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Copper Phthalocyanine MWCNTs Composites: Characterization and Evaluation for Sensor and Solar Cells interlayer

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Abstract

Copper Phthalocyanine (CuPc) thin film with and without multi-walled carbon nanotubes (MWCNTs) is prepared using the solution based method and used in gas sensor and solar cell applications. The structural characteristics of the CuPc thin films showed a single peak around 7^{o} with the preferred orientation for charge transportation. Using atomic force microscopy (AFM), morphological properties show a rough surface with some aggregates and ribbons. The optical absorption properties were determined using UV-Visible absorption spectroscopy; the optical band gap has varied after adding MWCNTs to CuPc. Electrical conductivity of CuPc:MWCNTs composite is higher than that of the pure CuPc. The CuPc thin film sensr have shown good response properties to ammonia gas. The solar cell performance of the P3HT:PCBM based solar cell was enhanced.

Keywords: CuPc; MWCNTs, Solar cells, Ammonia Sensor

متراكبات الثالوسايانين –نحاس وانابيب الكاربون النانوية متعددة الجدران :تشخيص وتقييم عملهم كمتحسسات او طبقات بينية للخلايا الشمسية

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الخلاصة:

تم تحضير أغشية رقيقة من مادة الثالوسايانين –نحاس (CuPc) مع وبدون الأنابيب النانوية الكربونية متعددة الجدران (MWCNTs) باذابتها بمحاليل عضوية ومزجها مع انابيب الكاربون النانوية. حيث تستخدم الاغشية المحضرة في مستشعر الغازات وتطبيقات الخلايا الشمسية. أظهرت الخصائص التركيبية للأغشية الرقيقة من CuPc ظهور قمة واحدة لطيف الاشعة السينية عند حوالي 7 درجات مع الاتجاه المفضل لنقل الشحنة. تظهر الخصائص التشخيصية للسطح باستخدام مجهر القوة الذرية ((AFM) سطحًا خشنًا مع بعض التكتلات والتحبب. تم تحديد خصائص الامتصاص البصري باستخدام منطقة مطيافية الامتصاص المرئي قبل وبعد اضافة انابيب الكاربون النانوية ودراسة الاختلاف بينهما؛ اختلفت فجوة الطاقة بعد إضافة MWCNTs إلى CuPc. تم قياس الموصلية الكهربائية لمركب CuPc: MWCNTs وتبين ان قيمها أعلى

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من CuPc النقي. أظهرت الأغشية الرقيقة لـ CuPc استجابة جيدة لغاز الأمونيا وتحسيين أداء الخلايا الشمسية لـ الخلية الشمسية القائمة على P3HT:PCBM.

1. Introduction

Phthalocyanine (Pc) is a macro-cyclic compound with formed π-electrons. It has unique physical and chemical properties, and thermal stability and as well as high sensitivity [1-3].Because of their properties, Pc has been examined in order to improve the effectiveness of organic electro-luminescent display [3]. Pc are prepared in a variety of methods depending on its type, metal-free, symmetrical and asymmetrical Pc. The synthetic process consists of many factors like precursor, solvent, catalyst and temperature. Pc is known as the blue-green pigment, because it is mainly absorbed by light in the UV region of the spectra [2]. Pc molecule has a mid-cavity that is filled with metal to form the metal Pc molecule (MPc). This has gotten a lot of attention because of its specific properties based on the type of metal (Fe, Cu, Co, Zn, Si, Au,…etc). During the past decades, a great deal of interest has been focused on the synthesis of metal Pc (MPCs)which has been used in several application such as sensors, solar cells and diodes [1,3]. Generally, Pc typically behaves as a p-type semiconductor [4]. It can easily be prepared as a thin film using various techniques [5] and solutions based thin film [6].These methods of preparation affect the electrical, optical and structural properties of the Pc thin film [7]. Copper phthalocyanine (CuPc) is one of the major candidates used as organic pigments [8]. The CuPc film shows three diverse crystallographic phases: α-metastable, β-stable and x-crystal phases, depending on deposition conditions, atomic direction, and crystal structures [9]. When thin films are deposited at room temperature and annealed to 100 or 200 degrees Celsius, the process displays an α- phase [10]. At a high temperature of 210°C and annealing temperatures of 275°C and 310°C, the ß phase of the CuPc thin film was observed [11] .The ß- structure is more stable than the α-form. The α-phase is converted to the ß-phase at a temperature above 240℃ [12]. Today, there is an increase interest in developing sensors for gas detection based on conductance techniques, which are based on the electrical properties of a material as they show significant response in the presence of the detected gas [13]. Generally, there are several gas sensitive materials with good properties owing to their good thermal and chemical stabilities. The change in conductivity of CuPc films due to adsorption of oxidizing gases is employed in the gas sensor material [14,15]. In the case of solar cells, the use of organic semiconductors allows the fabrication of large area devices at relatively low cost energy conversion and on flexible substrates [16]. CuPc has been extensively studied as a potential material for solar cells due to its better photo-voltaic and photo-conductive properties [17,18]. Multi-walled carbon nanotubes (MWCNTs) is a new class of nanostructures with unique electronic and mechanical properties that are used in different organic application [19-22].

In the present study, a preparation of CuPc with and without MWCNTs was carried out and the prepared samples were used as sensors and solar cells.

