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Single walled carbon nanotube anodes based high performance organic light-emitting diodes with enhanced contrast ratio

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ABSTRACT

Commercially-available single walled carbon nanotubes (SWCNTs) were used to fabricate SWCNT sheets for anodes of organic light-emitting diodes (OLEDs) by spray-coating process without any use of surfactant or acid treatment. A layer of DMSO doped PEDOT:PSS was spray-coated on the SWCNT sheets to not only lessen the surface roughness to an acceptable level, but also improve the conductivity by more than three orders of magnitude. For our SWCNT-based OLEDs of tris-(8-hydroxquinoline) aluminum (Alq_3) emission layers, a maximum luminance 4224 cd/m^2 and current efficiency 3.12 cd/A were achieved, which is close to the efficiency of ITO-based OLEDs. We further found out that our OLEDs based on the PEDOT:PSS covered SWCNT anodes tripled the contrast ratio of the conventional indium tin oxide (ITO) based OLEDs.

1. Introduction

Over the past decade, enormous efforts have been made to fabricate highly conductive, transparent, flat and flexible single-wall carbon nanotube (SWCNT) sheets for their potential to substitute and surpass the conventional transparent conducting oxide—indium tin oxide (ITO) in an extensive variety of optoelectronic devices [1–5]. For ITO suffers from the drawbacks of high cost, inherent brittleness, and need for high-temperature processing [6,7], it is not an ideal choice for large-area and flexible application. As transparent anode material for organic light-emitting diodes (OLEDs), SWCNT has a work function (of 4.5–5.1 eV) [8] similar to or even better than that of ITO (4.4–4.9 eV) [9]. In addition, the SWCNT sheet boasts key properties such as flexibility, transparency, high conductivity and fitness of solution process, which is a promising candidate to replace ITO in OLED technology for flexible applications and mass-manufacture. Several groups have reported SWCNT sheets parallel to ITO sheets with low sheet resistance below 200 Ω/sq accompanying high transmittance above 80% in visible region, using surfactant and acid treatment [3,10–14].

However, the OLEDs based on these SWCNT sheets had hardly acquired the satisfactory performance as the ITO-based OLEDs did [3,13,15]. Besides the attribution that the inherent excessive surface roughness of SWCNT sheets due to SWCNT's large aspect ratio should be responsible for the difference between SWCNT based and ITO based OLEDs, during the process of fabricating these SWCNT sheets, it is found that although some surfactants can result in stable dispersion by structureless random absorption on SWCNTs [16], they also cover up and denature the SWCNTs [17,18] in addition to more or less the toxicity they have. Moreover, the subsequent acid treatment has been reported to destroy most SWCNTs [19–21], poison the emissive layer for the presence of residual mobile counterions and can cause delamination from the underlying substrate, affecting the properties of devices based on these SWCNTs.

In this paper, we report a high performance OLED based on the SWCNT anode, which achieved a maximum luminance and current efficiency of 4224 cd/m^2 and 3.12 cd/A,

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respectively. The commercially-available SWCNTs were used to fabricate SWCNT sheets by spray-coating process with no use of any surfactant or acid treatment. Dimethyl sulfoxide (DMSO) doped poly(3,4-ethylenedioxythiophene): poly(styrenesulfonate) (PEDOT:PSS) [22] was used to improve the resistance and surface roughness of SWCNT sheets. Finally, the optical properties of the SWCNT anode based OLEDs were explored. The result demonstrated a triple contrast ratio higher than that of the conventional ITO-based OLEDs.

2. Materials and methods

The SWCNTs were purchased from Shenzhen Nanotech Port Co. Ltd. with CNT purity >90 wt.%, SWCNT purity >60 wt.%, outer diameter <2 nm and length in the range of 5–15 μm. The SWCNT sheets were fabricated by spray-coating process suitable for adjusting the sheet resistance and transmittance from 0% to 100% [4]. We started by dispersing the SWCNTs in ethanol solvent with the aid of ultrasonic treatment, and then the homogeneous dispersion (of 0.25 mg/ml SWCNTs) without further purification was spray-coated on the heated glass substrate at 120 °C, followed by 3-h drying at 85 °C. Through a patterned shadow mask, two SWCNT sheets were spray-coated on a glass substrate. On each of the four edges of the glass substrate, two rectangular ITO thin films were sputtered, acting as connecting electrodes to SWCNT sheets or to Aluminum electrodes. The inset image in Fig. 1 shows two SWCNT sheets with dimension of 5 × 25 mm spray-coated on the glass substrate.

