High-Efficiency Blue Organic Light-Emitting Diodes Using C$_{60}$ as a Surface Modifier on Indium Tin Oxide

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C$_{60}$ is a molecule with 60 carbons on spherical surfaces and is well known as an electron acceptor in solar cells. It can form a charge transfer complex with metals, organics and inorganics and interface dipole formation between C$_{60}$ and other materials has been reported in other works. There have been several works about using C$_{60}$ in organic light-emitting diodes (OLEDs). C$_{60}$ was used as an efficient electron transport material and it was also effective as a buffer layer on AI. The use of C$_{60}$ as a buffer layer on AI reduced the interfacial energy barrier between Al and N,N’,N’-di(1-naphthyl)-N,N’-diphenylbenzidine (NPB) from 1.2 to 0.3 eV. It was also used as a buffer layer on indium tin oxide (ITO) and low driving voltage was obtained after C$_{60}$ modification on ITO due to the reduced energy barrier between ITO and NPB. In our study, it was found that hole injection of C$_{60}$ modified devices greatly depended on the surface treatment of ITO and O$_2$ plasma treatment was effective to get a high current density, while hole injection was not affected by C$_{60}$ on untreated ITO.

In this work, we studied device performances of blue OLEDs with C$_{60}$ as a buffer layer on untreated ITO and O$_2$-plasma-treated ITO. The relationship between ITO surface treatment and device performances of C$_{60}$ modified devices was investigated and the mechanism for efficiency enhancement in C$_{60}$ modified devices was discussed.

Device configurations of ITO/C$_{60}$ (x nm)/NPB (50 nm)/MADN (30 nm)/Alq$_3$ (20 nm)/LiF (1 nm)/Al (200 nm) were used to study the effect of C$_{60}$ thickness on device performance. Two ITOs, untreated ITO and O$_2$-plasma-treated ITO, were used to obtain information about the relationship between surface properties of ITO and device performances. ITO glass substrates were cleaned with acetone and isopropl alcohol in an ultrasonic bath for 15 min, respectively, and were dried at 120°C for 2 h before use. The ITO substrates were exposed to oxygen plasma at a radio-frequency power of 100 W with O$_2$ flow rate of 50 sccm. After O$_2$ plasma treatment, C$_{60}$ was deposited at a deposition rate of 0.01 nm/s and the thickness of C$_{60}$ was controlled from 0 to 7 nm to correlate the C$_{60}$ thickness with device performances. AI was evaporated at a deposition rate of 5 Å/s and the devices were encapsulated with a glass lid and calcium oxide getter. Current density-voltage-luminance characteristics of the devices were measured with Keithley 2053A source measurement unit and PR 650 spectrophotometer. It was found in our previous work that surface dipole formation could be induced on O$_2$-plasma-treated ITO by C$_{60}$ modification, leading to efficient hole injection and high current density, while no reduction of energy barrier was observed on untreated ITO without O$_2$ plasma treatment even after C$_{60}$ modification. It is well known that high power efficiency can be obtained in OLEDs by lowering a driving voltage and improving electron-hole balance in a light-emitting layer. C$_{60}$ modification on ITO can give a driving voltage due to the reduced energy barrier between ITO and NPB and it can also give high recombination efficiency due to reduced hole flow in the device dependent on surface properties of ITO. Therefore, in this work, device performances of C$_{60}$ modified devices were investigated according to surface properties of ITO and C$_{60}$ thickness.

Figure 1 shows current density-voltage characteristics of C$_{60}$ modified devices with and without O$_2$ plasma treatment according to C$_{60}$ thickness. Current density of C$_{60}$ modified devices with O$_2$ plasma treatment (Fig. 1b) showed a maximum value at a C$_{60}$ thickness of 3 nm and then decreased. The high current density of C$_{60}$ modified devices can be explained by a surface dipole formation on ITO as reported in previous work. The surface dipole was induced between ITO and C$_{60}$ by O$_2$ plasma treatment and the energy barrier between ITO and NPB was lowered from 0.94 to 0.54 eV by C$_{60}$ modification, resulting in high current density in the devices. The decrease of current density at a C$_{60}$ thickness of 7 nm is due to low hole mobility and the highest occupied molecular orbital (HOMO) level of 6.2 eV of C$_{60}$. C$_{60}$ is known to have a high electron mobility of 1 cm$^2$/V s, while its hole mobility is only 1×10$^{-3}$ cm$^2$/V s compared with NPB hole mobility of 3×10$^{-3}$ cm$^2$/V s from our measurements. In addition, low-lying HOMO value (6.2 eV) of C$_{60}$ limits hole injection because of large energy barrier between ITO and C$_{60}$, C$_{60}$ acts as a separate layer at high thickness and it limits hole injection from ITO. Contrary to high current density of C$_{60}$ modified devices with O$_2$-plasma-treated ITO, current density of C$_{60}$ modified devices with untreated ITO was lowered by C$_{60}$ modification. Current density was gradually decreased according to the thickness of C$_{60}$, indicating that hole injection of C$_{60}$ modified devices was not facilitated by C$_{60}$ on untreated ITO. There was no energy barrier reduction between ITO and NPB by C$_{60}$ modification of untreated ITO and C$_{60}$ acted just as a hole transport material with a low hole mobility and high energy barrier, resulting in low current density after C$_{60}$ modification.

