



High-Efficiency Blue Organic Light-Emitting Diodes Using C₆₀ as a Surface Modifier on Indium Tin Oxide

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C₆₀ was introduced as a modifier on indium tin oxide (ITO) and the effect of C₆₀ modification on light-emitting efficiency of blue organic light-emitting diodes was investigated. Device performances of C₆₀ modified devices were greatly dependent on ITO surface properties and C₆₀ thickness. Power efficiency of blue devices was improved by 80% by C₆₀ buffer layer on ITO because of low driving voltage and balanced electron-hole recombination

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Manuscript submitted April 8, 2007; revised manuscript received May 16, 2007. Available electronically June 19, 2007.

C₆₀ is a molecule with 60 carbons on spherical surfaces and is well known as an electron acceptor in solar cells.^{1,2} It can form a charge transfer complex with metals, organics and inorganics and interface dipole formation between C₆₀ and other materials has been reported in other works.^{3,4}

There have been several works about using C₆₀ in organic light-emitting diodes (OLEDs).^{3,5-7} C₆₀ was used as an efficient electron transport material⁶ and it was also effective as a buffer layer on Al.⁵ The use of C₆₀ as a buffer layer on Al reduced the interfacial energy barrier between Al and *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 C₆₀ modification on ITO due to the reduced energy barrier between ITO and NPB.³ In our study, it was found that hole injection of C₆₀ modified devices greatly depended on the surface treatment of ITO and O₂ plasma treatment was effective to get a high current density, while hole injection was not affected by C₆₀ on untreated ITO.⁸

In this work, we studied device performances of blue OLEDs with C₆₀ as a buffer layer on untreated ITO and O₂-plasma-treated ITO. The relationship between ITO surface treatment and device performances of C₆₀ modified devices was investigated and the mechanism for efficiency enhancement in C₆₀ modified devices was discussed.

Device configurations of ITO/C₆₀ (*x* nm)/NPB (50 nm)/MADN (30 nm)/Alq₃ (20 nm)/LiF (1 nm)/Al (200 nm) were used to study the effect of C₆₀ thickness on device performance. Two ITOs, untreated ITO and O₂-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 isopropyl 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 (rf) power of 100 W with O₂ flow rate of 50 sccm. After O₂ plasma treatment, C₆₀ was deposited at a deposition rate of 0.01 nm/s and other organic materials were evaporated at a rate of 0.1 nm/s. The thickness of C₆₀ was controlled from 0 to 7 nm to correlate the C₆₀ thickness with device performances. Al 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 0253A source measurement unit and PR 650 spectrophotometer.

It was found in our previous work that surface dipole formation could be induced on O₂-plasma-treated ITO by C₆₀ modification, leading to efficient hole injection and high current density, while no reduction of energy barrier was observed on untreated ITO without O₂ plasma treatment even after C₆₀ modification.⁸ 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. C₆₀ modification on ITO can give a low 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 depending on surface properties of ITO. Therefore, in this work, device performances of C₆₀ modified devices were investigated according to surface properties of ITO and C₆₀ thickness.

Figure 1 shows current density-voltage characteristics of C₆₀ modified devices with and without O₂ plasma treatment according to C₆₀ thickness. Current density of C₆₀ modified devices with O₂ plasma treatment (Fig. 1b) showed a maximum value at a C₆₀ thickness of 3 nm and then decreased. The high current density of C₆₀ modified devices can be explained by a surface dipole formation on ITO as reported in previous work.⁸ The surface dipole was induced between ITO and C₆₀ by O₂ plasma treatment and the energy barrier between ITO and NPB was lowered from 0.94 to 0.54 eV by C₆₀ modification, resulting in high current density in the devices. The decrease of current density at C₆₀ thickness of 7 nm is due to low hole mobility and the highest occupied molecular orbital (HOMO) level of 6.2 eV of C₆₀. C₆₀ is known to have a high electron mobility of 1 cm²/V s,⁹ while its hole mobility is only 1 × 10⁻⁴ cm²/V s compared with NPB hole mobility of 3 × 10⁻³ cm²/V s from our measurements. In addition, low-lying HOMO value (6.2 eV) of C₆₀ limits hole injection because of large energy barrier between ITO and C₆₀. C₆₀ acts as a separate layer at high thickness and it limits hole injection from ITO. Contrary to high current density of C₆₀ modified devices with O₂-plasma-treated ITO, current density of C₆₀ modified devices with untreated ITO was lowered by C₆₀ modification. Current density was gradually decreased according to the thickness of C₆₀, indicating that hole injection of C₆₀ modified devices was not facilitated by C₆₀ on untreated ITO. There was no energy barrier reduction between ITO and NPB by C₆₀ modification of untreated ITO and C₆₀ acted just as a hole transport material with a low hole mobility and high energy barrier, resulting in low current density after C₆₀ modification.

