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The effect of different multiwall carbon nanotubes concentration on morphology, optical, and electrical properties used as flexible anode

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Abstract. Spin coating technique has been used to deposit various concentration of Multi-wall carbon nanotube (MWCNTs) thin films on flexible substrate of polyethylene terephthalate (PET) as electrode, the study shows the effect of (1, 2, 3 mg/ml) concentration of (MWCNTs) thin films, by AFM, optical and electrical measurements which indicate that the best concentration is 2 mg/ml according to (2, 3D) images, which shown widespread and regular spread of CNTs, low absorption of wavelengths (400, 550, 700 nm) at low concentrations, and compatible increase of responsivity with increased current for PET-MWCNTs/MEH-PPV:MWCNTs/AL as photodetector device.

Keywords. Polyethylene terephthalate; carbon nanotube; nanocomposite; Organic photodetector

1. Introduction

The growing use of transparent conducting films in the last decade due to popular devices like cell phone, touch screen, LCD displays and used as electrode for e-book readers and solar cell [1]. Generally, indium tin oxide (ITO) according to the large conductivity and high transparency used as electrode in OLEDs and other applications. However, with the passage time the surface of ITO physically and chemically considered weak, therefore degrade the performance of the electrode [2]. Actually, good properties ITO but it does not have the required flexibility in some application, expensive and limit the efficiency and performance of the device for expanded use in solar energy applications. On the other hand, CNTs considered as active alternative material used in the fabrication flexible CNTs thin conductive films (TCF) due to the high electrical conductivity, flexibility, as well as have a good optical property [3-5]. The geometry of Multi-wall carbon nanotube (MWCNTs) employs tremendously in the construction of highly porous three-dimensional (3D) electrodes [6-8]. And in photoelectron chemical devices with thickness approximately 100 nm can exhibit high level of optical transparency [9,10]. CNTs are considered as a new and advanced material thus attracted great interest from researchers in different scientific fields such as optoelectronic devices [11], cement pastes [12] and gas sensors [13].

The conjugated polymer MEH-PPV is known as poly (2-methoxy-5-(2'-ethylhexyloxy)-1,4-phenylenevinylene) and as a hole transport material [14]. MEH-PPV is common polymer used in optoelectronic devices as an excitation source [15]. To enhance the conductivity of the conjugated



polymer MEH-PPV, carbon nanotube is stuffed in the polymer matrix to increase the electric current, and it acts as a collective charge network of the thin film in the solar cells [14]. In our work, CNTs was used as filler in the bulk heterojunction MEH-PPV:MWCNTs nanocomposite thin films, the polymer has two peaks in the range (300-400 nm), (400-600 nm) Sequentially[16], and apply the effect of various concentration in the PET-MWCNTs/MEH-PPV:MWCNTs/AL as photodetector device.

2. Experimental

The Multi-wall carbon nanotube (MWCNTs) [3992 Rte 121E, Ste 3, Grafton, VT 05146, USA] was dissolved in (N, Ndimethylfromamide DMF) solvent to obtain the concentration of (1, 2, 3 mg/ml). The solution was placed in a magnetic stirrer for 5 hours and then sonicated for 5 hours to obtain a homogeneous thin film. The solution was coated on PET substrate by spin coating (10 sec and 500 rpm) after left the solution on substrate about 60 minutes and then dried at 66 °C for a half-hour to remove any residual of solvent.

The polymer (poly[2-methoxy-5-(2'-ethylhexyloxy)-1,4 - phenylenevinylene] (MEH-PPV) [Sigma-Aldrich; average Mn 40,000-70,000 MKBF2052V; Refrigerator stored, USA] was dissolved in (THF) solvent about 30 minutes to get (1 mg/ml). and MWCNT solution prepared at (0.1 mg/ml), mixing the two solutions at the volume ratio(0.9:0.1) ml respectively to deposit on (PET-MWCNTs) substrates by spin coating at (10 sec and 500 rpm) then dried at 66 °C for half-hour to remove any residual of solvent. At the last the aluminum AL contact metal was deposited on the top of the film using the thermal evaporation technique. A spin-coating system has been used in this study, surface of the thin films was carried out using an Atomic Force Microscope(SPM, Model AA3000), tip NSC35/AIBS from Angstrom Advanced Inc (USA), UV-Vis measurements were conducted using a (SHIMADZU CORPORATION UV-VIS 1650-PC spectrophotometer) with a wavelength range from 190-1100nm, Grating Monochromator LEOI-94 (∞ Lambda) was used with KEITHLEY 6517B electro Meter/ High resistance, to measure the photocurrent with the range of incident wavelengths (300-900nm) and I-V characteristics are measured in a forward and reverse bias circuit using a DIGITAL Multimeter (VICOR-86C) with QJE(DC REGULATED power supply QJ3005x.

