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Effects of single walled carbon nanotubes on the electroluminescent performance of organic light-emitting diodes

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ABSTRACT

Effects of single walled carbon nanotubes (SWNTs) on the electroluminescent performance of organic light-emitting diodes (OLEDs) have been investigated by mixing them in a hole-conducting layer and in a light-emitting layer in OLEDs. We found that SWNTs play different roles when used as polymer:SWNT composites in OLEDs. When used in a hole-conducting layer, SWNTs facilitate the charge transport in the transport layer and on the other hand they also act as the exciton quenching centers at the transporting/emitting interface provided their concentration is high enough. When used in a light-emitting layer, SWNTs act as an n-type dopant to increase electron transport in p-type electroluminescent film and subsequently improve the balancing degree of bipolar injection, leading to an enhancement in the electroluminescence efficiency.

1. Introduction

Recently, much attention has been paid to use nanomaterials for improving the electroluminescent (EL) performance of organic light-emitting diodes (OLEDs) [1–4]. Among those nanomaterials, single walled carbon nanotubes (SWNTs) are expected to be useful in improving OLEDs due to their well-established synthesis process, excellent mechanical properties, and good carrier-transporting ability. Although SWNTs have been reported to improve the EL efficiency when used as polymer:SWNT composites, their role in OLEDs is not clear yet. Several possible explanations have been proposed, including (a) improving hole injection and transport [5], (b) improving the conductivity of polymer films [6], (c) hole-blocking in the polymer composite [7], and (d) hole trapping of SWNTs in a hole-conducting polymer [8]. However, these explanations are not suitable for explaining all the phenomena reported in the literature.

In this paper, we investigated the roles of SWNTs on the EL performance of OLEDs when mixing them with a hole-conducting material and a light-emitting material. Our findings provide a clear understanding of the role of SWNTs in OLEDs and will be helpful for improving OLED performance by using SWNTs.

2. Experimental

The SWNTs were synthesized by a laser ablation method [9], and was purified by hydrothermal and chemical treatments. The SWNTs contain two-third semiconducting and one-third metallic nanotubes [10]. As a result, the SWNTs can exhibit both charge transport and electron withdrawing abilities. The hole injection material poly(3,4-ethylenedioxythiophene) doped with poly(styrene sulfonate) (Baytron P 4083) (PEDOT) was acquired from the Bayer Company. The hole-transporting material (PVK) and the electron-transporting material (PBD) were

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purchased from Sigma–Aldrich Company and used as received. The light-emitting conjugated polymer polyfluorene (PFO, purchased from H.W. Sand Company) and Super-Yellow (purchased from Merck Company) were used as received. The electrophosphorescent material Iridium (III) tris(2-(4-totyl)pyridinato-N,C^2) [Ir(mppy)$_3$] was purchased from American Dye Source Inc. In order to investigate the role of SWNTs on the performance of the OLEDs, three types of device architecture were fabricated. The first type of devices have the structure of ITO/PEDOT:SWNT (*x* wt.%, 40 nm)/PFO (80 nm)/Ca (20 nm)/Al (80 nm), where *x* is 0, 0.001, 0.01, and 0.02, relative to solid PEDOT content. The second one is ITO/PEDOT:SWNT (0.01 wt.% relative to solid PEDOT content, 40 nm)/PVK:PBD:Ir(mppy)$_3$ (69 wt.%:30 wt.%:1 wt.%, 60 nm)/Ca (20 nm)/Al (80 nm), which use Ir(mppy)$_3$ as a phosphorescent emissive material. The third one has a structure of ITO/PEDOT (40 nm)/Super-Yellow:SWNTs (*x* wt.%, 80 nm)/Ca (20 nm)/Al (80 nm), where *x* is 0 and 0.005.

