Organic light-emitting diodes with carbon nanotube cathode-organic interface layer

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(Received 2 August 2008; accepted 24 November 2008; published online 8 January 2009)

Improved performance of organic light-emitting diodes (OLEDs) was achieved by implementing a carbon nanotube (CNT) layer at the cathode-organic interface, spin coated between the organic layer and the cathode. The small geometry of CNTs could enable the enhancement of the electric field around them, thus increasing electron injection efficiency from the cathode to the organic layer. In addition, as measured from the x-ray absorption and emission spectroscopy, incorporation of CNT could reduce the lowest unoccupied molecular orbital of the organic material at the cathode-organic interface, thus effectively decreasing the barrier for electron injection. Increased electron injection and luminance characteristics were demonstrated for both polymer and small molecule based OLED devices. © *2009 American Institute of Physics*. [DOI: 10.1063/1.3049605]

Organic light-emitting diodes (OLEDs) are attracting much attention due to their potential applications for solid-state lighting and flat-panel displays.[1–6] Although much effort has been devoted to the optimization of OLED performance, carrier injection barriers between the organic materials, and the electrodes remain a limiting factor. The simplest method to reduce these barriers is to use low work function cathode materials for electron injection and high work function anode materials for hole injection.[7] Although this approach works relatively well for hole injection using transparent indium-tin-oxide (ITO) anode in combination with hole-transport layers, effective injection of electrons with stable low work function materials at the cathode side remains a challenge. Low work function elemental metals,[1,7,8] such as magnesium (Mg), calcium (Ca), and lithium (Li), are reactive with ambient oxygen and water. They also tend to create quenching sites in areas near the cathode-organic interface, which are detrimental to the efficiency and stability of the device.[9] It is therefore highly desirable to develop alternative stable materials or structures that would enable efficient electron injection cross OLED's cathode-organic interface.

In our previous effort,[10] microimprinting technology was utilized to realize structured cathodes for improving electron injection of OLEDs. The localized electric field at the cathode-organic interface was increased as a result of the structured cathode geometry.[11–13] The current density and luminance of the device was improved by enhanced electron tunneling at the cathode-organic interface. As an alternative to microimprinting and lithographically defined structures, carbon nanotubes (CNTs) have generated tremendous excitement for a wide range of applications due to their advantageous electrical, thermal, and mechanical properties.[14] Enhanced field emission has been reported from CNTs where the small geometric features of CNTs yield substantial local enhancement of the electric field.[15,16] CNTs have been introduced into the structures of OLEDs, for example, in the form of CNT-polymer composite to improve transport properties of polymer materials,[17–19] or as potential anode material of OLEDs.[20,21] In this letter, we demonstrate that a CNT layer can act as an electron injection enhancer at the cathode-organic interface. These OLEDs exhibited better electron injection and luminance characteristics as compared to similar devices without the use of CNTs.

Organic materials used for fabricating OLEDs include poly[2-methoxy-5-[(2′-ethylhexyl)oxy]-*p*-phenylenevinylene] (MEH-PPV), *N*,*N*′-di-[(1-naphthyl)-*N*,*N*′-diphenyl]-1,1′-biphenyl)-4,4′-diamine (NPB), 8-hydroxyquinoline aluminum (Alq_3), and poly(3,4-ethylenedioxythiophene): poly(styrenesulfonate) (PEDOT:PSS), acquired from Sigma-Aldrich Inc. The ITO-coated glass substrate (200 nm, 20 Ω/□) was cleaned with the ultrasonic wave in acetone, ethanol, and purified water. PEDOT:PSS was coated by spin casting and dried at 150 °C for 30 min. MEH-PPV films (approximately 100 nm thick) were coated by spin casting from a chloroform solution with a concentration of 4 mg/ml. NPB and Alq_3 were thermally evaporated with a thickness of about 30 nm in a vacuum chamber under a pressure of $\sim 8 \times 10^{-7}$ Torr. Multiwall CNTs of diameters on the order of 10 nm were synthesized using chemical vapor deposition approach.[22] CNTs were coated by spin casting from a hexane solution with a concentration of 0.05 mg/ml. LiF and other electrode materials (Al and Ca) were also thermally evaporated in the vacuum environment. The current density-voltage characteristics of the OLEDs were determined with a Keithley source meter (model 2420). The luminance values were measured with a Minolta luminance meter (model LS-110). All the measurements were performed in a glovebox under nitrogen atmosphere.

