Conducting nano films based on multi-walled carbon nanotubes and poly(3,4-ethylene dioxy thiophene-poly(styrene sulfonate) for organic light-emitting diode

Phuong Hoai Nam Nguyen
Faculty of Engineering Physics and Nanotechnology, University of Engineering and Technology, Vietnam National University, 144 Xuan Thuy road, Cau Giay District, Hanoi, Vietnam
E-mail: namnph@vnu.edu.vn

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Abstract
It is well known that multi-walled carbon nanotubes (MWCNTs) are an excellent nanomaterial. In this paper, the nanocomposite ultra-thin films were fabricated consisting of MWCNTs and poly (3,4-ethylene dioxy thiophene-poly(styrene sulfonate) (PEDOT-PSS) for organic light-emitting diode (OLED). The field-emission scanning electron microscopy (FESEM) images of MWCNTs thin films show that the diameter of MWCNTs are 10–30 nm and their length is 300–500 nm. Electrical and optical properties of the films are investigated and the sheet resistance can reach minimum value at 36.5 $\Omega\text{sq}^{-1}$ and the transparency of the film is about 80%. The current density–voltage ($J–V$) characteristics of the devices were also studied.

Keywords: MWCNTs, PEDOT-PSS, thin film, OLED, nanocomposite, conductive polymer
Classification numbers: 4.10, 5.04, 5.10, 5.14

1. Introduction
Conductive polymers are organic materials that conduct electricity. They have conjugated double bonds in their molecular structure and are also called organic semiconductors. As in inorganic semiconductors, charge carriers in organic semiconductors are electrons and holes [1]. Motion of charge carriers in organic semiconductors depend on $\pi$ bonds and super position of quantum mechanical wave function.

Poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate) (PEDOT-PSS) is a good transparent and conductive polymer with high stability and moderate band gap. On the basis of these advantages, it has been used for many applications in semiconducting devices. Multi-walled carbon nanotubes (MWCNTs) have excellent properties [2], so nanocomposite thin film of PEDOT-PSS and MWCNTs is a kind of material having excellent conduction and high mechanical strength. Nanocomposite thin film of PEDOT-PSS:MWCNTs at MWCNTs weight concentration of 0.01% slightly reduces transparency but decreases sheet resistance about five times compared with the film of PEDOT-PSS [3, 4]. The use of intermediate poly(ionic liquid) (PIL) to link poly(3,4-ethylenedioxythiophene) (PEDOT) with MWCNTs leads to the increase of the conducting properties of the nanocomposite thin films. The sheet resistance of the thin film PEDOT-PIL/MWCNTs (MWCNTs weight concentration at 0.2%) decreased 65 times compared to the thin film of PEDOT [5]. In this work, ultra-thin films of PEDOT-PSS:MWCNTs have been fabricated and characterized. Some kinds of organic light-emitting diode (OLED) have been fabricated and the properties of devices were compared with each other. Ultra-thin film PEDOT-PSS:MWCNTs were introduced between the emission layer...
and the anode. The blend conducting polymer films of poly(9-vinylcarbazole) (PVK) and poly(2-methoxy-5-(2-ethoxyhexyloxy)-1,4-phenylenevinylene) (MEH-PPV) with optimal weight ratios of PVK:MEH-PPV have been fabricated and used as the emitting layer [6]. The device configuration of ITO/PEDOT-PSS:MWCNTs/PVK:MEH-PPV/TiO$_2$/Al is shown in figure 1. The current density–voltage (J–V) characteristics of the device were also studied. It provides an improved performance as compared to the control device.

2. Experimental

The MWCNTs, supplied from Shenzhen Nanotech Port Co. Ltd., were further purified with strong acid to remove the impurities. The acid-modification of CNTs was based on a mixture of concentrated nitric and sulfuric acids in a molar ratio of 3 : 1, respectively [5]. The suspended MWCNTs were added into the mixture of the acids and refluxed at 80°C for 20 min. After washing with de-ionized water until the supernatant attained a pH around 7, the samples were dried in a vacuum oven at 100°C. The infrared (IR) spectra of the acid-treated MWCNTs were determined by Fourier transform infrared (FTIR) spectrometer (GX-PerkinElmer—USA). The conducting polymers PVK and MEH-PPV were purchased from Aldrich Chemical Co. and used as-received. Indium tin oxide (ITO) and Al were used as the anode and the cathode, respectively. The sheet resistance of the ITO/PEDOT-PSS:MWCNTs/PVK:MEH-PPV/TiO$_2$/Al is shown in figure 1. The current density–voltage (J–V) characteristics of the device were also studied. It provides an improved performance as compared to the control device.

Figure 1. The structure of the OLED.

3. Results and discussion

Figure 2 shows the IR spectra of the MWCNTs before acid treatment (black curve) and after acid treatment (red curve).

