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Lambertian white top-emitting organic light emitting device with carbon nanotube cathode

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We demonstrate that white organic light emitting devices (OLEDs) with top carbon nanotube (CNT) electrodes show almost no microcavity effect and exhibit essentially Lambertian emission. CNT top electrodes were applied by direct lamination of multiwall CNT sheets onto white small molecule OLED stack. The devices show an external quantum efficiency of 1.5% and high color rendering index of 70. Due to elimination of the cavity effect, the devices show good color stability for different viewing angles. Thus, CNT electrodes are a viable alternative to thin semitransparent metallic films, where the strong cavity effect causes spectral shift and non-Lambertian angular dependence. Our method of the device fabrication is simple yet effective and compatible with virtually any small molecule organic semiconductor stack. It is also compatible with flexible substrates and roll-to-roll fabrication. © *2012 American Institute of Physics*. [http://dx.doi.org/10.1063/1.4767439]

INTRODUCTION

Top-emitting organic light emitting devices (OLEDs) hold a couple of key advantages, which make them very attractive for OLED lighting and OLED display applications.[1–4] Top-emitting OLEDs are better suited for active-matrix applications as they can be more easily integrated with a non-transparent transistor CMOS backplane. Another important advantage of top-emitting OLEDs is that they can be deposited onto virtually any substrate, including flexible substrates such as metal foils and plastics. While few electrode options are available for bottom-emitting OLEDs, it is particularly challenging to fabricate top-emitting OLED, due to lack of suitable (semi-) transparent electrode materials, which can be deposited directly on top of organic stack, without damaging the soft and sensitive organic layers. Indium tin oxide (ITO) is a benchmark for thin film transparent electrodes for bottom electrode small molecule OLED devices. However, the deposition of top-electrodes using sputter deposition processes usually damages the upper organic layers and leads to high leakage current[5] as well as low lifetime[6] of the device. Therefore, top electrodes made from sputtered ITO are not well suited for top-emitting OLED devices. Another well-studied option for ITO replacement is a conducting polymer (e.g., poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate) (PEDOT:PSS)). However, conducting polymers are typically applied from solution[7] (e.g., water) and thus are not compatible with small molecules utilized in OLED devices. This leaves thin metallic films as only choice for top OLED electrode.

Generally top-emitting devices–incorporating two highly reflecting electrode contacts–are showing microcavity effects. As a result of this microcavity layer structure, the emission shows a very small-band full width at half maximum (FWHM). FWHM strongly depends on the reflectivity of both organic/electrode interfaces and can be estimated as[8]

$$FWHM = \frac{\lambda^2}{2L} \times \frac{1 - \sqrt{R_1 R_2}}{\pi (R_1 R_2)^{1/4}}, \quad (1)$$

where R_1 and R_2 are the reflectivity of the two electrodes and L is the optical length between the two electrodes. For metal electrodes with high reflectivity, the emission spectra thus show limited spectral emission range and strong angle dependent emission spectra. This can–so far–only be partly alleviated by using a specially tuned organic layer structure in combination with a dielectric outcoupling layer[9] or dielectric/metal/dielectric multilayer, which suppresses metal reflection.[10–12] Nevertheless, color stability and color control of white light emission from top-emitting layer structures remain a great challenge.

In this work, we demonstrate that carbon nanotubes (CNTs) provide a viable alternative for small molecule top-emitting white OLEDs. CNTs have attractive properties such as mechanical durability and flexibility, chemical stability, transparency, and high conductivity. Unlike brittle ITO, CNTs are fully compatible with flexible substrates and can be applied via room temperature roll-to-roll processing. Many applications of CNT for OLEDs electrode were demonstrated. Typically CNT films are used for ITO bottom replacement.[13–21] Fabrication of CNT top electrode OLEDs is very challenging since organic semiconductors are very sensitive to processing conditions (solvents, temperature, oxygen, etc.). To the best of our knowledge, only one group so far reported on OLED with CNT top electrodes.[22] CNTs were applied on top of the polymer using polydimethylsiloxane

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(PDMS) soft stamp. In all previous reports, CNT electrode was only used for single emitter OLED devices. Angular emission dependences of fabricated devices were not reported so far.

