Surface-Modified Zinc Oxide Nanoparticles for Electron Injection Layers in Organic Light-Emitting Devices

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We report the application of two surface modifiers, 2-(2-hydroxyphenyl)benzothiazole (BTz) and 8-quinolinol (8Qn), to electron-transporting layers (ETLs) comprising zinc oxide nanoparticles (ZnO NPs) to improve the efficiency of electron injection into light-emitting layers in organic light-emitting devices (OLEDs). BTz and 8Qn were respectively added to ZnO NP dispersions; these surface modifiers then reacted with the ZnO NPs and changed their optical properties, proving the interaction between the ZnO NPs and modifiers. The modified ZnO NPs were employed as ETLs in fluorescent polymer-based OLEDs. The BTz-device showed a slightly lower driving voltage and a slightly higher luminous efficiency than the unmodified ZnO device, whereas the 8Qn-device showed a much lower driving voltage and a much higher luminous efficiency than the unmodified ZnO device. The device driving stability was evaluated, and both of the modified devices showed improved lifetimes compared with the unmodified device. In particular, a more than five-fold improvement in lifetime was obtained for the BTz-device.

Keywords: OLED, ZnO, Modifier, Organic–inorganic hybrid

1. Introduction

Solution-processed organic light-emitting devices (OLEDs) have attracted much attention because of their potential for easy production of large-area devices and low fabrication cost. One of the biggest problems in solution-processed OLEDs is their low device performance. For a long time, solution-processed OLEDs have lagged behind evaporation-processed OLEDs in terms of their performance. However, vigorous recent research and development is gradually improving their luminous efficiency and driving stability [1-3]. For achieving high luminous efficiency, high carrier recombination probability is essential, which means that high electron and hole injection efficiencies from the electrodes are required. In general, electron injection is more difficult than hole injection because the electron-injection barrier from the electrode to an organic functional layer is larger than the hole-injection barrier. Many researchers have attempted to develop efficient solution-processable electron-transporting and electron-injection materials [4-8]. In recent years, highly transparent and conductive inorganic electron-transporting materials (iETMs) have attracted great attention. There are various reports on iETMs [9-12], and zinc oxide (ZnO) is one of the most popular iETMs because of its low cost and intrinsically high stability [9,10,13-18]. ZnO electron-transporting layers (ETLs) have a deep conduction band energy level of ca. 4.0 eV, making it easy for electron injection from high work function (WF) cathodes. However, there are energy barriers between the ZnO ETLs and light-emitting layers (EMLs), which have the lowest unoccupied molecular orbital (LUMO) levels of 2.7–3.5 eV. Therefore, ZnO ETLs have often been modified by surface modifiers such as solution-processable small molecules or polymer amines [16,17], small organic or inorganic salts [13-15], and a metal complex [14], to improve the efficiency of electron injection into EMLs. We have previously synthesized ZnO nanoparticles (NPs)
dispersed in alcohol solvents and applied them as ETLs in solution-processed OLEDs [14]. 8-Quinolinolato lithium (Liq) was employed as a surface modifier for the ZnO ETL. The Liq-modified ZnO was spin-coated on a fluorescence-emitting polymer EML, poly(9,9-dioctylfluorene-alt-benzothiadazole) (F8BT). The Liq-modified ZnO device exhibited higher electron-injection efficiency and air stability than the conventional Cs2CO3-modified ZnO device.

In this study, we report applications of two surface modifiers, 2-(2-hydroxyphenyl)benzothiazole (BTz) and 8-quinolinol (8Qn), on ZnO NPs to improve the efficiency of electron injection into EMLs in OLEDs. The chemical structures of BTz and 8Qn are shown in Fig. 1(a). BTz and 8Qn were respectively added to ZnO NPs dispersed solutions, and these surface modifiers then reacted with the ZnO NPs and changed the optical properties of the ZnO NPs, proving the interactions between the ZnO NPs and the modifiers. The modified ZnO NPs were employed as the ETL in F8BT-based OLEDs. The BTz-device showed a slightly lower driving voltage and a slightly higher luminous efficiency than the unmodified ZnO device, whereas the 8Qn-device showed a much lower driving voltage and a much higher luminous efficiency than the unmodified ZnO device. Both of the modified devices exhibited improved lifetimes compared with the unmodified device. In particular, a more than five-fold improvement in lifetime was obtained for the BTz-device.

2. Experimental
2.1. Materials.
Spherical-shaped ZnO NPs with particle diameters of 6–8 nm were synthesized according to an established procedure [14]. The synthesized ZnO NPs were dispersed in alcohol solvents at 5 mg/mL. BTz and 8Qn were purchased from Tokyo Chemical Industry Co., Ltd. and Kanto Chemical Co., Inc., respectively, and were used as received. BTz and 8Qn were respectively added to ZnO NPs dispersion solutions, where the weight ratio of ZnO NPs:(BTz or 8Qn) was 9:1. The dispersion solutions were stirred at 80 °C for 1 h. Poly(3,4-ethylenedioxythiophene):poly(4-styrenesulfonate) (PEDOT:PSS) (Clevios P VP CH 8000) was purchased from Heraeus Materials Technology. Poly(9,9-dioctylfluorene-alt-N-(4-butylphenyl)-diphenylamine) (TFB) was purchased from American Dye Source, Inc. F8BT was provided by Sumitomo Chemical Co., Ltd.