Fig. 1 shows the structure of a photodetector device. To calculate the responsivity as a function of wavelength, as shown in the following equation:

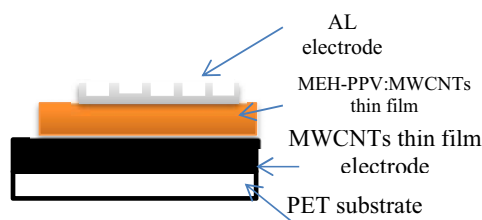
$$(1) \quad R(\lambda) = J_{ph}(\lambda) / P_{in}(\lambda)$$

where $J_{ph}(\lambda)$ is the photocurrent density from the test detector and $P_{in}(\lambda)$ is the incident power density [17].

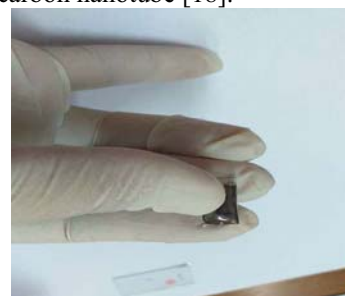
To calculate the absorption coefficient from Beer's equation:

$$(2) \quad B = \xi dc$$

where B is the absorbance, ξ is the absorption coefficient, d is the distance that the light beam travels through the solution, and c is the concentration of Multiwall carbon nanotube [18].



a



b

Figure 1. (a) Structure of the photodetector device, (b) photograph of PET-MWCNTs thin film.

3. Results and Discussion

3.1. Atomic Force Microscope (AFM)

The morphology of dispersion MWCNTs was verified by analyzing the surface morphology, using AFM images obtained on an area approximately ($2.05 \times 2.06 \mu\text{m}^2$). Fig. 1a illustrates (2D) and (3D) images of surface morphologies, the dispersion of CNTs is regularly as indicated by blue arrows in (2D) image, that's what corresponds to an image (3D).

It is clear from the Fig. 1b and with increasing the concentration of CNTs widespread and regular spread over the measured area and this agrees with the increase current in the measurement of (I-V) and this is due to the role of the conductive CNTs network of increasing conductivity.

Fig. 1c shows the agglomerate of CNTs is very clear and this is corresponds to a decrease in the current of (I-V) measurement and roughness increases with increased CNTs concentration (1.16, 2.48, 17.2 nm) respectively. Increasing the concentration of CNTs and by Van Der Waals forces forming a stack randomly overlapping CNTs structure, thus caused low optically transparent level and a solid conductor, while at low concentration forming a porous interconnected network of CNTs, and thus caused fast charge transport between the conductive pathways interconnecting of CNTs and a high optically transparent level [19].