Figure 2 shows luminance-voltage curves of C₆₀ devices with untreated ITO and O₂-plasma-treated ITO. Luminance was improved in O₂-plasma-treated devices, while it was decreased in the devices with untreated ITO except 1 nm C₆₀ modified devices. The high luminance in O₂-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 C₆₀ because of reduced current density as shown in Fig. 1. Compared with O₂-plasma-treated devices, C₆₀ modified untreated ITO devices except for a device with 1 nm thick C₆₀ showed lower luminance value than C₆₀ free device as expected from current density data. The high luminance in 1 nm thick C₆₀ modified de-

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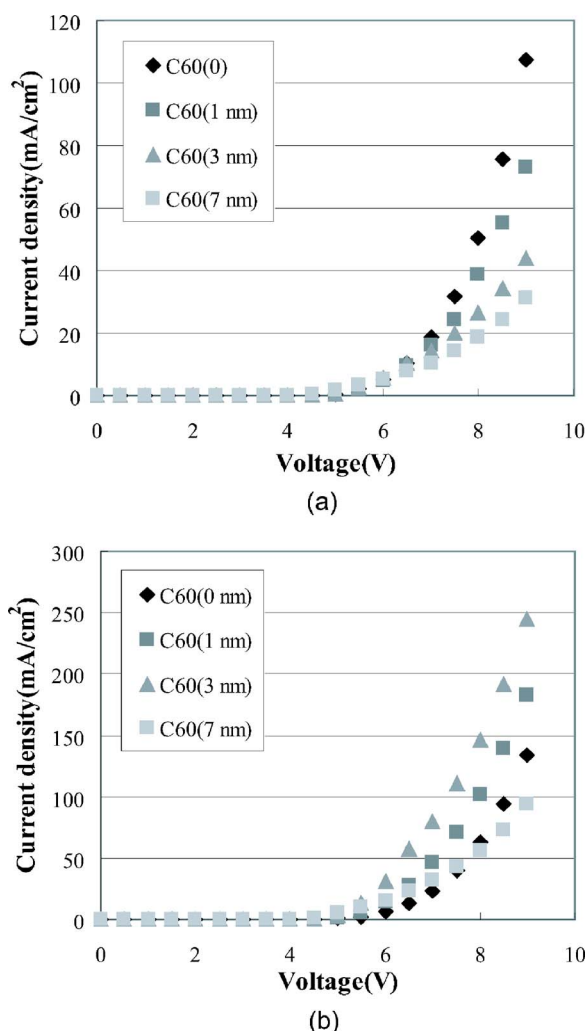


Figure 1. (Color online) Current density-voltage curves of C₆₀ modified devices with and without O₂ plasma treatment. (a) C₆₀ devices with untreated ITO. (b) C₆₀ devices with O₂-plasma-treated ITO.

