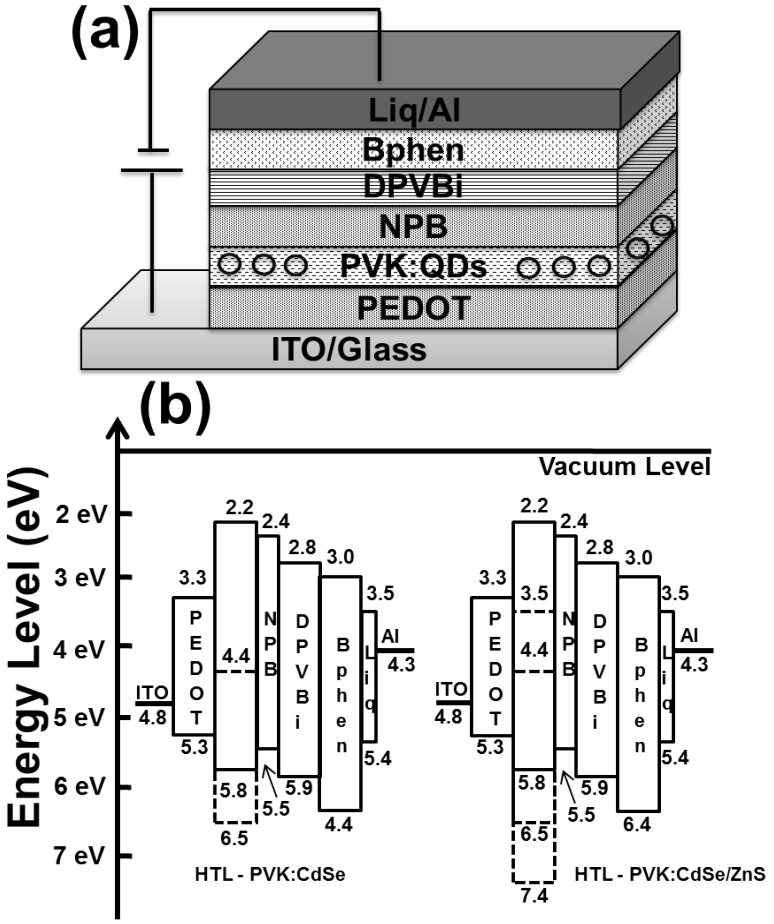

Fig. 1. Schematic diagrams of the (a) blue organic light-emitting device (OLED) structure and (b) corresponding energy bands of the OLEDs containing CdSe quantum dots (QDs) or CdSe/ZnS QDs.

3. Results and discussion

Figure 2 shows the absorption and the photoluminescence (PL) spectra of (a) the CdSe and (b) the CdSe/ZnS QDs in toluene, respectively. The dominant absorption peaks around 450 nm shown in Figs. 2(a) and 2(b) correspond to the CdSe and the CdSe/ZnS QDs. The dominant PL exciton peaks at 598 and 600 nm shown in Figs. 2(a) and 2(b) are also related to the CdSe and the CdSe/ZnS QDs, respectively. While the shapes of the PL peaks for the CdSe and the CdSe/ZnS QDs are similar, the peak position of the CdSe/ZnS QDs is slightly shifted to longer wavelength in comparison with that of the CdSe QDs. The red shift of the PL peak for CdSe/ZnS QDs is attributed to an enhancement of the carrier traps in the CdSe core QDs with a ZnS shell, resulting in an increase in the generation and the injection of carriers in the CdSe core QDs [17,18]. The full width at half maximum (FWHM) of the PL spectrum for the CdSe/ZnS QDs is larger than that for the CdSe QDs due to the interaction between the CdSe core and the ZnS shell [19].