We demonstrate that CNT can be deposited on top of small molecule p-i-n OLED devices. Utilization of p-i-n device concept together with room temperature direct lamination process effectively allows depositing CNT electrode onto virtually any organic stack. We further show that due to the non-reflective nature of CNT electrodes, white OLEDs with top CNT electrodes show almost no microcavity effect and nearly Lambertian emission. The devices fabricated show external quantum efficiency (EQE) values of 1.5%, which is similar to devices with top thin metal electrodes. Thus, we demonstrate that the use of non-reflective carbon based semitransparent electrodes (e.g., carbon nanotube, graphene, etc.) can solve the issues of color control and color stability for top-emitting white OLEDs.

OLED STRUCTURE AND LAYER DEPOSITION

The organic stack–depicted in Figure 1–consists of several organic layers on top of a 60 nm thick Al anode deposited on top of a glass substrate. The organic layers are arranged in a pin-sequence starting with 20 nm 2,2-(perfluoronaphthalene-2,6-diylidene) dimalononitrile (F6-TCNNQ) 4 wt. % doped MeO-TPD (N,N,N′,N′-Tetrakis(4-methoxyphenyl)-benzidine) electron transport layer (ETL) which is followed by 10 nm NPB (N,N′-Di(naphthalen-1-yl)-N,N′-diphenyl-benzidine) as electron blocking layer (EBL). The successive emission layer (EL) consists of 10 nm Ir(MDQ)$_2$(acac) (Iridium(III)bis(2-methyldibenzo-[f,h]chinoxalin) (acetylacetonat)) (5 wt. %) doped NPB for phosphorescent red emission, 3 nm Ir(ppy)$_3$ (Tris(2-phenylpyridin) iridium(III)) (5 wt. %) doped TCTA (4,4′,4″-tris(carbazol-9-yl)-triphenylamine) for phosphorescent green emission and 10 nm TPBe (2,5,8,11-Tetra-tert-butylperylene) (1 wt. %) doped MADN (2-Methyl-9,10-bis(naphthalen-2-yl)anthracene) for fluorescent blue emission. Thereby, the fluorescent and phosphorescent emission systems are separated by a 1.5 nm thick interlayer (IL) from TCTA and TPBi (2,2′,2″-(1,3,5-Phenylen)tris(1-phenyl-1H-benzimidazol)) with a ratio of 1:2 to hinder mutual exciton quenching. The multi-emission layer system is followed by a 10 nm thick hole blocking layer (HBL) from the material NET5 (Novaled electron transporter) and the ETL consisting of NDN1 (Novaled n-dopant) (8 wt. %) doped NET5 with a thickness d of 35 nm (**1**), 95 nm (**2**), or 122 nm (**3**). On top of the organic layer stack the top-electrode is deposited. CNT electrodes and Ag (15 nm) are used for comparison. The deposition of the organic layers and the metal electrodes is realized by thermal evaporation in a UHV chamber (J. K. Lesker) at a pressure of 10^{-7} mbar. The white top-emitting OLED devices with the new CNT cathode are denoted with **A**, whereas commonly used thin Ag cathode layer are denoted with **B**.

layer	material	thickness (nm)
cathode	Ag or CNT	15/d(CNT)
ETL	NET5:NDN1	d
HBL	NET5	10
EML3	MADN:TBPe	10
IL	TCTA:TBPi	1.5
EML2	TCTA:Ir(ppy)	3
EML1	NPB:Ir(MDQ) (acac)	10
EBL	NPB	10
HTL	MeO-TPD:F6-TCNNQ	20
anode	Al	60

FIG. 1. OLED stack using either CNT or thin Ag as cathode.

CNT CATHODE DEPOSITION

Free standing CNT sheets were obtained as described elsewhere.[18] For this study, we used CNTs with sheet resistance of 1500 Ω/□ and a high transparency in the visible range of 380–780 nm (75% at 550 nm) depicted in Figure 2. Furthermore, both CNT samples on top of glass substrates show very low reflectivity values, which were hardly measurable with our spectrometer ($R_{CNT} < 5\%$). Low optical reflection and scattering was shown before for different semi-transparent CNT based films.[23–25] The CNT cathode layers–used for devices **A**–are self-laminated onto the organic ETL layer in inert atmosphere as shown in Figure 3. Subsequently, all devices are encapsulated with glass cover lids and UV-curing glue.