To get the uniform dispersion of SWNTs in PEDOT, we suspended the SWNTs functionalized by with crown ether, making them dispersible in deionized water [11]. They were then ultrasonicated the SWNTs solution 30 min, and then we mixed the SWNT solution with PEDOT solution and deionized water to form the composites at designed doping concentration. For the Super-Yellow:SWNTs composite preparation, SWNTs dispersed in chloroform were added into Super-Yellow chloroform solution to give the desired doping concentrations. The PEDOT:SWNTs composites were spin-coated onto ITO-coated glass substrate and the thickness of the film was 40 nm. The light-emitting layers for the three types of devices were all formed by spin coating from their chloroform solutions. Finally, the calcium (Ca) and aluminum (Al) electrode were deposited sequentially by thermal evaporation under the vacuum of 2×10^{-6} Torr, and the deposition rate was typically about 1 Å/s. The thicknesses and the morphology of the films and were measured by a Veeco atomic force microscopy (AFM) using a tapping mode. The resistivity and conductivity of PEDOT:SWNTs composite films on glass substrates were measured by a four-probe method with a Keithley source meter. The current and voltage characteristics of the OLEDs were measured with Keithley 2400 source meter. The EL spectra of OLEDs were recorded by a HORIBA Jobin Yvon spectrometer. The luminance and efficiency of OLEDs were measured by an OLED testing system calibrated by the National Institute of Standards and Technology.

3. Results and discussion

We investigated the roles of SWNTs in a hole conducting layer on the performance of OLEDs at first. Fig. 1a shows the current density–voltage (*J*–*V*) characteristics of OLEDs employing PEDOT:SWNTs composites with various doping concentrations under a forward bias. With increasing the SWNTs concentration in PEDOT, the current density of devices becomes higher under the same voltage, which means the hole injection and/or transport are improved by introducing SWNTs in the PEDOT layer of devices. However, the EL intensity did not show a monotonous increase when increasing the SWNTs concentration in PEDOT under the same current density. From Fig. 1b we can see that when the SWNTs concentration in PEDOT is no higher than 0.01 wt.%, then the higher the doping concentration, the stronger the EL intensity. But when the doping concentration of SWNTs reaches 0.02 wt.%, the EL performance of the devices deteriorates, and the EL intensity becomes lower than that of the device without SWNTs doping. Our results have some differences compared to those reported by Woo et al. [8]. In their case, the doping concentration of SWNTs in PEDOT is no less than 0.05 wt.%. Although they also observed the enhancement of current density when increasing the SWNTs doping concentration in PEDOT, they only found that EL brightness in devices employing PEDOT:SWNTs composites was reduced relative to the device without using SWNTs. As a result, their explanation of SWNTs as hole traps in PEDOT film should be reconsidered, since there would be no EL intensity enhancement in our case if the injected holes were initially trapped by SWNTs in PEDOT film.

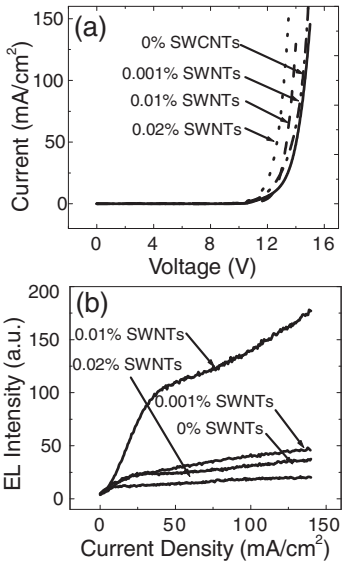

Fig. 1. The *J*–*V* curves (a) and the EL intensity–current density curves (b) of devices with the structure of ITO/PEDOT:SWNTs (*x* wt.%, 40 nm)/PFO (80 nm)/Ca (20 nm)/Al (80 nm).

We investigated the conductivity of PEDOT:SWNTs composite films with different doping concentration of SWNTs. It is shown in Table 1 that when the SWNTs

Table 1
The resistivity (ρ) and conductivity (C) of PEDOT:SWNT composite films with various SWNT concentration.

SWNT concentration (%)	ρ (Ω cm)	C (S/cm)
0	44,902	2.23×10^{-5}
0.0004	40,778	2.45×10^{-5}
0.0042	31,709	3.15×10^{-5}
0.0010	29,775	3.36×10^{-5}
0.6622	23,666	4.23×10^{-5}