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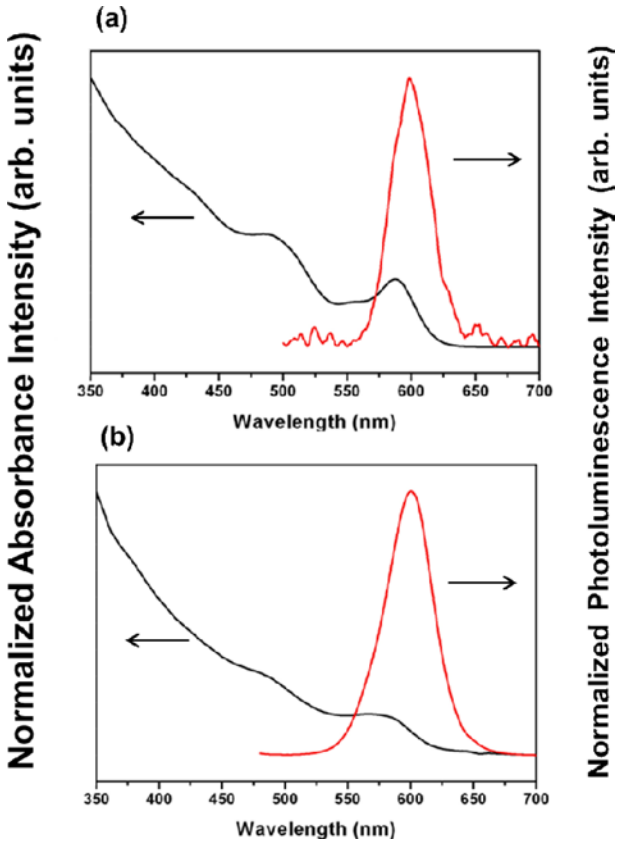

Fig. 2. Normalized absorption and photoluminescence spectra of the (a) CdSe quantum dots (QDs) and (b) CdSe/ZnS QDs.

Current densities as functions of the applied voltage and luminances as functions of the applied voltage for blue OLEDs are shown in Figs. 3(a) and 3(b), respectively. Two samples were fabricated for each device, and four measurements were performed to obtain the device characteristics of the samples. The effects on the hole-injection and -transport properties of the embedded color conversion HTL were investigated by using the results for the current densities as functions of the applied voltage, which can be attributed to the ohmic, trap-limited space-charge-limited current (SCLC), trap-filled SCLC, and trap-free SCLC characteristics [20,21]. The variation in the current density of device II was related to trap-limited SCLC above 6 V, resulting in a decrease in the current density because CdSe/ZnS QDs played an important role in enhancing the trapping of holes while that of device I represented trap-filled SCLC between 6 and 9 V and eventually shaped trap-free SCLC above 9 V. The brightness of device II at 9 V was much lower than that of device I because the carrier trapping and optical absorption forces of the CdSe/ZnS QDs were stronger than those of the CdSe QDs resulting from the existence of the ZnS shell.

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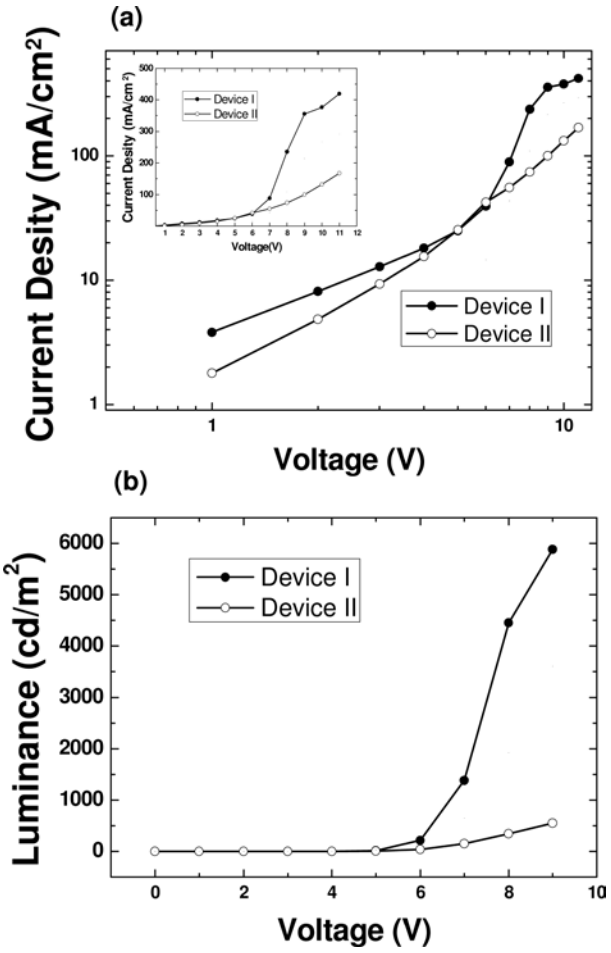

Fig. 3. (a) Current densities as functions of the applied voltage and (b) luminances as functions of the applied voltage for devices I and II. Filled circles and opened circles represent devices I and II, respectively.

The luminance efficiencies as functions of the current density for devices I and II are shown in Fig. 4. The luminance efficiencies of devices I and II increased rapidly with increasing current density to approximately 100 mA/cm^2, after which they remained fairly constant at values of 1.10 and 0.14 cd/A, respectively. The lower efficiency of device I in comparison with that of device II originated from the decrease of the current density and the brightness due to the strong carrier trapping and optical absorption forces resulting from the existence of the ZnS shell.