Figure 2 shows luminance-voltage curves of C$_{60}$ devices with untreated ITO and O$_2$-plasma-treated ITO. Luminance was improved in O$_2$-plasma-treated devices, while it was decreased in the devices with untreated ITO except 1 nm C$_{60}$ modified devices. The high luminance in O$_2$-plasma-treated devices is due to high current density in the devices which is induced by low hole injection barrier between ITO and NPB. However, the luminance was lowered at 7 nm thick C$_{60}$ because of reduced current density as shown in Fig. 1. Compared with O$_2$-plasma-treated devices, C$_{60}$ modified untreated ITO devices except for a device with 1 nm thick C$_{60}$ showed lower luminance value than C$_{60}$ free device as expected from current density data. The high luminance in 1 nm thick C$_{60}$ modified de-
vices is due to efficient recombination of holes and electrons in the emission layer, which will be described in detail in current efficiency data.

Based on the current density and luminance of C60 modified devices, current efficiency was calculated and was plotted against C60 thicknesses (Fig. 3). Current efficiency of blue devices was almost constant at low C60 thickness and then increased at a thickness of 7 nm after O2 plasma treatment, while it showed a maximum value at 3 nm and was saturated without O2 plasma treatment. High efficiency of 3.7 cd/A at 1000 cd/m² could be obtained in blue devices with 3 nm C60 buffer layer on untreated ITO. 80% improvement of current efficiency was observed by C60 modification on untreated ITO. The high efficiency of C60 modified devices can be explained by efficient hole-electron recombination in the emitting layer.10,11 In general, hole injection is more efficient than electron injection in OLEDs and hole is the dominant charge carrier in the devices.11 Therefore, less hole flow in the device can improve hole-electron balance in the device, enhancing recombination efficiency. In spite of high driving voltage, the hole and electron charge balance improved current efficiency of C60 modified device with untreated ITO. A decrease of current efficiency at 7 nm C60 modification on untreated ITO indicates that electron-hole balance is optimized at 3 nm C60 thickness. Similar results could be obtained in blue devices with O2-plasma-treated ITO. High efficiency of 3.1 cd/A could be observed in C60 devices with O2 plasma treated ITO at a
O$_2$-plasma-treated devices. Hole-electron charge balance was not improved at low C$_{60}$ thickness even though driving voltage was lowered by C$_{60}$ modification.

Figure 4 shows the power efficiency of C$_{60}$ modified devices according to C$_{60}$ thickness. As can be expected from the current efficiency of C$_{60}$ devices, power efficiency of C$_{60}$ devices was greatly enhanced by C$_{60}$ modification. Power efficiency as high as 1.5 lm/W could be obtained in C$_{60}$ devices with 3 nm C$_{60}$ on untreated ITO, while C$_{60}$ devices with 3 nm C$_{60}$ on O$_2$-plasma-treated ITO showed only 1.2 lm/W at 1000 cd/m$^2$. Even though the driving voltage of C$_{60}$ devices was reduced by O$_2$ plasma treatment, the power efficiency was not improved remarkably due to moderate current efficiency of O$_2$-plasma-treated C$_{60}$ devices. O$_2$-plasma-treated C$_{60}$ devices showed a maximum power efficiency value of 1.4 lm/W at a C$_{60}$ thickness of 7 nm because of the high current efficiency at high C$_{60}$ thickness in spite of similar driving voltage with devices without C$_{60}$. On the other hand, power efficiency of C$_{60}$ devices with untreated ITO was decreased at high C$_{60}$ thickness due to the high driving voltage in spite of high current efficiency. In short, power efficiency was high at low C$_{60}$ thickness because of moderate driving voltage and high current efficiency in C$_{60}$ modified devices with untreated ITO, while power efficiency was rather low at high C$_{60}$ thickness because of high driving voltage in spite of high current efficiency. In the case of C$_{60}$ modification on O$_2$-plasma-treated ITO, power efficiency was high at high C$_{60}$ thickness due to high current efficiency even though the driving voltage was similar to that of C$_{60}$ free devices, while it was not improved greatly at low C$_{60}$ thickness due to rather low current efficiency in spite of low driving voltage.

In summary, current efficiency and power efficiency of C$_{60}$ devices were greatly improved by C$_{60}$ modification of ITO. C$_{60}$ retarded hole flow in C$_{60}$ devices with untreated ITO, while it facilitated hole injection in O$_2$-plasma-treated devices. 80% improvement of current and power efficiency was observed in C$_{60}$ devices and the use of C$_{60}$ as a buffer layer on ITO can freely control device performances of OLED by combined management of ITO surface properties and C$_{60}$ thicknesses.

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References