Solution-Processed Carrier Injection Layer for Microfluidic Organic Light-Emitting Diodes

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(Received March 10, 2020; accepted May 22, 2020, published June 26, 2020)

Abstract
We investigated an effect of a solution-processed electron injection layer (EIL) on an electroluminous (EL) performance of organic light-emitting diode with a liquid emitting layer (Liquid OLED). A pyrene-based liquid organic semiconductor, 1-pyrenebutyric acid 2-ethylhexyl ester (PLQ), was used as a greenish-blue emitter. Zinc oxide nanoparticles (ZnO NPs) were deposited on an indium tin oxide (ITO) cathode by a spin-coating method. We fabricated two kinds of liquid OLEDs with ITO anode/PLQ/ITO cathode and ITO anode/PLQ/ZnO NPs (EIL)/ITO cathode. Current density and luminance were increased significantly by inserting the ZnO NPs between the ITO cathode and PLQ. We expect that the solution-processed ZnO NPs can be useful in developing microfluidic OLED displays.

Keywords: Liquid Organic Semiconductor, ZnO Nanoparticles, Electron Injection Layer, Microfluidic OLED, Liquid OLED

1. Introduction
In recent years, organic light-emitting diodes (OLEDs) have been successfully commercialized in display applications such as mobile phones and TVs. The OLED device typically consists of solid-state functional layers sandwiched between two electrodes, including an electron injection layer (EIL), an electron transport layer (ETL), an emitting layer (EML), a hole transport layer (HTL), and a hole injection layer (HIL). In order to facilitate electron injection from a cathode into EML or ETL, several EIL materials such as lithium fluoride (LiF) and zinc oxide nanoparticles (ZnO NPs) have been used in state-of-the-art OLEDs.[1–5] In addition, at least one of the electrodes is required to be transparent. An indium tin oxide (ITO) film, which has a work function of about 4.7 eV, has been widely used as an anode or a cathode because of its high transparency.

On the other hand, solvent-free organic fluids such as liquid organic semiconductors (LOSs) have attracted attention for flexible organic electronic device applications.[6, 7] In 2009, Xu and Adachi demonstrated a liquid OLED, in which a LOS-based emitting layer was sandwiched between two ITO-coated glass substrates.[8] In order to integrate multiple liquid OLEDs on a substrate, our research group proposed and investigated microfluidic OLEDs.[9–11] In that work, single-micrometer-thick microchannels sandwiched between the ITO anode and cathode were fabricated by a microelectromechanical systems (MEMS) process and a heterogeneous bonding technique. Multi-color electroluminescence (EL) emissions were successfully obtained using a pyrene-based LOS (1-pyrenebutyric acid 2-ethylhexyl ester (PLQ)) in the microchannels. However, in comparison with solid-state OLEDs, the EL performance of the microfluidic OLEDs is still primitive and needs to be improved particularly in terms of luminance.

In this study, in order to enhance the luminance of PLQ, we investigated an effect of a solution-processed EIL on the EL performance of liquid OLED consisting of two ITO-coated glass substrates. The ZnO NPs were used as the EIL and spin-coated on the ITO cathode.
2. Experiments

We fabricated two kinds of liquid OLEDs with ITO anode/PLQ (EML)/ZnO NPs (EIL)/ITO cathode (Device 1) and ITO anode/PLQ (EML)/ITO cathode (Device 2). Figure 1 shows a chemical structure of PLQ and a design of the liquid OLED (Device 1) with an active area of 4 mm² (2 mm × 2 mm). An ionic liquid, tributylmethylphosphonium bis(trifluoromethanesulfonyl)imide, was also doped into PLQ (Nissan Chemical Corporation) at its concentration of 0.25 wt% to enhance the carrier injection from the electrodes. [9] PLQ was sandwiched between the ITO anode and the ZnO NPs-coated ITO cathode. A fabrication process of the liquid OLED is as follows. To form the electrode pattern, ITO was etched by aqua regia. The anode and cathode surfaces were cleaned in 2-propanol and then treated by 172 nm xenon excimer lamp (Ushio, SUS713). The ZnO NPs (Avantama, N-10), which have an average diameter of 10-15 nm and are dispersed in 2-propanol at a concentration of 0.6 wt%, were spin-coated on the cathode at 4,000 rpm for 30 s. Then, the cathode substrate was annealed at 140 °C for 10 min. After PLQ was dropped on the cathode, two substrates were fixed with clips.

The current density–voltage–luminance (J–V–L) characteristics of the liquid OLEDs were measured using a source meter (Keithley Instruments, Model 2400) and a luminance meter (Konica-Minolta, LS-160). EL spectra were taken with a spectrometer (Ocean Optics, Flame-S).

3. Results and Discussion

Figure 2 shows the J–V–L characteristics of liquid OLEDs with and without the ZnO NPs. It was found that both the current density and luminance were increased more than 10 times in comparison with Device 2. In addition, the turn-on voltage decreased by inserting the ZnO NPs between the ITO cathode and PLQ. The maximum luminance reached 32.3 cd/m² at 82 V for Device 1. This result indicates that the electron injection from the cathode to PLQ was enhanced, and consequently, the recombination of electron-hole pairs was significantly increased. The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) levels of PLQ were reported to be 5.8 and 2.6 eV, respectively. [12] The barrier height of the electron injection was found to be larger than that of the hole injection since the work function of ITO was 4.7 eV. Furthermore, Zhang et al. reported that the work function of the ZnO NPs was 4.1 eV. [3] Therefore, the electron injection barrier height was reduced by the insertion of the ZnO NPs. A maximum current efficiency of Device 1 was measured to be 0.18 cd/A at 22 V. The solid-state OLED using pyrene derivatives as EML was reported to exhibit the current efficiency of 2.2 cd/A. [13] Therefore, in order to maximize the EL performance of PLQ, we will fabricate the liquid OLED having EIL, ETL, and HIL.

The photographs and EL spectra at 45 V are shown in Fig. 3. The EL spectra of both the devices were recorded with an integration time of 400 ms and an average of 2 times. It can be seen that Devices 1 and 2 exhibited greenish-blue EL emission, and the obtained EL spectra were almost identical to each other with a maximum wavelength at 500 nm. Therefore, we can conclude that the ZnO NPs can contribute to enhance the luminance of PLQ. In the near future, we will investigate a fabrication methodology for microfluidic OLEDs with the ZnO NPs-based EIL.

4. Conclusion

We fabricated the liquid OLED with the ZnO NPs-based EIL. Compared to the liquid OLED without the ZnO NPs,
the current density and luminance were increased significantly. Since the ZnO NPs can be simply deposited on the electrodes by a solution process, we expect that the ZnO NPs can be applied as EIL in the microfluidic OLEDs.

Acknowledgment

The authors would like to acknowledge Prof. Toshihiro Nakamura (Hosei University) for valuable discussions. This research was partially supported by JSPS KAKENHI Grant Number JP19K15424, the IMRA Japan Award, and Toshiba Electronic Devices & Storage Corporation.

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