OLED CHARACTERIZATION

All devices are electrically and optically characterised using an automated measuring setup, consisting of a calibrated array-spectrometer (CAS 140CT-153) in combination with a Keithley 2400 Source Meter as well as a self-made goniometer setup, detecting the angle dependent emission spectra from 0° to 90°. From the measurement data, the efficiencies are calculated using the procedure presented by Meerheim *et al.*[26] The optical properties of CNT electrodes are measured using a spectrophotometer Perkin-Elmer Lambda 900.

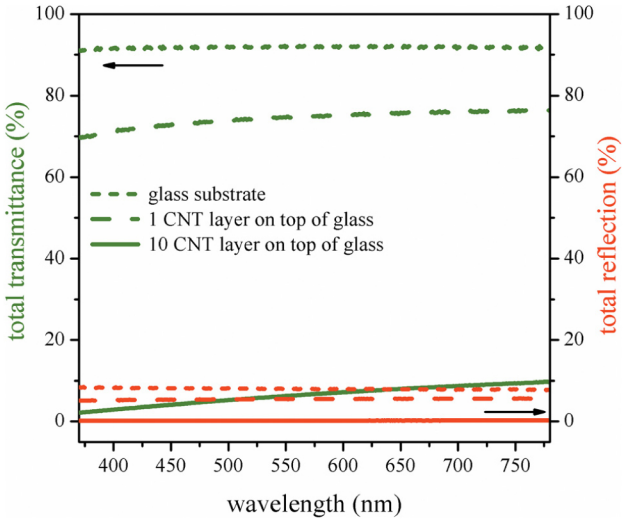

FIG. 2. Un-polarized total transmission and reflection of a CNT layer used as cathode for devices type **A** and a sheet of 10 CNT layer on top of glass. The measurements were performed with a spectrometer Solid Spec-3700.

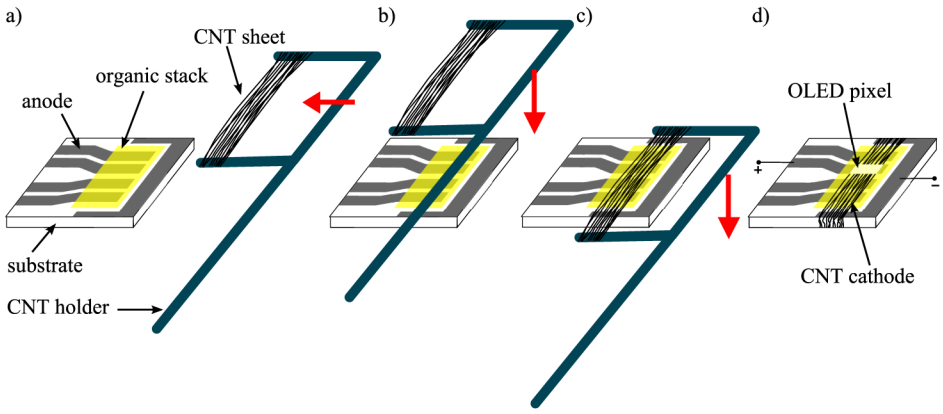

FIG. 3. Self-lamination of a CNT cathode. (a) Prepared OLED sample with deposited organic layers (yellow) on top of four anode contacts and prepared CNT-sheet. (b) and (c) Process of self-lamination: The CNT-sheet holder is moved downwards to the prepared substrate laminating the CNT-sheet on top of the organic layers. (d) The CNT sheet acts as cathode to the OLED.

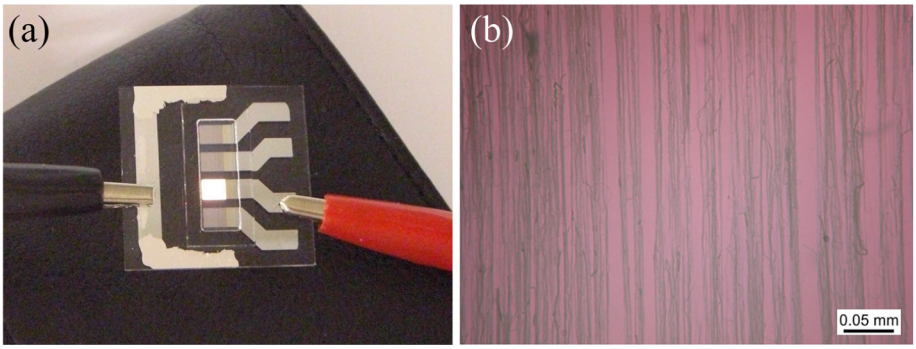

FIG. 4. (a) Photograph of the white-emitting OLED with CNT top electrode under operation and (b) microscope picture of the top-emitting OLED surface with parallel aligned CNT tubes forming the cathode but leave space between each other.

