Highly Conductive Flexible Transparent Polymeric Anode and its Application in OLEDs

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Abstract

Highly conductive flexible transparent polymeric anode was fabricated by inclusion of single-wall carbon nanotubes (SWCNTs) into aqueous poly(3,4-ethylene dioxythiophene: poly(styrene sulfonate) (PEDOT:PSS) system. The transmittance and conductivity of the PEDOT:PSS/SWCNTs anode was studied as a function of the SWCNTs loading. Flexible transparent anode with low sheet resistance was fabricated and organic light-emitting devices fabricated using this PEDOT:PSS/SWCNTs as the anode exhibited a close performance to that obtained using indium tin oxide (ITO) anode.

1. Introduction

Indium tin oxide (ITO) has been by far one of the most common transparent anode materials for organic light-emitting device (OLEDs) because of its high work function, high transparency and availability related to its application in the liquid crystal displays (LCD) industry. However, ITO is not the ideal choice for fully flexible OLEDs because flexible devices fabricated on flexible substrates with ITO are too easy to be broken arising from the crack of the ITO when the substrate is bent [1]. Therefore, a great deal of interest has been paid to replacement of ITO for fully flexible OLEDs. Polymeric anode [2], metal anode [3, 4], modified oxide anode [5], and carbon nanotubes sheets [6], etc., have been adopted in flexible OLEDs or other optoelectronic devices to replace the traditional ITO anode. Among them, polymeric anode has been regarded as one of a most promising one for OLEDs because its low cost and high flexibility. Up to now, polymeric anodes still suffer low conductivity which limits its application in the electrode materials of OLEDs and other optoelectronic devices. It has been shown that conductivity of polymer can be highly improved by inclusion of high conductivity materials into the polymer matrix, as conductivity pathway through out the polymer matrix can be created by the highly conductive materials [7]. In this research, poly(3,4-ethylene dioxythiophene:poly(styrene sulfonate) (PEDOT:PSS), which was firstly developed by Bayer AG research laboratories [8] was adopted as its good film-forming properties, high conductivity, high visible light transmittance and excellent environmental stability. Single wall carbon nanotubes (SWCNTs) [9, 10] were selected as highly conductive doping materials due to its high aspect ratio, high conductivity, low percolation threshold and low absorption in visible region. Herein, we report the fabrication of highly conductivity transparent flexible polymeric anode and OLEDs based on the polymeric anode. Our devices based on the flexible polymeric anode exhibit high performances, which are close to those of the devices using ITO as anode.

2. Experimental

Poly(ethylene terephthalate) (PET) films with a thickness of 175μm (DuPont Teijin Films/Melinex® ST506) were adopted as flexible substrate. The 120Ω/□ sheet resistance of the PET coated with ITO films (CPFilms Inc.) was used for reference. The patterned ITO/PET substrates and PET substrate were cleaned by sequential rinsing in non-ionic detergent, de-ionized water, acetone and isopropyl alcohol each for 10 minutes with ultrasonic baths and dried in a vacuum oven for 12 hours at 60°C. The PET substrate was treated by O_2 plasma for 8 minutes.

Dimethyl sulfoxide (DMSO) was added into the dispersion of PEDOT:PSS (BAYTRON® PH 500) to improve its conductivity. Different concentration of the DMSO was adopted to achieve an optimal value. Before spin-coating, the solution was filtered by 0.45μm polyvinyl difluoride (PVDF) syringe filter. Films with a thickness of 100nm were obtained. Different baking temperature was conducted on the DMSO treated PEDOT:PSS films and the conducted of the films was tested.

An optimal concentration of DMSO and SWCNTs (Nanocs Inc.) were added into the PEDOT:PSS solution and disturbed for a few hours. Thin nanocomposite films of PEDOT:PSS and SWCNTs with a thickness of 100nm were obtained by spin-coating method. The films were baked at an optimal condition obtained.

Transmittance of the PEDOT:PSS and SWCNTs nanocomposite films on PET substrate was measured by a UV/VIS spectrometer (Perkin-Elmer Lambda 18). The sheet resistance of the films was determined with a multi-meter by measuring the resistance (R) between two parallel silver electrodes, which were fabricated by vacuum evaporating method through a shadow mask, as shown in Fig. 1. In this research, W and L were adopted as 10mm. The conductivity tests were conducted in glove box with N_2 at room temperature.