Figure 1(a) shows measured current density versus voltage (*I-V*) results of a polymer based OLED device having the structure ITO/PEDOT:PSS/MEH-PPV/CNT/Ca/Al. This device exhibits an increased current density as compared to a conventional OLED without incorporating CNTs [Fig. 1(a)]. The threshold voltage is reduced slightly from 2.0 to 1.8 V after a CNT layer is incorporated. Note that Ca is a low work function cathode material that can yield a low threshold, but it is unstable upon exposure to air or moisture. When Al was used as the cathode material instead of Ca, the threshold voltage was lowered from approximately 3 to 2 V after implementing a CNT layer, as shown in Fig. 1(b). Fig-

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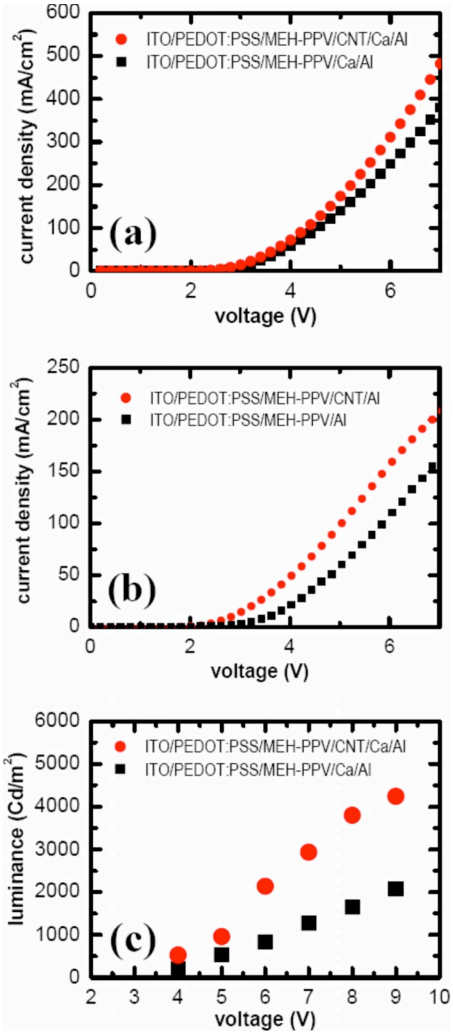

FIG. 1. (Color online) *I-V* measurements of MEH-PPV-based OLEDs, (a) ITO/PEDOT:PSS/MEH-PPV/CNT/Ca/Al and (b) ITO/PEDOT:PSS/MEH-PPV/CNT/Al, as compared to the baseline devices. (c) *L-V* measurements of MEH-PPV-based OLED, ITO/PEDOT:PSS/MEH-PPV/CNT/Ca/Al, as compared to the baseline device. The baseline devices have similar structure except CNTs were not incorporated at the cathode-organic interface.

ure 1(c) shows measured luminance versus voltage (*L-V*) curves of the same two devices as for Fig. 1(a); the luminance of the device implemented with CNTs is significantly higher when the applied voltage exceeds the threshold. There is no apparent change of the emission spectra after CNT incorporation.

Experiments were also performed by implementing CNTs at the cathode-organic interface of small organic molecule based OLEDs, which has a structure ITO/PEDOT:PSS/NPB/Alq_3/CNT/LiF/Al. The measured *I-V* and *L-V* results are shown in Fig. 2, along with the results of a corresponding baseline device without the incorporation of CNTs at the cathode-organic interface. Similar to the case for polymer based OLEDs, both current density and luminance of the device having a CNT cathode-organic interface are increased.