2.2. Opto-electronic properties.
Ultraviolet–visible (UV–Vis) spectra of solutions with modifier concentrations of 10−4–10−2 mg/mL and films of thickness 10 nm were measured using a Shimadzu UV-3150 UV–Vis–NIR spectrophotometer. WF values of the films of thickness 10 nm were measured using a Thermo Fisher Scientific Theta Probe X-ray and UV photoelectron spectrometer system. Photoluminescence (PL) spectra of the solutions were obtained using a HORIBA JOBIN YVON Fluoromax-4 fluorometer. The concentration of each PL sample solution was determined to be 10−4–10−2 mg/mL so as to not cause concentration quenching and saturation of the PL detector. PL excitation wavelengths were 330 nm for ZnO, 326 nm for BTz, 300 nm for 8Qn, and 375 nm for ZnO:BTz and ZnO:8Qn.

2.3. Device fabrication and evaluation.
ITO substrates were cleaned using an ultrasonic sonicator and a UV-ozone cleaner. OLEDs with a structure of [ITO (130 nm)/PEDOT:PSS (30 nm)/TFB (20 nm)/F8BT (80 nm)/ETL (10 nm)/Al(100 nm)] were fabricated. The device emitting area was 2 mm × 2 mm. The employed ETLs comprised unmodified-, BTz-modified-, and 8Qn-modified-ZnO NPs. A PEDOT:PSS water dispersion solution was spin-coated onto the ITO substrates followed by annealing at 200 °C for 10 min in air. The substrates were then transferred into a nitrogen-filled glove box. TFB was spin-coated onto the PEDOT:PSS layer from p-xylene solution followed by annealing at 180 °C for 60 min. F8BT was spun-coated onto the TFB layer from p-xylene solution followed by annealing at 130 °C for 10 min. Al cathodes were vacuum evaporated onto the unmodified or modified ZnO layer. Current density–voltage (J–V) characteristics of the OLEDs were measured using a current source meter, Keithley 2400. Luminance–voltage (L–V) characteristics of the OLEDs were measured using a luminance meter, Konica Minolta CS-200. Electroluminescence (EL) spectra were measured using a photonic multichannel analyzer, Hamamatsu PMA-11. Quantum efficiencies were calculated based on the Lambertian assumption. Device lifetimes were tested at a constant current.
3. Results and discussion

Figures 1(b)-(f) show the UV–Vis absorption and PL spectra of the solution samples. The ZnO:(BTz or 8Qn) solutions exhibited different peaks in their UV–Vis absorption spectra compared with both the ZnO and the modifier spectra. The changes in the UV–Vis spectra indicated that the surface modifiers, BTz and 8Qn, reacted with the ZnO NPs. In the ZnO:(BTz or 8Qn), a new absorption band from 350 nm to 410 nm appeared. The shapes and positions of the new absorption band were similar in both solutions, suggesting that the generated band was resulted from ZnO defects filling by the surface modifiers. The ZnO:(BTz or 8Qn) solutions also showed different PL spectra peaks from both the ZnO and the modifier ones with a broad structureless spectrum shape. The short wavelength edges of the PL spectra overlapped with the absorption edges of the UV–Vis spectra, which implied that the PL emissions were derived from defect-filled ZnO surface excitons. Although the UV–Vis absorption spectra showed a similar absorption band shape in both solutions, the PL spectra peaks were different between each modified sample. In the ZnO:BTz solution, the PL spectrum showed a peak at 450 nm, which is a shorter wavelength than that for the ZnO and longer wavelength than that for the BTz (495 nm). In the ZnO:8Qn solution, the PL spectrum showed a peak at 500 nm, which is a shorter wavelength than that for the ZnO and longer wavelength than that for the BTz (420 nm). The different PL wavelengths indicate that the PL emissions are related to the electronic states of the surface modifiers. Together, the PL emissions are related to defect-filled ZnO surface excitons and the electronic states of the modifiers. It is possible that an exciplex-like complex comprising the ZnO surface and the modifier is the origin of the PL emission. The structureless shape of the PL spectra supports this supposition.

Figure 2 shows the UV–Vis absorption spectra of the films. The ZnO:BTz film showed a longer wavelength absorption band from 370 nm to 430 nm than the ZnO film. This band is similar to that of the solution sample, suggesting that BTz successfully modified the ZnO surface in the film state. Surprisingly, the ZnO:8Qn film did not show a longer wavelength absorption band than the ZnO film. Furthermore, the strong peak at 260 nm is similar to that at 240 nm in the PL spectrum of the 8Qn solution. There is a possibility that the 8Qn did not modify the ZnO surface in the film state. The peak position and shape at 260 nm in the ZnO:8Qn film should be compared with those of a peak in an 8Qn-film. Unfortunately, we could not fabricate films made of BTz and 8Qn modifiers because of their low film-forming capability, and therefore, we did not measure the UV–Vis spectra of the corresponding films. WF values were obtained from the secondary electron cutoff values in the ultra-
Fig. 2. Normalized UV–Vis absorption spectra of film samples of ZnO, ZnO:BTz, and ZnO:8Qn.