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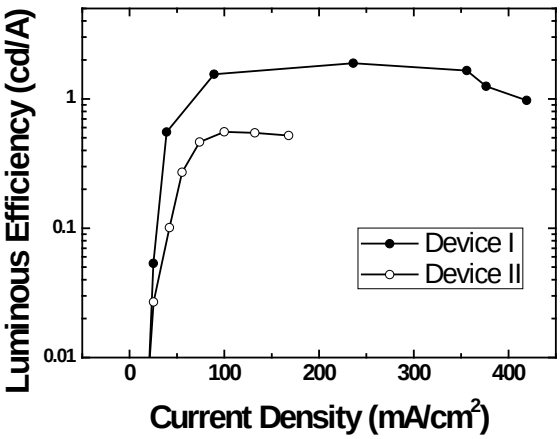

Fig. 4. Luminance efficiencies as functions of the current density for devices I and II. Filled circles and opened circles represent devices I and II, respectively.

The EL spectra of the OLEDs were related to the absorption and PL spectra of the CdSe and the CdSe/ZnS QDs, as shown in Fig. 5. Because the emission efficiency of the QD is lower than that of the blue OLED, the emission peaks related to the QDs were not clear. The difference in the EL spectra between devices I and II indicates the absorption and re-emission of the QDs. The peak position of the EL spectrum for device II is shifted to long wavelength in comparison with that for device I, which is in reasonable agreement with the absorption and the PL spectra shown in Fig. 2. The FWHM value of the EL spectra for device II is larger than that for device I. The differences in the peak positions and in the FWHMs for the EL spectra between the OLEDs containing CdSe and CdSe/ZnS QDs are attributed to the color conversion effects resulting from the insertion of the CdSe and the CdSe/ZnS QDs into the HTL.

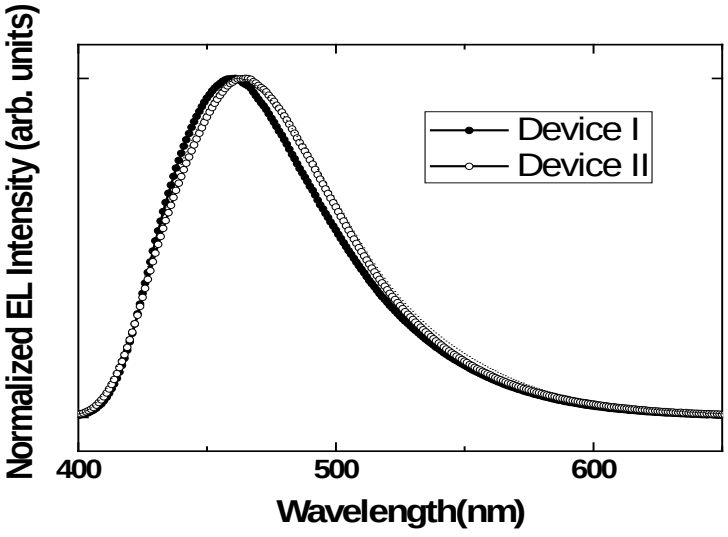

Fig. 5. Electroluminescence spectra of devices I and II. Filled circles and opened circles represent devices I and II, respectively.

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4. Summary and conclusions

The electrical and the optical properties of OELDs fabricated with a PVK HTL containing CdSe and CdSe/ZnS QDs were measured. PL spectra for the CdSe and the CdSe/ZnS QDs showed dominant exciton peaks. Current densities as functions of the voltage showed that the enhanced hole trapping and decreased hole current in the OLEDs could be attributed to the existence of the ZnS shell. The brightness of the OLEDs with CdSe/ZnS QDs was much lower than that of OLEDs with CdSe QDs because CdSe/ZnS QDs had strong carrier trapping and optical absorption force than CdSe QDs resulting from the ZnS shell. EL spectra for blue OLEDs containing CdSe and CdSe/ZnS QDs showed that the differences in the peak positions and the FWHMs were color conversion effects resulting from the insertions of the CdSe and the CdSe/ZnS QDs in the HTL. Even though the brightness of device II was lower than that of device I, the color conversion efficiency of the device II was higher than that of device I demonstrated by slight red-shifted EL emission spectra. The red-shift magnitude of the PL peaks for OLEDs dependent on the host materials and the type of the QDs affected the device performance. These results can help improve understanding of blue OLEDs based on color conversion QDs embedded in a HTL.

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