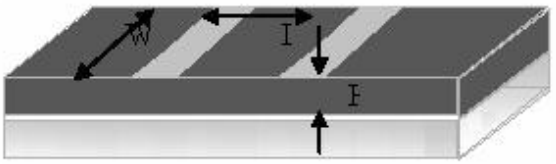

Fig. 1 Measuring the sheet resistance of thin PEDOT:PSS films. W, L, H are the contact length between silver electrode and PEDOT:PSS film, distance between the two sliver electrodes and thickness of the PEDOT:PSS film, respectively. When W=L, we obtain the sheet resistance of the film with a thickness of H.

The basic structure of the OLED devices is two layer structure with a hole transport layer of TPD and emitting/electron transport layer of Alq_3 film sandwiched between a transparent ITO anode or PEDOT:PSS/SWCNTs anode and a LiF/Al cathode, as shown in Figure 2. The TPD,

Alq_3, LiF and Al films were deposited under a vacuum of 2×10^{-6} Torr with a deposition rate of 0.5nm/s, 0.2nm/s, 0.3nm/s and 0.5nm/s, respectively. The thickness of each layer was measured by quartz oscillating thickness monitors. The effective size of the devices is $10mm^2$. The steady-state current-voltage-luminescence (I-V-L) characteristics and electroluminescence (EL) spectra of the devices were measured using 814 photomultiplier detection system Photon Technology International (PTI) under ambient environment at room temperature.

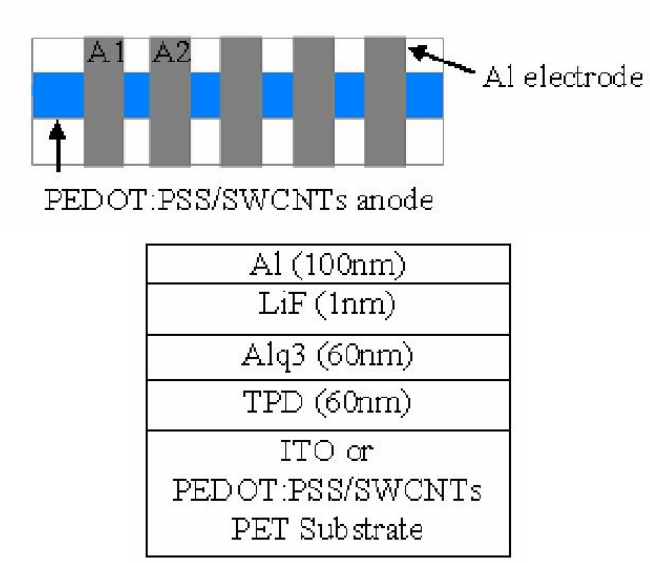

Fig. 2 Schematic diagram showing the OLEDs with a configuration of transparent anode/TPD/Alq_3/LiF/Al on flexible PET substrate

3. Results and discussion

The conductivity of PEDOT:PSS films as function of DMSO concentration under different baking temperature is shown in Fig. 3. It was found that the conductivity of the PEDOT:PSS can be dramatically increased by a degree of three orders after solvent treatment together with temperature treatment. The conductivity of the PEDOT:PSS films can reach a relatively stable value as the concentration of DMSO be to about 5%. When a DMSO treated PEDOT:PSS was dried in a vacuum at room temperature, no conductivity enhancement was observed, which indicated that both the post-treatment temperature and the solvents treatment are very important parameters for the conductivity enhancement of the PEDOT:PSS film. Further increase the temperature over 200°C, decrease of the conductive was observed at the PEDOT:PSS films. With increase of the baking temperature, the decrease of the conductivity was even more obvious, which might due to the decomposition of the PEDOT:PSS at a higher temperature.