Fig. 3. Organic light-emitting device (OLED) structure and chemical structures of used materials.

violet photoelectron spectroscopy spectra. The WF values were determined to be 4.19 eV for the unmodified ZnO, 4.34 eV for the BTz-modified ZnO, and 4.11 eV for the 8Qn-modified ZnO. The BTz-modification increased the WF value of the unmodified ZnO, whereas the 8Qn-modification reduced the WF value of the unmodified ZnO. This difference in WF shift probably resulted from the directions and magnitudes of the surface modification-generated dipoles.

We fabricated OLED devices with a structure of [ITO (130 nm)/PEDOT:PSS (30 nm)/TFB (20 nm)/F8BT (80 nm)/ETL (10 nm)/Al(100 nm)] (Fig. 3). The employed ETLs were unmodified-, BTz-modified-, and 8Qn-modified-ZnO NPs. The light-emitting polymer F8BT has a LUMO level of ca. 3.5 eV. Figures 4(a)-(c) show the $J-V-L$, $J$-external quantum efficiency (EQE) characteristics, and the EL spectra of the devices. The BTz-device showed a slightly lower driving voltage and a slightly higher luminous efficiency than the unmodified ZnO device, whereas the 8Qn-device showed a much lower driving voltage and a much higher luminous efficiency than the unmodified ZnO device. The 8Qn-device showed a maximum EQE of 4.5% at around 40 mA/cm². The 8Qn-device with the lowest ETL WF value of 4.11 eV showed the lowest driving voltage. However, the difference of the driving voltages cannot be explained by only the WF shift effect, because the BTz-device with the largest ETL WF value of 4.34 eV showed a lower driving voltage than the unmodified device. In addition, a large electron-injection barrier of 0.59 eV still remains between the 8Qn-modified ZnO and F8BT. It is important to take into account the LUMO levels of the surface modifiers. The LUMO levels were estimated to be −2.65 eV for BTz and −3.2 eV for 8Qn based on the corresponding LUMO levels of the metal complexes previously reported [19-21]. The 8Qn LUMO level matches the F8BT LUMO level of 3.5 eV, whereas the BTz LUMO level is too shallow to match the F8BT LUMO level. The matched LUMO level of 8Qn probably contributed to the improved driving voltage in the 8Qn-device.

We also tested the device lifetimes at a constant current density of 10 mA/cm². Figure 4(d) shows the lifetime test results of the devices. The devices showed LT50 values, which is the time taken to reach half the initial luminance, of 220 h for the unmodified ZnO NPs, 1140 h for the BTz-device, and 370 h for the 8Qn-device. Both the BTz- and 8Qn-devices showed longer lifetimes than the unmodified device. The BTz-modification significantly improved the device lifetime by more than a factor of five. The reasons why both the surface modifications improved the device lifetimes are not clear from the experiments. However, we assume that the unstable defects in the ZnO NPs were passivated by the modifiers, and the stabilized ZnO exhibited longer device lifetimes. The lifetime difference between the BTz- and 8Qn-devices probably resulted from the difference between the ZnO–modifier interactions mentioned above. The film UV–Vis absorption spectra implied that the ZnO–BTz interaction is stronger than the ZnO–8Qn interaction, and the stronger ZnO–BTz interaction greatly improved the device lifetime.

4. Conclusion

We modified ZnO NP surfaces using BTz and 8Qn to improve their capability of electron injection into the F8BT EML. Both BTz and 8Qn-modifications
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Fig. 4. OLED characteristics. (a) Current density–voltage and (b) luminance–voltage characteristics. (c) Electroluminescence spectra at 25 mA/cm². (d) Lifetime test results at a constant current density of 10 mA/cm².

Successfully changed the optical properties of the ZnO NPs, which indicates that the BTz and 8Qn modifiers reacted with the ZnO NPs. The BTz modification increased the WF value of the ZnO NPs by 0.15 eV, whereas the 8Qn modification reduced the WF value of the ZnO NPs by 0.08 eV. However, a large electron-injection barrier between the 8Qn-modified ZnO and F8BT still existed after modification. We applied the BTz- and 8Qn-modified ZnO NPs as the ETL in solution-processed OLEDs. The BTz-device showed a slightly lower driving voltage and a slightly higher luminous efficiency than the unmodified ZnO device, whereas the 8Qn-device showed a much lower driving voltage and a much higher luminous efficiency than the unmodified ZnO device. The matching of the 8Qn LUMO level with the F8BT LUMO level probably contributed to the lower driving voltage. In the lifetime tests, both the BTz and 8Qn devices exhibited longer lifetimes than the unmodified device. In particular, the BTz-device exhibited a more than five-fold longer lifetime. Despite the good progress made in the present study, there is still room to improve the device characteristics, and the development of new surface modifiers is desirable.

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