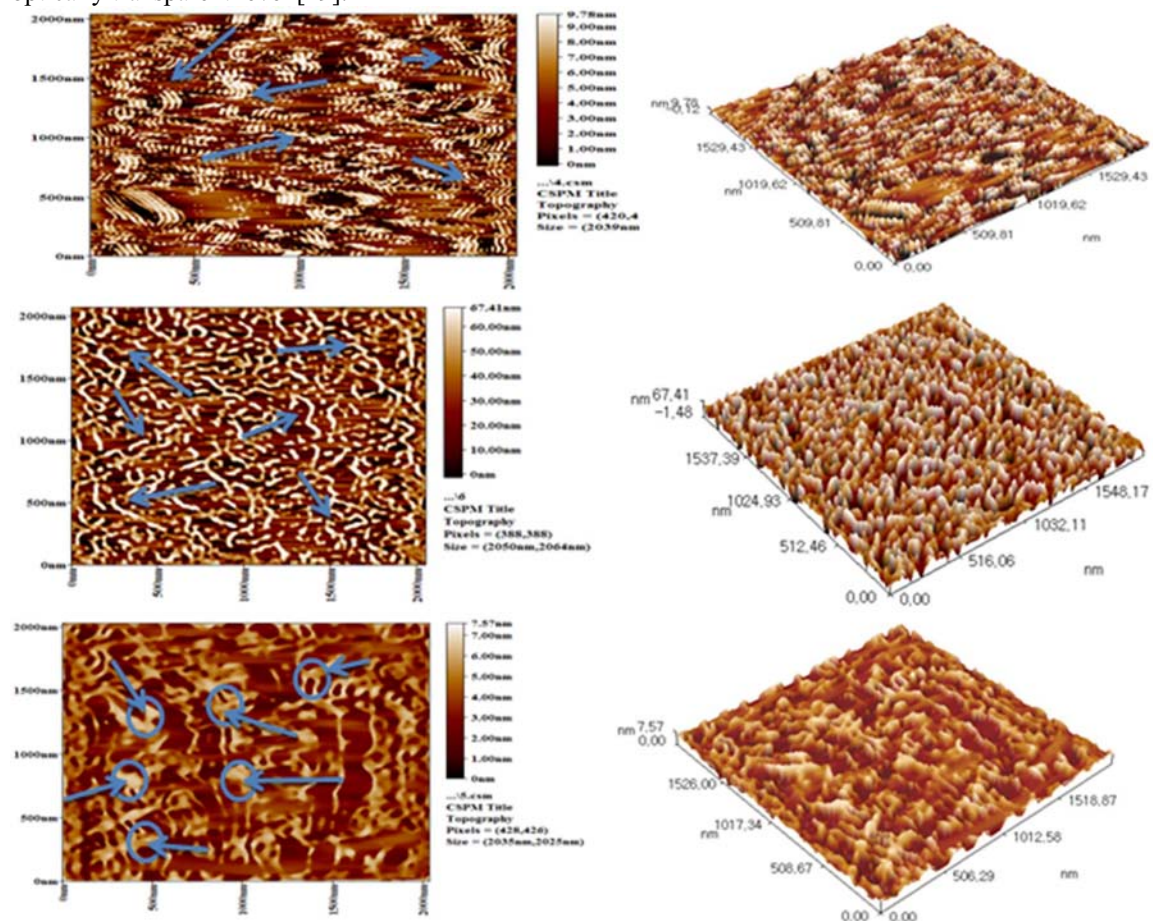


Figure 2. AFM images 2D to the left side and 3D to the right side of MWCNT thin films at concentration. of MWCNTs 1,2,3 mg/ml, (a-c) respectively.

3.2. Optical characterization

Absorption spectra of the multiwall carbon nanotube thin films were carried out. The absorption spectrum of the MWCNTs increased with increasing the concentration of MWCNTs and an intensive absorption peaks at around (222, 328 nm) (5.58, 3.74 eV) for (1, 2, 3 mg/ml) concentration of CNTs respectively.

The plasmon resonances are attributed to the far-UV and UV regions of $((\pi + \sigma)$ and (π) plasmon [20,21]. The transition between the pins in the electronic densities states of the CNTs, is due to collective excitations of (π) free-electron cloud that caused different plasmon absorbance peaks in the electron transition $(\pi - \pi^*)$ of Multiwall carbon nanotube and occurred at around ((310-155 nm) (4-8 eV)) [22,23]. Our result peak agrees with previous report [24,25].

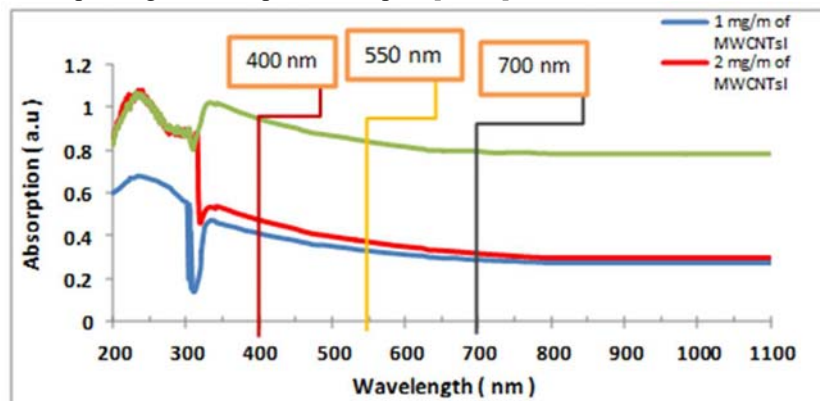


Figure3. UV-Vis. absorbance spectra of Multiwall carbon nanotube thin films, with a different concentration of MWCNTs (1,2,3 mg/mL).

Fig.3 shows the relation between Absorbance and concentration of MWCNTs and due to Beer's law (eq.2) to calculate the slope from this figure, the slope equal to $(\Delta B/\Delta C)$ and absorption coefficient ϵ equal to $(\text{slope (ml/mg)/d (nm)} * 10^{-7} \text{ (cm/nm)})$. The absorption coefficient ξ has the maximum value at the wavelength 400 nm as shown in Table1, the absorption coefficient decreases with increase the wavelength at the visible range, this means 700 nm has the higher transmittance. Our result agrees with [26].