As demonstrated in our previous work[10] the measured increase of both the total current density and luminance implies that the injected electrons have to be increased with the introduction of CNTs at the cathode-organic interface. According to the Fowler-Nordheim tunneling theory,[23,24] the

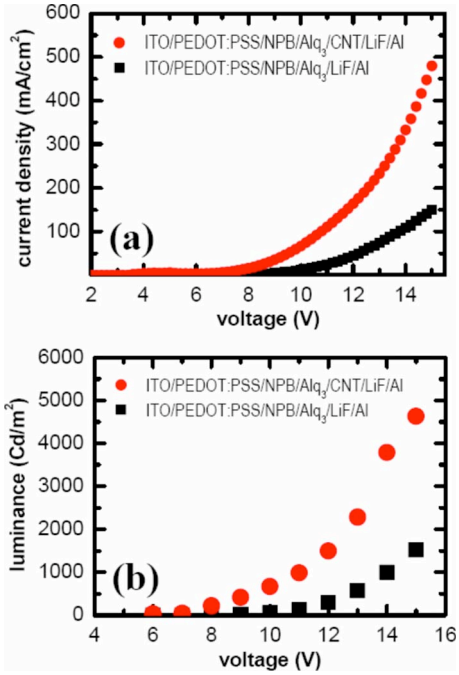

FIG. 2. (Color online) (a) *I-V* and (b) *L-V* measurements of Alq_3-based OLED device, ITO/PEDOT:PSS/NPB/Alq_3/CNT/LiF/Al, as compared to the baseline device. The baseline device has similar structure except CNTs were not incorporated at the cathode-organic interface.

electron current density across a barrier such as the one at the cathode-organic interface of an OLED depends strongly on the local electric field. Therefore, the electron injection current density of OLEDs can be improved by even slightly increasing the electric field at the cathode-organic interface. Based on the Poisson equation, we estimated the electric field distribution when CNTs are incorporated at the cathode-organic interface. Figure 3 shows calculated electric field intensity E at the top of nanotubes lying on a flat cathode as a function of nanotube diameter. Without nanotubes, $E=1\times10^8$ V/m for a flat cathode.

Other than an enhancement of local field at the cathode-organic interface, we attempted to examine the influence of CNT incorporation on the lowest unoccupied molecular orbital (LUMO) and highest unoccupied molecular orbital (HOMO) levels of the organic material.[25] Utilizing the x-ray photon beam from the synchrotron radiation facility at the Berkeley Advance Light Source, we obtained x-ray absorption spectra (XAS) and x-ray emission spectra (XES) of Alq_3 samples. The test samples have structures glass/ITO/Alq_3

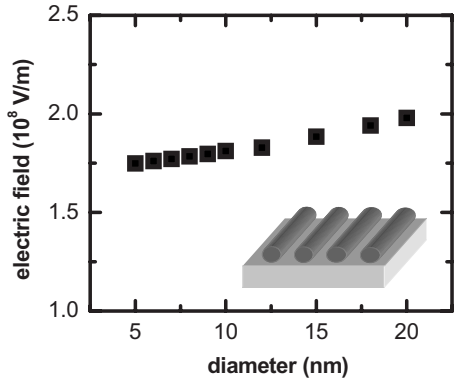

FIG. 3. Calculated electric field intensity at the top of nanotubes lying on a flat cathode, as a function of nanotube diameter.