In order to improve the conductivity and solve the problems like short-circuit or nonuniform injection of holes caused by the excessive surface roughness of SWCNT sheets, a 150 nm, 60 Ω/sq with 83.1% transmittance (at λ = 538 nm) planarization layer of PEDPT:PSS was directly spray-coated on the SWCNTs sheets. A concentration of 5 wt% DMSO was added continuously into the solution of PEDOT:PSS (BAYTRON® PH500) while being stirred, by which an improvement in conductivity of more than three orders of magnitude could be achieved [23]. Previously, the planarization layer was commonly spin-coated on the SWCNT sheet's surface [3,13–15,24]. Considering that the uniformity and morphology of SWCNT sheets spray-coated on the glass substrate may be degraded by spin-coating process, where the spin-coated solution is dipped on the surface of SWCNT sheets, and to some extent, disperses the SWCNT sheet, resulting in the degradation of the form and structure of it, we spray-coated the PEDOT:PSS solution on the SWCNT sheets at 110 °C, after mixing one PEDOT:PSS solution with nine ethanol followed by 30-min ultrasound. Finally, the PEDOT:PSS covered SWCNT sheets were put into the drying oven at 80 °C for three hours.

The OLEDs were eventually completed using a stake of small molecular organic layers and metal cathode in multisource organic molecular vapor deposition system at 3.0×10^{-4} Pa. The organic stack consists of 50 nm *N*,*N*′-diphenyl-1,1-bihyl-4,4-diamine(NPB) and 60 nm tris-(8-hydroxquinoline) aluminum (Alq_3). The cathode layer consists of 0.5 nm lithium fluoride (LiF) and 100 nm aluminum on the organic layer deposition. On one piece of glass substrate, 4 diodes were fabricated with dimension of 5 × 5 mm for each. Fig. 2(c) and (d) show the schematic diagram of the device structure and the photograph of an operating SWCNT-based OLED device.

The transmittance of the SWCNT sheets was obtained from the ratio of the measured transmittance of SWCNTs-coated glass, by MODEL U-3900H Spectrophotometer, to that of the glass substrate prior to spray-coating. The sheet resistance was measured by a four point method with CT5601Y Sheet Resistivity Meter. The AFM images and the

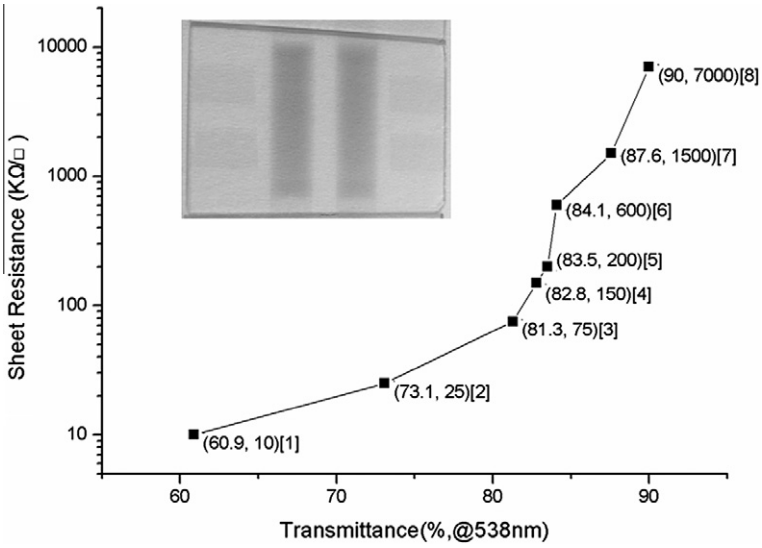

Fig. 1. The sheet resistance of spray-coated SWCNT sheets as a function of the transmittance at a wavelength of 538 nm (corresponding to the peak emission of OLEDs in our experiments). The inset image is the photograph of spray-coated SWCNT sheets on a glass substrate.