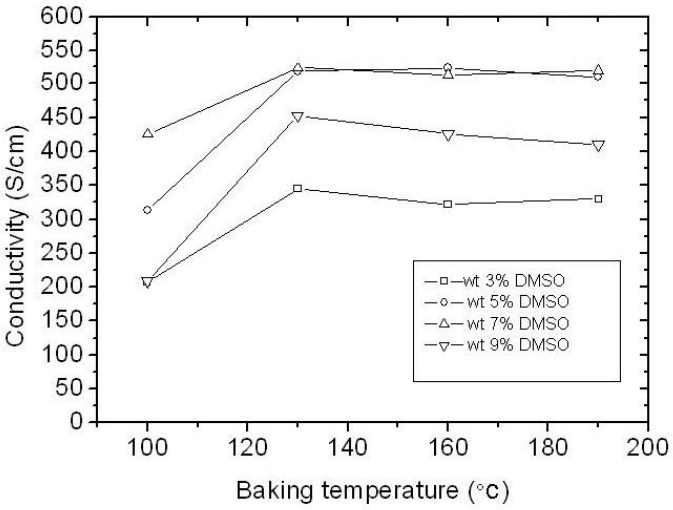

Fig. 3 Conductivity of thin (about 100nm) PEDOT:PSS films with different doping ratio of DMSO under different baking temperature with a baking time of 10 minutes

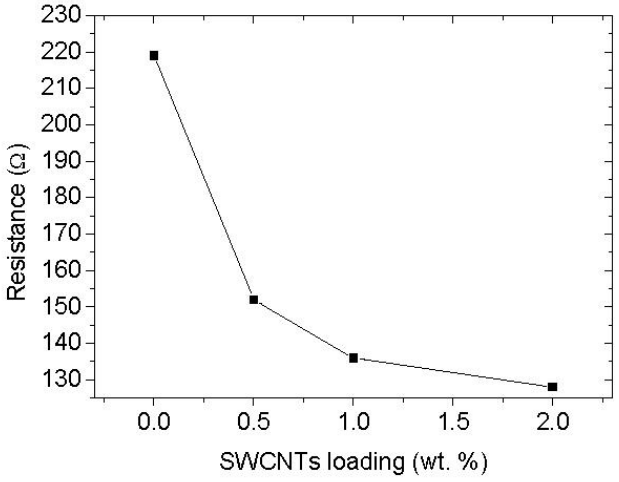

Fig.4 Sheet resistance of thin (about 100nm) PEDOT:PSS/SWCNTs films (with a concentration of wt. 5% DMSO doping) as function of SWCNTs loading

Fig.4 shows the sheet resistance of thin PEDOT:PSS films with a thickness of 100nm as function of SWCNTs loading. It was found that the conductivity of the PEDOT:PSS was improved with the increasing of the SWCNTs loading, which indicated that the conductivity pathway of SWCNTs was formed in the PEDOT:PSS system. However, the conductivity was increased not in orders degree as shown in other polymer/SWCNTs system [7, 9]. Possible explanation is that the conductivity difference between the different polymer systems. Sheet resistance of Batron VP AI 4083 is in the degree of MΩ, and those of poly(m-phenylenevinylene-co-2,5-dioctyoxy-p-phylenevinylene) (PmPV) and polyvinylalcohol (PVA) are in thousands of MΩ degree, while sheet resistance Batron PH500 is in several hundreds. When the SWCNTs conductive pathway formed, low conductive polymer systems contribute very little to the

conductivity, with the increase of conductive SWCNTs loading, several orders degree of conductivity increase was obtained in the polymers. As in our PEDOT:PSS and SWCNTs system, polymer matrix has a relative high conductivity and conductivity difference between polymer system and SWCNTs is little, therefore, the conductive of the nanocomposites was determined by both the polymer system and SWCNTs network. In a result, the conductivity of PEDOT:PSS was not dramatically increased with the increase of SWCNTs loading.

Fig.5 shows the transmittance of thin PEDOT:PSS film, PEDOT:PSS/SWCNTs films and the PET substrate adopted in this research. It was found that the transmittance of the PEDOT:PSS film slightly decreased with the increased of the SWCNTs loading. Flexible polymeric anode with a sheet resistance of 136.2Ω and a transmittance of 80% in the visible region was obtained with thin PEDOT:PSS/SWCNTs films, as shown in Fig.6.