It was found that after acid treatment, the MWCNTs have higher purity than raw MWCNTs. These spectra have the same peaks as those of CNTs because they correspond to the same carbon ring bonds. The peak at 1627 cm$^{-1}$ presents the carbon ring bond (C=C) in the structure of CNTs, the peak at 2923 cm$^{-1}$ presents the bond (C-H), the peak at 1830 cm$^{-1}$ presents the bond (C=O), the peak at 1109 cm$^{-1}$ presents the bond (C=N) [5, 8, 9]. These bonds were formed in the processing for the fabrication of MWCNTs. The difference between the IR spectra of raw MWCNTs and acid-treated MWCNTs is the appearance of same carbon ring bonds. The peak at 1627 cm$^{-1}$ presents the bond (C=C) in the structure of CNTs, the peak at 2923 cm$^{-1}$ presents the bond (C-H), the peak at 1830 cm$^{-1}$ presents the bond (C=O), the peak at 1109 cm$^{-1}$ presents the bond (C=N) [5, 8, 9]. These bonds were formed in the processing for the fabrication of MWCNTs.

The device configuration of ITO/PEDOT-PSS:MWCNTs/PVK:MEH-PPV/TiO$_2$/Al is shown in figure 1. The current density–voltage (J–V) characteristics of the device were also studied. It provides an improved performance as compared to the control device.

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Figure 2. IR spectra of raw MWCNTs and acid-treated MWCNTs.

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Figure 3. FESEM of PEDOT-PSS:MWCNTs thin films.

Figure 4. Transmittance of nanocomposite thin films of PEDOT-PSS:MWCNTs.

The transmittance of the nanocomposite thin films in the range from near ultraviolet to near infrared light are shown in figure 4. It was found that the transmittance of the PEDOT-PSS films was slightly decreased after inclusion of MWCNTs fillings. The nanocomposite film of PEDOT-PSS:MWCNTs = 100:0.5 (weight fraction) shows the transmittance about 80%.

Figure 5 presents the sheet resistance of the nanocomposite thin films. The resistance of the films decreases rapidly when increasing MWCNTs concentration and goes to minimum value of 36.5 $\Omega$ sq$^{-1}$ at PEDOT-PSS:MWCNTs = 100:0.5 due to the excellent conduction of the MWCNTs. However, the resistance of the films increases back when MWCNTs concentration exceeds the optimal value (PEDOT-PSS:MWCNTs = 100:0.5). The increase of the resistance of the films can be attributed to the increase of defects of the films when the concentration of MWCNTs is higher than the optimal point.

Figure 6 shows the current density–voltage ($J-V$) characteristics of the single layer device (A) and the multilayer devices using the PEDOT-PSS and PEDOT-PSS:MWCNTs films as the anode buffer layer (B and C). The multilayer device (C) was fabricated consisting of a transparent ITO electrode, the conducting nanocomposite ultra-thin film which has a thickness of 25 nm, the blend conducting polymer film and an aluminum (Al) electrode: ITO/PEDOT-PSS:MWCNTs/PVK:MEH-PPV/Al.

From figure 6 we see that the $J-V$ performances of the devices are strongly dependent on the presence of the nanocomposite thin film PEDOT-PSS:MWCNTs between the anode and the emitting layer. It can be seen that the current density of the multilayer devices (B and C) are much higher compared with those of the single-layer device (A) at the same operating voltage. Also, the threshold field of the multilayer devices strongly decreases to a value lower than 2 V. The single layer device performed very poorly. This result suggests that the tunneling of charge carriers between
ITO and PVK:MEH-PPV can highly enhance the injection of holes due to the large potential drop across the ultra-thin conducting layer; hence, the turn-on voltage is reduced and overall current density increases [11]. It also shows that the bias voltage to obtain the same current density for the OLEDs with PEDOT-PSS buffer layer is higher compared with that of the device with PEDOT-PSS:MWCNTs buffer layer. This is probably because the hole injection ability of the PEDOT-PSS might be improved by the MWCNTs fillings [12]. As the result, the PEDOT-PSS:MWCNTs thin layer enhances most of the holes injected from the anode to the emitting layer (PVK:MEH-PPV). In addition, the resistance decrease of the nanocomposites PEDOT-PSS:MWCNTs will reduce the bulk resistance of the OLEDs, which might be attributed to the increase of the current density. Therefore, great improvement in the performances of the devices were achieved with the use of nanocomposites of PEDOT-PSS and MWCNT as hole injection layer of the OLEDs.

4. Conclusion

We have prepared with nanocomposite thin films of PEDOT-PSS:MWCNTs for use in OLEDs. The performance of the device is improved in decreasing turn-on voltage (to lower 2 V) and increasing current density (to 0.8 mA mm$^{-2}$), leading to increase in the luminance and efficiency of the device. The nanocomposites of PEDOT:PSS and MWCNTs were fabricated by inclusion of acid-treated MWCNTs into aqueous PEDOT:PSS solution. The nanocomposite increases the hole injection at the nanocomposite–anode interface, therefore enhancing the internal quantum efficiency. The conduction properties of the MWCNTs might contribute to the improvement of the nanocomposites of PEDOT-PSS and MWCNTs, which leads to the improvement of the OLEDs.

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