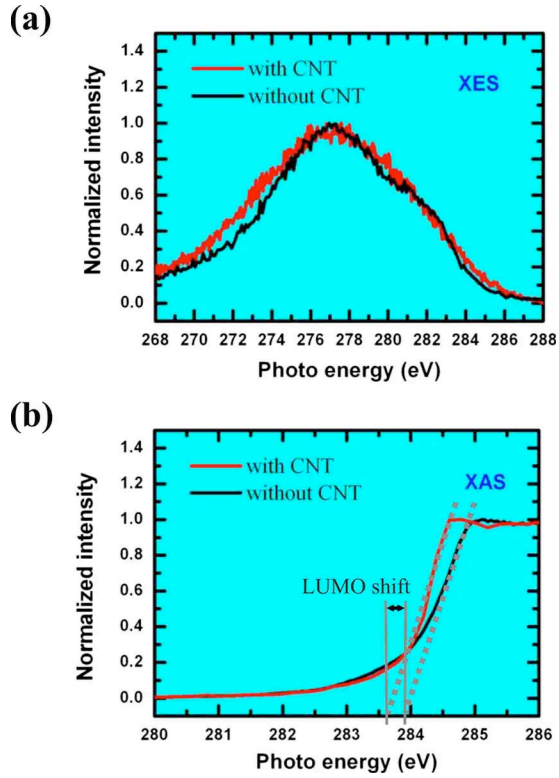

FIG. 4. (Color online) (a) XES and (b) XAS spectra of Alq_3 film incorporated with CNTs. A schematic illustration of how the shift of LUMO level is shown in (b).

and glass/ITO/Alq_3/CNT, respectively. The thickness of the Alq_3 films under study was about 200 nm. As shown in Fig. 4, the XES spectra of Alq_3, which are used to yield the HOMO level of molecules, do not show any significant change after incorporating CNTs. In contrast, the LUMO level as derived from the XAS spectra exhibits a reduction of approximately 0.3 eV after CNT incorporation. This result indicates that, in addition to localized field enhancement that enables improved electron injection from the cathode to the organic layer, a reduction of the LUMO level at the cathode-organic interface could yield a lower barrier for electron injection, thus contributing to the improved OLED device performance. The reduction of LUMO level of Alq_3 when CNTs are implemented could result from the modification of the molecule polarization, yielding new surface states.[26] Further experiments as well as theoretical model are needed in order to identify the exact microscopic mechanism.

To verify improved electron injection characteristics of a CNT layer at the cathode-organic interface, electron-dominant OLEDs with the structure of Al/MEH-PPV/CNT/Ca/Al were fabricated and tested.[7] Due to the very large energy barrier at the anode side, no light emission was observed from this device at the applied voltage up to the values reported in Fig. 5, which shows the *I-V* curve of the electron dominant device. Compared to the conventional device without CNTs, incorporation with CNTs at the cathode-organic interface leads to distinctly improved current density with lower turn-on threshold voltage. We also constructed OLED devices by spin coating the solvent (hexane) without incorporating CNTs. We found that the performance of the device with hexane coating alone does not show any improvement as compared to the baseline device without spin coating. This observation indicates that the layer of CNTs is

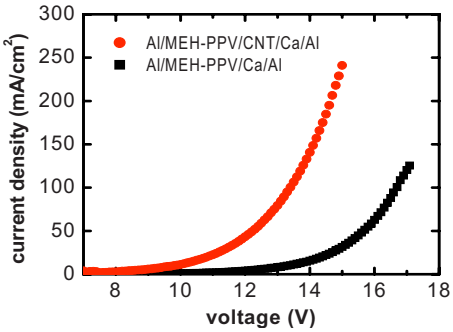

FIG. 5. (Color online) *I-V* measurements of an electron-only device having the structure Al/MEH-PPV/CNT/Ca/Al. For comparison, the baseline device has similar structure except CNTs were not incorporated at the cathode-organic interface.

at the origin of device improvement when they are incorporated at the cathode-organic interface of OLEDs.

This research has been supported by the U.S. Department of Energy, Office of Energy Efficiency and Renewable Energy, under Contract No. DE-AC02-05CH11231.

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