RESULTS AND DISCUSSION

A photograph of the fabricated device **A** under operation is depicted in Figure 4(a). A very homogeneous light emission can be seen from the whole OLED pixel area, which shows that the deposited CNT film provides a quite uniform coverage of the organic stack (see Figure 4(b)).

The current density-voltage characteristics for the prepared devices are depicted in Figure 5. For the devices **B** with metal cathode, the ETL thickness has a negligible effect on the jV-characteristics due to relatively high conductivity of the ETL layer. The situation is, however, different for CNT cathodes: Penetration of CNT bundles through the ETL leads to complete electrical short of device **A1** with thinner ETL layer thickness (not shown in Figure 5) and high leakage current equivalent to partial electrical short of device **A2**. Device **A3** with highest ETL layer thickness of 122 nm on the other hand shows reverse-current values similar to Ag references devices, which allows us to conclude that ETL thickness of 122 nm is sufficiently large to prevent electrical shorts of the OLED with CNT cathode.

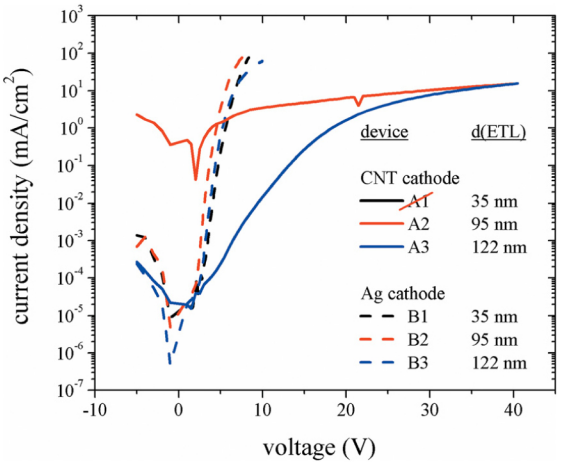

FIG. 5. *jV*-characteristics of the fabricated devices with different ETL layer thicknesses *d* and different cathodes. Device **A1** is not shown due to an electrical short.

Table I summarizes the key values of some devices. The external quantum efficiency of device **A2** at a driving current of 1 mA is about 1.5% (474 cd/m^2) as calculated from angle dependent emission spectra (Figure 6). Due to the high resistance of the carbon nano tubes, much higher voltages are needed for CNT devices compared to the low resistive thin Ag cathode layer. This results in a low power efficiency. Better conductivity of CNT film could substantially improve power efficiency of the OLED device. Devices **A3** and **B3** with a ETL layer thickness of 122 nm show values of 0.55% and 2.97%, respectively. A low electrical conductivity severely limits the practical application of the fabricated

TABLE I. Key values of the running devices at a driving current of 1 mA.

Parameter	Unit	**A2**	**A3**	**B3**
Thickness *d* of ETL	nm	95	122	122
Top-cathode-material		CNT	CNT	Ag
External quantum efficiency	%	1.46	0.55	2.97
Luminous efficacy	lm/W	0.2	0.1	1.43
Luminance	cd/m^2	474	203	360
CIE x		0.470	0.455	0.353
CIE y		0.372	0.384	0.264
CRI		70.1	72.6	55.8
CCT	K	2272	2549	3826

