Transparent and Conductive Properties of Nanocomposite Thin Film of MWCNTs and PEDOT-PSS for Applications in OLED

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Abstract: It is known that Multi-walled Carbon Nano Tubes (MWCNTs) are an excellent conduction nanomaterial while Poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT-PSS) is a conductive and transparent polymer. In this paper, we mix MWCNTs with PEDOT-PSS to create a new type of nanocomposite thin film which has both excellent conduction and transparency of each composition materials for applications in electronics and optoelectronics. The nanocomposite is synthesized by modifying MWCNTs in an acid solution then mix with PEDOT-PSS. The field emission scanning electron microscopy (FESEM) images of the fabricated thin film with 0.3 Wt% of MWCNTs show that the diameter and length of the MWCNTs are ca. 10-30 nm and 300-500 nm, respectively. Electrical and optical properties of thin film are also investigated: the sheet resistance reaches the minimum value of $36.5 \Omega/\square$ with the transparency of ca. 76% at the wave length of 600 nm. Furthermore, I-V characteristics of organic light emission diodes (OLEDs) made by the synthesized nanocomposite thin films are analyzed. The ITO/PEDOT-PSS:CNTs/PVK:MEH-PPV/Al multilayer OLED exhibits well improving performance with the work function of 0.8 V corresponding with the current of 0.4 mA while the ITO/PVK:MEH-PPV/Al simple OLED has the work function of 3 V and the current of only 0.01 mA.

Key words: MWCNTs, PEDOT-PSS, thin film, OLED, nanocomposite, conductive polymer.

1. Introduction

Conductive polymers are organic polymers that conduct electricity [1]. They have conjugated double bonds in their molecular structure and called organic semiconductor. Such as inorganic semiconductors, charge carriers in organic semiconductors are electrons and holes. Motion of charge carriers in organic semiconductors depend on π bonds and superposition of quantum mechanical wave function.

In energy band structure, an organic semiconductor has the Highest Occupied Molecular Orbital band (HOMO) and the lowest unoccupied molecular orbital band (LUMO), these two bands such as the valence band and the conduction band in an inorganic

semiconductor. In the ground state, the HOMO band exist electrons while the LUMO band do not exist electrons. When stimulating factors appear such as light or temperature, electrons in the HOMO band absorb energy so they become an excited state. If absorbed energy is equal or higher than band gap, electrons could jump up into the LUMO band. This processing is the same as electrons in the valence band jump up into the conduction band when electrons are excited in an inorganic semiconductor [2].

A typical conductive polymer is Poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate) (PEDOT-PSS). It has good transparency and conduction, high stability and moderate band gap. Base on these advantages, this polymer has many applications in semiconductor industry.

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A nanomaterial can be used to create a composite with PEDOT-PSS is Multi-walled Carbon Nano Tubes (MWCNTs). They are excellent conduction, high mechanical strength and hardness nanomaterial. Therefore, nanocomposite thin film of PEDOT-PSS with MWCNTs may possess excellent conduction, good transparency and high mechanical strength. Moon reported that the nanocomposite thin film of PEDOT-PSS: MWCNTs at 0.01 Wt% of MWCNTs reduced slightly its transparency but decreased its sheet resistance about 5 times compared with the thin film of PEDOT:PSS [3]. In addition, using intermediate poly(ionic liquid)(PIL) to link between PEDOT-PSS and MWCNTs, conduction of nanocomposite thin film of PEDOT-PSS:MWCNTs could be improved significantly: the nanocomposite thin film of PEDOT-PSS:MWCNTs at 0.2 Wt% of MWCNTs had sheet resistance which decreased 65 times compared with the thin film of PIL-PEDOT-PSS [4].

Due to properties of excellent conduction, good transparency, and high stable, the nanocomposite thin film of PEDOT-PSS:MWCNTs can be applied in electro-optic devices and one of favorite applications is to utilize it as an electron transport layer (ETL) or a hole transport layer (HTL) in organic light emitter (OLED). In our work, we synthesized the nanocomposite thin films of PEDOT-PSS:MWCNTs with various Wt% of MWCNTs. The obtained thin films are then used to fabricate organic light emission diodes (OLEDs). The detailed data of the fabricated OLEDs are investigated and reported.

2. Experiments

2.1. Clean and Modification of MWCNTs

Processing of clean and modification of MWCNTs were carried out accordingly with the reported procedures from literature [2]. Briefly, MWCNTs were oxidized in a solution of 3:1 of HNO_3 : H_2SO_4 , stirring for 3 h at 80 °C by a magnetic stirrer. After cooling down to room temperature, they were washed with DI

water and then dried in a vacuum oven for 24 h at room temperature.

2.2. Synthesizing of Nanocomposite Solution of PEDOT-PSS:MWCNTs

Acid-treated MWCNTs were mixed in a solution of PEDOT-PSS 70% , and several samples with 0.1, 0.2, 0.3, 0.4, and 0.5 Wt% of MWCNTs were prepared. All five samples were synthesized as following: The MWCNTs were dispersed in the PEDOT-PSS solution by a magnetic stirrer for 48h and shaking in ultrasonic machine for 6h at room temperature to made the nanocomposite solution of PEDOT-PSS:MWCNTs. Shaped substrate glasses of 1×1 cm were cleaned, then spin-coating method was utilized to obtain the thin films of PEDOT-PSS: MWCNTs on the cleaned glasses.