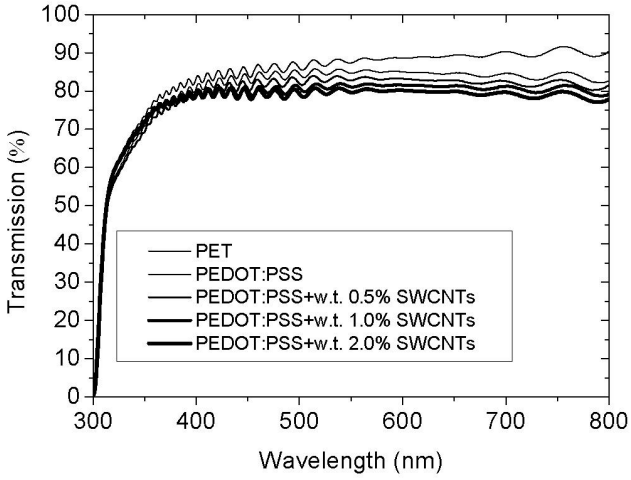

Fig.5 Transmittance of the thin PEDOT:PSS/SWCNTs films on flexible PET substrate

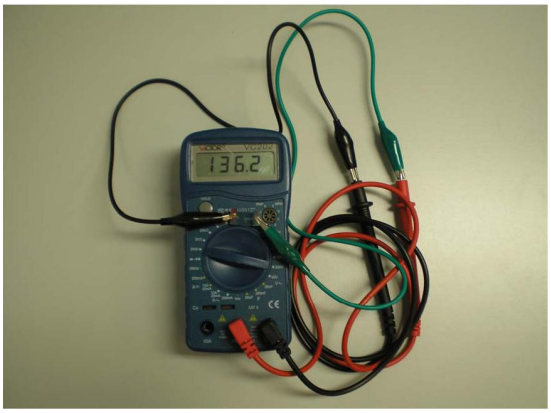

Fig. 6 Flexible transparent PEDOT:PSS with wt. 1% SWCNTs (with a concentration of wt. 5% DMSO doping) on PET substrate, the sample has a dimension of 10mm*10mm and a thickness of 100nm (sheet resistance: 136.2Ω)

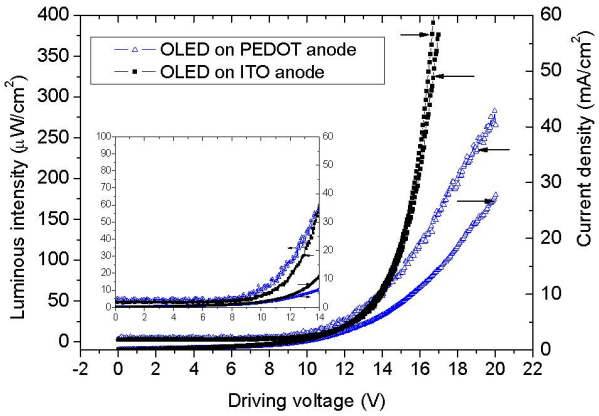

Fig.7 I-V-L curve of the OLEDs based on PEDOT:PSS/SWCNTs anode and ITO anode

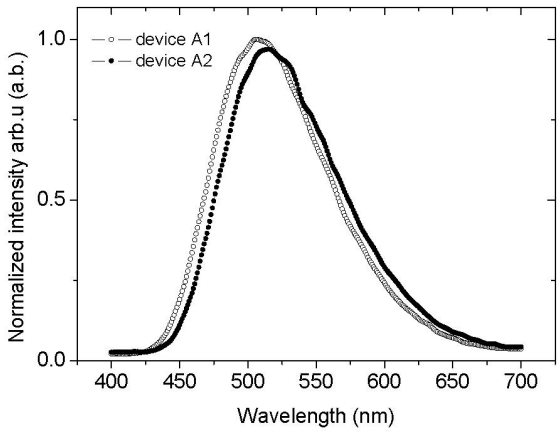

Fig.8 Normalized EL spectra of OLEDs based on PEDOT:PSS/SWCNTs anode, A1 is the device near the anode contact when applied an operating voltage, A2 is the one far from the anode contact that A1