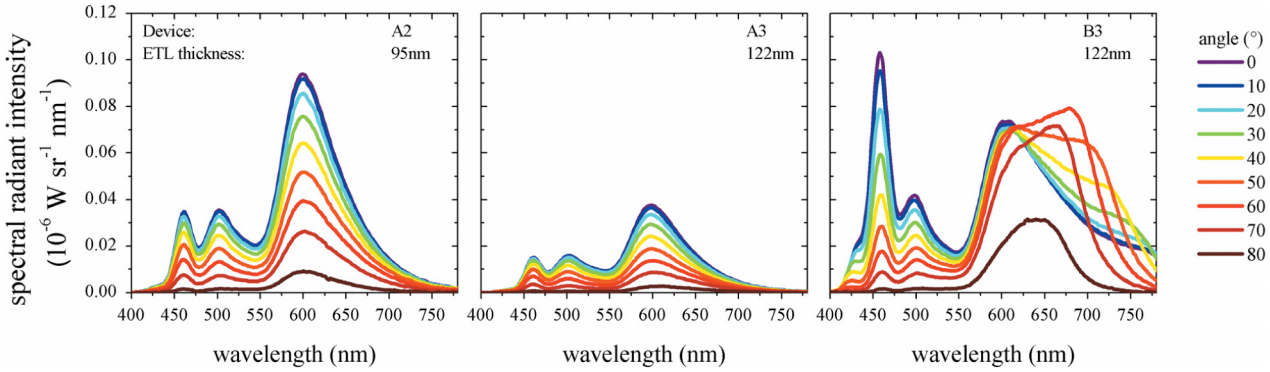

FIG. 6. Spectral radiant intensity of devices **A2**, **A3**, and **B3** driven at a current of 1 mA. As reference, device **B3** shows very strong microcavity effect.

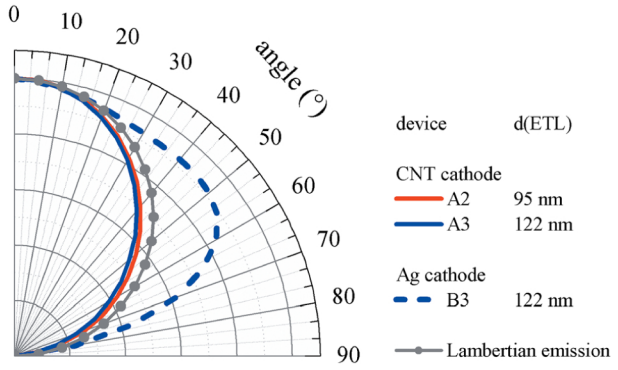

FIG. 7. Polar-diagram of the devices **A2**, **A3**, and **B3**. CNT devices **A** show emission characteristics very close to ideal Lambertian emission.

devices due to the low device power efficiency (Table I). Straightforward the idea of stacking many CNT layers together brings the sheet resistivity down. However, in the same time, the optical transmission also goes down (see Figure 2), which degrades the utility of this approach due to the loss of EQE of the OLED device. Consequently, other methods to improve the CNT film conductivity have to be considered, e.g., the improvement of the CVD method for a better control of individual CNT properties (diameter, length, amount of structural defects, doping, etc.[25]).

Based on the OLED spectra at an angle of 0°, the chromaticity coordinates (CIE 1931), color rendering indices (CRI), and correlated color temperature (CCT) are calculated. For both CNT devices, color rendering indices above 70 are reached, which is quite high for white lighting device and similar to the best values reported for semitransparent metal electrodes.[10,27]

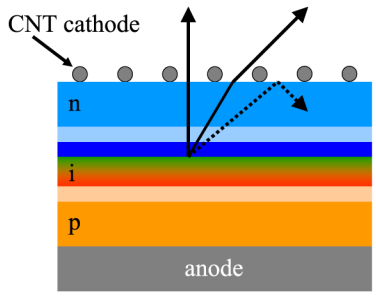

FIG. 8. Scheme of the light outcoupling mechanism of the white top-emitting OLED with porous carbon nanotube cathode.

Figure 7 shows the polar-diagram of the samples **A2**, **A3**, and **B3**. It can be seen that both CNT OLEDs **A** with ETL thickness variations of 95 and 122 nm show essentially Lambertian emission, compared to devices **B**.

Minor deviations (reduction) of the intensity of CNT devices at large angles is caused by internal total reflection of the light at the N_2/organic interface (see Figure 8). Furthermore, due to the strong microcavity effects for reference device **B3**, a strong angle dependence can be detected. This results in a shift of the EL peaks as well as the change in the ratio between the peaks. For the organic layer thickness of device **B3**, the cavity emission shows a minimum for the visible emission wavelength leading to a low and unbalance emission spectrum.

SUMMARY

In summary, we fabricated top-emitting white organic light emitting devices with a carbon nanotube film cathode. Carbon nanotube electrodes were deposited by direct lamination from free standing multiwall carbon nanotube sheets onto small molecule OLED stack. The usage of CNT layer hereby realizes white OLEDs without any strong cavity effects as known from OLEDs where both electrodes are made from metal layers. Thus, CNT OLED devices avoid complicated optical design to alleviate the undesired microcavity effect, which is particularly problematic for white emission. Fabricated top-emitting white OLEDs with CNT show nearly Lambertian emission, well balanced white emission with CRI of 70 and negligible spectral change with higher viewing angle.

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