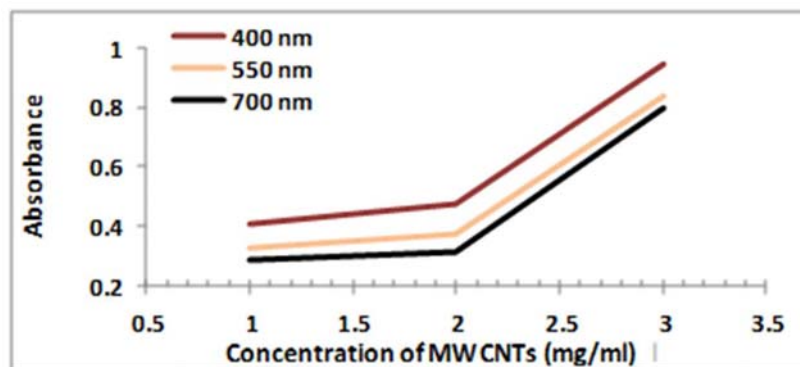


Figure 4. shown the absorbance versus the concentration of Multiwall carbon nanotube in(mg/ml), at the range of visible wavelengths of 400, 550, 700 nm.

Table 1. showing the various concentration of MWCNTs with respect to absorption coefficient ξ at 400, 550, 700 nm.

Concentration of MWCNTs range mg/ml	ξ at 400 nm ml/mg cm ⁻¹	ξ at 550 nm ml/mg cm ⁻¹	ξ at 700 nm ml/mg cm ⁻¹
1-2	6809	4468	3020
2-3	47400	46800	47800

To calculate the energy gap (E_g) by Tauc equation which used to find the type of transition and value of energy gap by plotting the relation of $(\alpha h\nu)^2$ versus photon energy ($h\nu$). Fig. 4(a-c) illustrate the energy gap is direct and the value of energy gap for (1, 2, 3 mg/ml) concentration of MWCNTs at the range of (3.5-4) eV, and our results are consistent with the researcher [23].

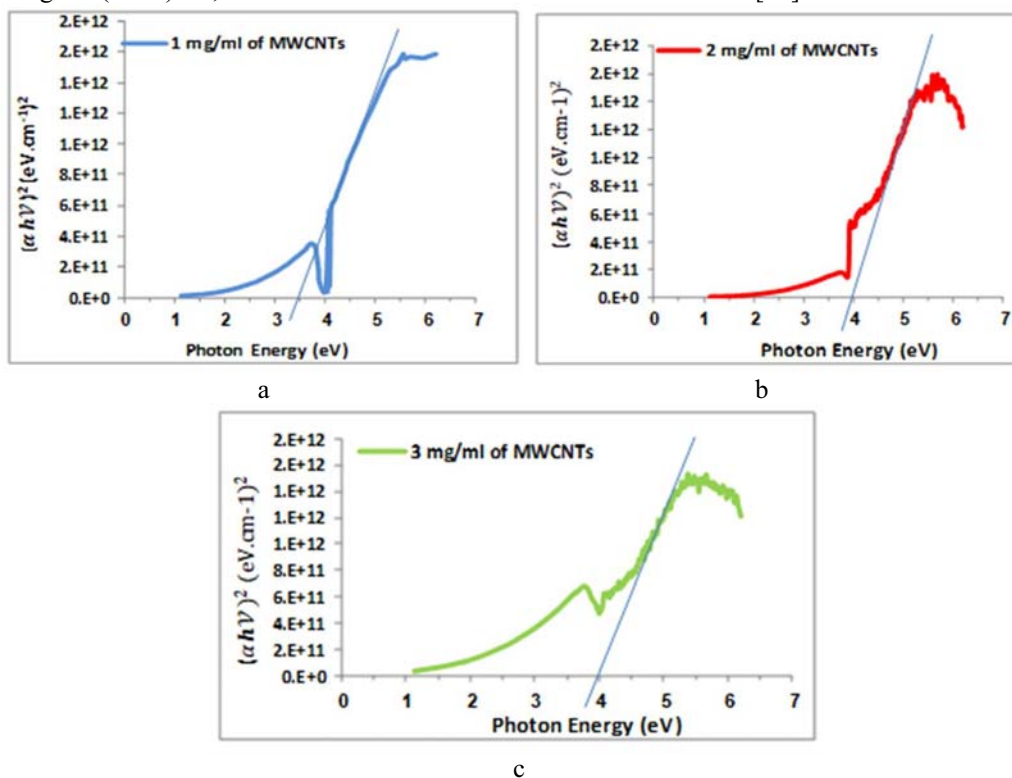


Figure 5. $(\alpha h\nu)^2$ versus photon energy ($h\nu$) of incident radiation for Multiwall Carbon Nanotube thin films, (a) 1 mg/ml, (b) 2 mg/ml, (c) 3 mg/ml of MWCNTs.