ices 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

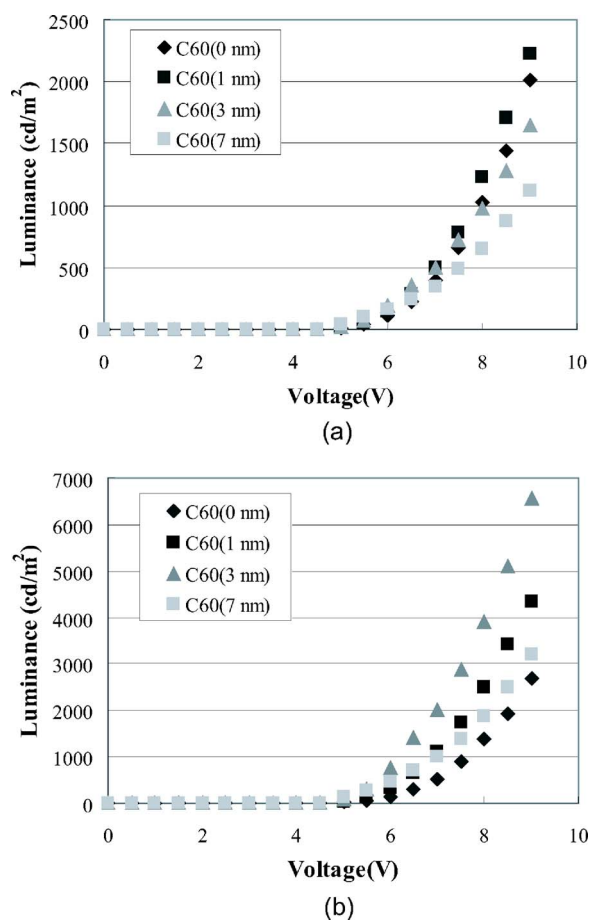


Figure 2. (Color online) Luminance-voltage curves of C₆₀ modified devices with and without O₂ plasma treatment. (a) C₆₀ devices with untreated ITO. (b) C₆₀ devices with O₂-plasma-treated ITO.

C₆₀ thickness of 7 nm, which is also due to improved hole-electron balance in the device caused by less hole flow in the device. Current efficiency was not increased at low C₆₀ thickness because hole injection was efficient due to the low energy barrier in

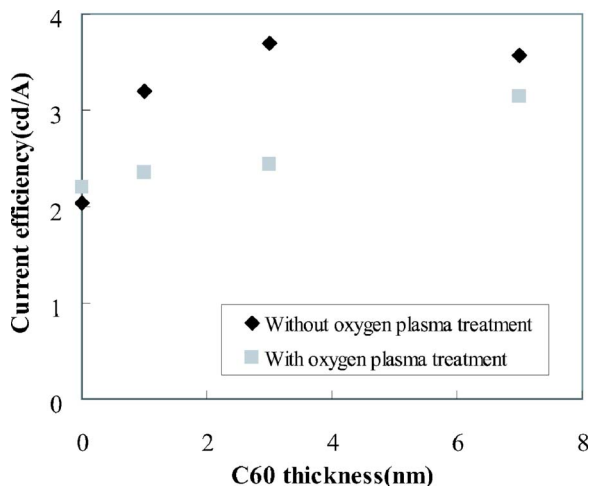


Figure 3. (Color online) Current efficiency of C₆₀ devices according to C₆₀ thickness.

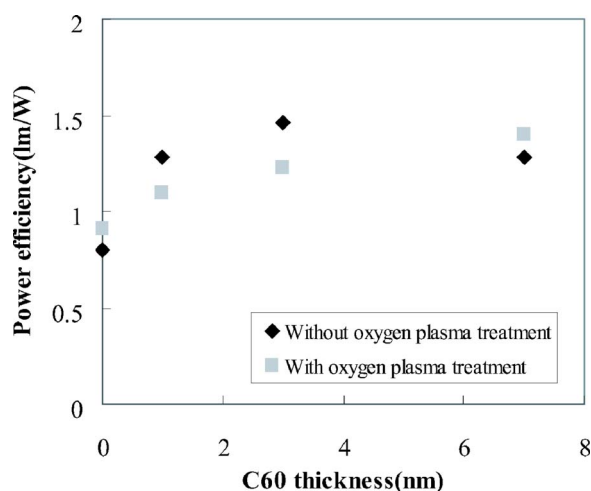


Figure 4. (Color online) Power efficiency of C_{60} devices according to C_{60} thickness.

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/m². 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.

Dankook University assisted in meeting the publication costs of this article.

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