2.3. Fabrication of OLED

2.3.1 Fabrication of the Simple OLED Structure

ITO electrodes were prepared as show in Fig.1. Emission layer of MEH-PPV:PVK was coated on ITO electrodes, followed by coating of Al electrode on the emission layer to form simple OLED structure. In our work, the emission layer MEH-PPV:PVK was coated on the ITO electrodes by using the spin-coating method with the diagram presented in Fig. 3. While Al electrode was formed on the emission layer by the conventional vacuum thermal evaporation technique. Fig. 2 shows the simple OLED structure.

2.3.2 Fabrication of the Multilayer OLED Structure

In order to improve performance and lifetime of the OLED, ETL or HTL or both layers could be inserted into a simple OLED structure to obtain a multilayer OLED structure. Fig. 4 depicts them ultilayer OLED structure which was coated with PEDOT-PSS:MWCNTs thin film such as HTL in its structure. The diagram of formation of PEDOT-PSS:MWCNTs layer and MEH-PPV:PVK layer in the multilayer OLED structure is shown in

Fig. 1 A configuration of the ITO electrodes on the substrate.

Fig. 2 The simple OLED structure.

Fig. 3 The diagram of formation of MEH-PPV:PVK layer in the simple OLED structure.

Fig. 5. Al electrode was formed by the vacuum thermal evaporation technique as reported in fabrication of the simple OLED structure.

2.4. Characterization and Instrumentation

The IR spectrums were determined by using FT-IR spectrometer (GX-PerkinElmer - USA). The sheet resistances were measured by fourpoint probe resistivity measurements (JANDEL - UK) at room

temperature. And transparencies were measured by UV-Vis Spectrometer (JASCO V-570). Field emission scanning electron microscopy (FESEM) images were recorded by HITACHI S-4800 instrument.

3. Results and Discussion

3.1. Analysis Structure of MWCNTs

IR spectrum of raw MWCNTs and acid-treated MWCNTs are presented in Fig. 6. Clearly, these two spectrum shave the same peaks: the peak at 1627 cm^{-1} identifies CNTs because it presents carbon ring bond (-C=C-) –the main bond in structure of CNTs; while the peak at $3,435\text{ cm}^{-1}$ presents (-OH) functional group due to existence of water; the peak at $2,923\text{ cm}^{-1}$ presents (-C-H-) bond; the peak at $1,380\text{ cm}^{-1}$ presents (-C-O-) bond; and finally the peak at $1,109\text{ cm}^{-1}$ presents (C-N) bond [5-7]. These bonds were formed in processing of fabrication of MWCNTs. The only difference between the raw MWCNTs and the acid-treated MWCNTs is that the IR spectrum of acid-treated MWCNTs has the peak at $1,253\text{ cm}^{-1}$ which presents (-C=O) bond due to existence of the

(-COOH)functional group[8] but the IR spectrum of MWCNTs do not exist. Presence of the (-COOH) functional group in acid-treated MWCNTs is due to the below reaction:

3.2. Structure of the Synthesized Thin Films

Structure of nanocomposite thin film of PEDOT-PSS and structure of nanocomposite thin film of PEDOT-PSS:MWCNTs are presented in Fig. 7a and Fig. 7b, respectively. Fig. 7a shows that structural morphology of the nanocomposite thin film of PEDOT-PSS has a little roughness while structural morphology of the nanocomposite thin film of PEDOT-PSS:MWCNTs with 0.2 Wt% of MWCNTs is relatively flat. This observation demonstrates that MWCNTs are distributed fairly uniform in the composited material. Fig. 7b also reveals that diameters of MWCNTs are in range 10 – 30 nm with their lengths are in range 300 – 500 nm.

3.3. Electrical and Optical Properties of the Fabricated Thin Films

Fig. 8 presents sheet resistance and optical transparency at wave number of 600 nm of the nanocomposite thin films of PEDOT-PSS: MWCNTs with Wt% of MWCNTs varying from 0.0% to 0.5%.

Investigation of the sheet resistance of the obtained thin films as a function of MWCNTs concentrations shows that it decreases rapidly when MWCNTs concentration increases from 0.0 to 0.3 Wt%: at 0.3 Wt% of MWCNTs, the sheet resistance has a minimum value of 36.5 $\Omega/\square$. However, the sheet resistance increases slightly when MWCNTs concentration continue to increase. MWCNTs are known for their excellent conduction nanomaterial while PEDOT-PSS is also a good conductive polymer, therefore when we combine two materials to form a new nanocomposite

Fig. 7 FESEM images of (a) PEDOT-PSS thin film and (b) PEDOT-PSS: MWCNTs thin film.