3.3. Electrical Properties

Fig.5 shows the I-V characteristics of Multiwall carbon nanotube in dark state. The Al metal contact and MWCNTs thin film form Ohmic connect and the current increase linearly as the applied voltage was given from -4V to 4V with increasing the concentration of CNTs, the current increase until 2 mg/ml then the current decrease. The important role of alignment the distribution of MWCNTs is the electrical conductivity and optical transparency of multiwall carbon nanotube networks, where the resistance decreases with increase of the concentration of CNTs, due to the increased number of pathways that the electrons can travel through [27]. The decreased current is due to aggregation of MWCNTs, it's known that the adjacent Multiwall carbon nanotube increases the quality of electrical conductivity by quantum tunneling effect, which decreases exponentially as the distance far away between the MWCNTs [28].

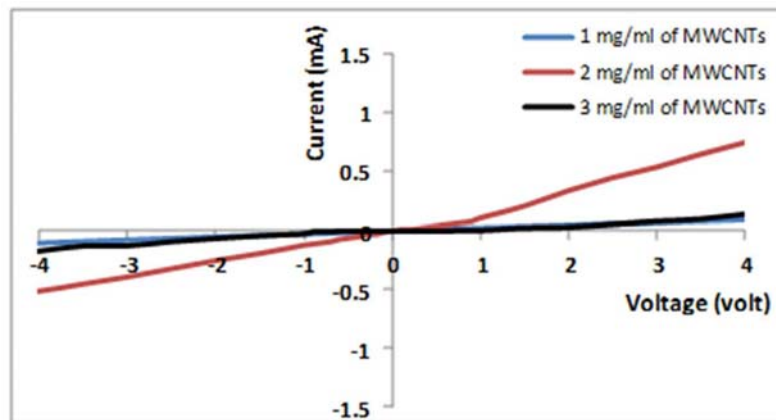


Figure 6. the current-voltage (I-V) characteristic of MWCNTs at concentration of (1, 2, 3 mg/ml).

Fig.6 shows the responsivity of MEH-PPV:MWCNTs thin film by using various concentration of Multiwall carbon nanotube as electrode under illumination condition at (300-900 nm). The effect of MWCNTs is increasing the conductivity of the photoconductivity that created by incident light on MEH-PPV:MWCNTs nanocomposite thin film, and works on generating pair of (electron-hole) [29]. The responsivity increases with increase the concentration of MWCNTs until 2 mg/ml then decrease. This is due to concentration, alignment, and formation of an interconnected structure of MWNTs [30]. This result is consistent with AFM and (I-V) measurements.

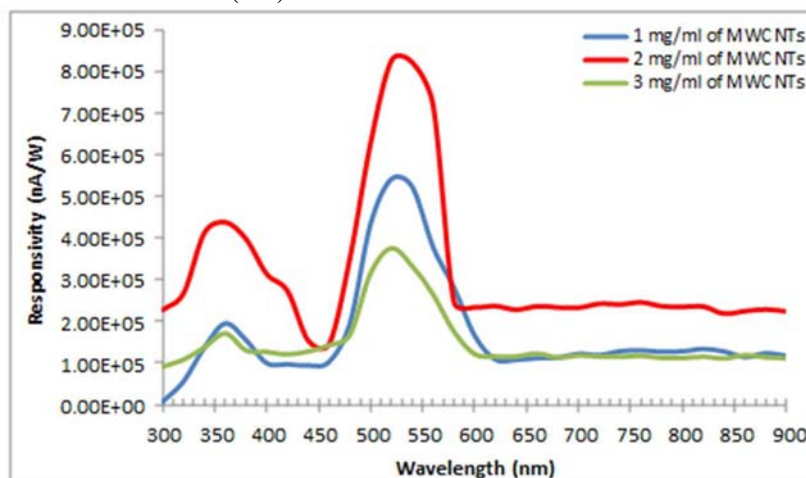


Figure 7. The spectrum of responsivity of (MEH-PPV:MWCNTs) versus wavelength with various concentration of MWCNTs as an electrode.

4. Conclusion

Through the dispersion time of Multiwall carbon nanotube in DMF solvent, the deposition time and speed rotation of spin coating, the effect of all these factors is to improve the characteristics of MWCNTs thin film as electrode anode, the responsivity values of the active layer at 2 mg/ml are 5×10^5 and 8×10^8 nA/W of PET-MWCNTs/MEH-PPV:MWCNTs/AL as photodetector device.

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