Fig.7 shows the I-V-L curve of the OLEDs based on PEDOT:PSS/SWCNTs anode and ITO anode, respectively. It has been found that the OLEDs based on the PEDOT:PSS/SWCNTs has a close performance to the OLEDs based on ITO anode below a drive voltage of 14V. In addition, the OLEDs on PEDOT anode have a higher external efficiency than those OLEDs on ITO anode. As the work function of PEDOT:PSS is higher than that of ITO, therefore, holes can be more easily injected into the hole transport layer, which might result in the higher luminous intensity and higher external efficiency in the OLEDs based on PEDOT:PSS/SWCNTs anode. With the increasing of the drive voltage, higher luminous intensity was found in the OLEDs based on ITO anode. From the I-V cure, it was found that current density in these devices in much higher than those with PEDOT:PSS/SWCNTs anode. As the resistance of the PEDOT:PSS/SWCNTs anode is higher than those of ITO, therefore, the whole resistance of the devices based on

polymeric anode is higher, which leads to the lower current density in the OLEDs. Therefore, lower luminous intensity was obtained in the polymeric anode based OLEDs with a drive voltage above 14V.

Another phenomenon in the OLEDs based on PEDOT:PSS/SWCNTs anode is the red-shift of the EL spectra and decreasing of light intensity with the increasing the anode length, as shown in Fig.8 where the normalized EL spectra of device A1 and A2 measured at a drive voltage of 15V are depicted, which was not found in OLEDs based on ITO anode. According to the diode property of OLEDs, the total resistance of the devices is extremely large when the applied voltage is lower than the threshold voltage. The resistance of the PEDOT:PSS/SWCNTs anode is too small to affect the distribution of the applied voltage. The resistance of the devices decreases rapidly with the increase of the applied voltage, when the applied voltage is higher than the threshold voltage of the devices. The higher the applied voltage, the lower the whole resistance is. Therefore, the resistance of the anode is large enough to redistribute the applied voltage. With increasing of the anode length, voltage-drop will increase. In the PEDOT:PSS/SWCNTs/TPD/LiF/Al structure device subjected to a forward bias, holes and electrons will be injected from the anode into the TPD layer and Alq_3 layer, respectively, and move towards the interface between the TPD and Alq_3 layer. As a result of carrier injection, hole and electron accumulation in the TPD region and Alq_3 region near the interface will occur, respectively, since the barriers for holes and electrons exist at the interface between Alq_3 and TPD. As the bias voltage is increased, more electrons and holes can transit through the Alq_3 and TPD layer to reach their respective accumulation regions near the interface, respectively. The carrier densities near the interface thus increase with increasing the applied voltage. The continuous increase of the carrier density will give rise to occupation of the electronic states at higher energies; that is the band filling effect. When there is an applied voltage on A1 and A2, as A2 has a longer anode length, more voltage-drop occurs in A2 as the relative higher resistance of the anode. In addition, hole-trapping properties of the SWCNTs [11] will also decrease the hole mobility and prohibit more holes be injected into the hole transport layer of TPD. As same drive voltage is applied on the different device A1 and A2, the effective drive voltage on A1 will higher than those on A2. As a result of the different band filling effect, the red-shift of EL peak and decrease of light intensity were found in device A1 and A2.

4. Conclusions

In conclusion, different concentration of DMSO and baking temperature was studied to improve the conductivity of spin-coating PEDOT:PSS films. It was found that a higher conductive of PEDOT:PSS films can be obtained with a weight concentration of 5% DMSO and baking temperature of 130°C for 10 minutes. Further improvement of the PEDOT:PSS conductivity was achieved by inclusion of highly conductive SWCNTs into PEDOT:PSS system. The transmittance and conductivity of the anode as a function of SWCNTs loading were studied. The conductive of the PEDOT:PSS films was improved with the increase of the SWCNTs concentration together with a slightly decrease in the transmittance. Flexible polymeric anode with a thickness of 100nm on PET substrate was obtained and a transmittance of 80% and a resistance of 136.2Ω were achieved. OLEDs based on this polymeric anode have a very close performance to those on ITO anode. This flexible polymeric anode is a very promising anode for fully flexible OLEDs or other optoelectronics.

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