Fig. 8 Dependence of sheet resistance and optical transparency of the obtained thin films with the MWCNTs concentrations.

material, a perfect conductive material is obtained. However, the sheet resistance of the nanocomposite thin films decreases to a minimal value then it does not decrease further although we still increase MWCNTs concentrations. Even the sheet resistance slightly increases with the increasing of the MWCNT concentrations. This observation can be explained that when MWCNTs concentrations are exceeded a critical value, defects of MWCNTs in the thin films also increase and these defects may block transportation of charge carriers lead to increasing of the sheet resistance. Moreover, we also know that charge carriers move along carbon nanotubes, so that when MWCNTs concentrations are high enough then MWCNTs are in a messy which may block moving of

charge carriers, subsequently lead to a slight increase of the sheet resistance.

Investigation of optical transparency of the obtained films at a wave number of 600 nm we observe that the optical transparency of thin films decrease when MWCNTs concentrations are increased. This is caused by fact that MWCNTs block light transmission. Therefore, more MWCNTs in nanocomposite material, light is blocked more lead to the decrease of the optical transparency of the synthesized films.

At 0.3 Wt% of MWCNTs, sheet resistance of the nanocomposite thin film reaches the minimal value of $36.5\Omega/\square$, decrease 5 times compare to that of the PEDOT-PSS thin film. Also at this MWCNT concentration, the synthesized nanocomposite thin film has the optical transparency of ca. 76% which is good for transmission of light.

Furthermore, Fig. 9 presents optical transparencies of the nanocomposite thin films of PEDOT-PSS: MWCNTs in range from near ultraviolet to near infrared.

Curve a shows the optical transparency of thin film of PEDOT-PSS which decreases from wave length of 300 nm to wave length of 800 nm. Curves b-fin the Fig. 9 are optical transparencies of the nanocomposite thin films of PEDOT-PSS: MWCNTs with different MWCNTs concentrations. The obtained results show that the optical transparencies decrease rapidly from wavelength of 300 nm to wave length of 350 nm: the

Fig. 9 Optical transparency spectra of nanocomposite thin films of PEDOT-PSS:MWCNTs.

optical transparencies reaches a minimal value at wavelength of 350 nm then they increased slowly in range wavelength from 350 nm to wavelength of 800 nm. The optical transparencies of curves b-f reach minimal value at wavelength of 350 nm demonstrate that MWCNTs absorbed light at wavelength of 350 nm. This is a major difference between the thin film of PEDOT-PSS and the nanocomposite thin films of PEDOT-PSS:MWCNTs.

3.4. I-V Characteristics of OLEDs

The nanocomposite thin film of PEDOT-PSS:MWCNTs has been used in many applications in electro-optic devices due to its excellent electrical conduction and good transparency properties. Among many possible applications, one of interesting application is that it is applied in fabrication of OLED.

Fig. 10 is I-V characteristics of the simple OLED structure. It can be seen that work function of this OLED is 3V with corresponding current of 0.01 mA. This work function value is quite high but corresponding current is rather small.

In order to improve performance of OLED, multilayer OLED structure is used. The configuration of this OLED is shown previously in the Fig. 4. Fig. 11 shows I-V characteristics of the multilayer OLEDs structure. Curve a is the I-V characteristics of ITO/PEDOT-PSS: MWCNTs/PVK-MEH:

Fig. 10 I-V characteristics of simple OLED structure: ITO/PVK:MEH-PPV/Al.

Fig. 11 I-V characteristics of OLEDs: (a) ITO/PEDOT-PSS:MWCNTs/PVK-MEH:PPV/Al OLED structure with 0.3 Wt% of MWCNTs; (b)ITO/PEDOT-PSS/PVK: MEH-PPV/Al OLED structure.

PPV/AlOLED structure with 0.3 Wt% of MWCNTs, while I-V characteristics of ITO/PEDOT-PSS/PVK:MEH-PPV/Al OLED structure is shown incurve b.

The Fig. 11a and 11b show that work functions of the multilayer OLEDs structure are low but currents are high in comparison with that of the simple OLED structure. The work function of the device showed in curve b is ca. 1.5V corresponding with the current of 0.15 mA, while the work function of the device showed in curve a is only 0.8V but the corresponding the current is 0.4 mA. It can be said that the

nanocomposite thin film of PEDOT-PSS:MWCNTs is made the HTL in the multilayer OLED this not only helps to decrease contact resistance but also to reduces a potential barrier between the ITO electrode and the emission layer. As a result, holes can move easily from ITO electrode to emission layer so that the work function is reduced and the current is increased. Furthermore, this advantage also increases possibility of recombination of electrons and holes in the emission layer, thus photons are emitted more. All of the mentioned advantages lead to the better performance of the multilayer OLED structure.

4. Conclusions

In this work, the nanocomposite thin films of PEDOT-PSS:MWCNTs are fabricated successfully. The nanocomposite thin film with 0.3 Wt% of MWCNTs has both excellent conduction and good transparency for many applications in electro-optic devices. In this research, it is applied in fabrication of the multilayer OLED structure with improved performance.

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