2. Experimental and Details

2.1. Material

CuPc blue pigment (of purity 99% and of molecular weight 576.07g/mol)(purchased from Sigma Aldrich) were used in the current study. CuPc powder is blue in color and easily soluble in organic solvent such as chloroform.

Multi-walled carbon nanotubes used as additives was purchased from Sigma Aldrich (98% carbon bases, D*L=110-170nm*5-9μm). All the regents were purchased from Sigma Aldrich and used without any further purification.

2.2. Preparation of Solution

20mg CuPc was dissolved in 10ml chloroform of (2mg/ml) concentration. The mixture was stirred at 60^{o}C until it reached a high homogeneous state and a complete CuPc dissolution. The final solution was stored in dark dissector for future use. On the other hand, (0.5mg) of

MWCNTs was suspended in 1ml chloroform using ultrasonic bath, and the MWCNTs:CuPc samples were prepared by mixing 100µl of MWCNTs suspension with 1ml of the prepared CuPc solution.

2.3. Sample Preparation

CuPc thin films were deposited on ITO and glass substrates using the spin coating process, which involved spinning the samples at 2000 rpm for 15 seconds in air before heating them at 60°C for 10 minutes.

3. Results and discussions:

3.1. Optical Characteristics

Figure 1 shows the absorption spectra of CuPc and CuPc:MWCNTs composite thin films. The absorption spectrum of CuPc shows absorption bands around the wavelengths: 640nm, 700nm and 850 nm, which are attributed to Q-band. This band is ascribed to the first π-π* electronic transition of the macrocyclic ring from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) (transition from the ground state to the first excited state) [23]. The observed Q-band is broadened and divided into three bands, which could be attributed to the molecular packaging [6]. CuPc crystals can be reduced to tilted dimers, and the molecular transitions are split due to Davydov splitting [24] suggesting an out of plane bonding [25]. On the other hand, a band around 383nm is observed and ascribed to the B-band. The latter is attributed to the second π-π* transitions of the macrocyclic ring of metal Pc (transition from the ground state to the second excited state). The band around 383nm is called the B-band which corresponds to the fundamental absorption band that can be used for the determination of the band gap of the material. After adding MWCNTs to the CuPc, no apparent change in the absorption peaks was observed. However, low intensity was revealed in the spectrum. Generally, carbon nanotubes have flattened absorption spectra [26].

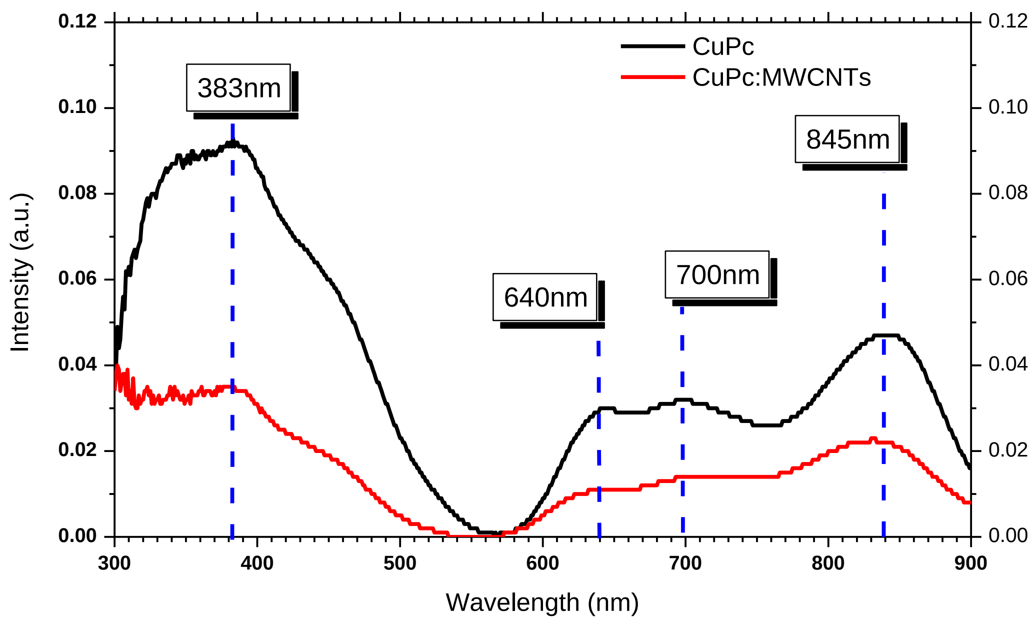

Figure 1-Absorption spectra of CuPc and CuPc:MWCNTs composite thin films.

The position of the conduction band minimum and the valance band maximum is the main concern between the two types of the transitions in Tauc model. In a direct band gap semiconductor, there is no change in the momentum, and the electron jumps from the HOMO to LUMO by absorbing a photon. While, in an indirect transition, there is a change in the momentum, and the transition contains a phonon for momentum conservation [27]. The absorption coefficient (α) of CuPc-based thin film can be determined using the following equation:

$$\alpha = \frac{1}{Td} \qquad (1)$$

Where: (T) is the transition and (d) is the thin film thickness. While, the optical band gap can be determined using Tauc equation :

$$\alpha h\nu = A(h\nu - E_g)^n \qquad (2)$$

Where: (A) is a constant, (h) is Plank's constant, (ν) is the frequency and (n) classifies the type of electronic transition between the energy bands based on its values [28].

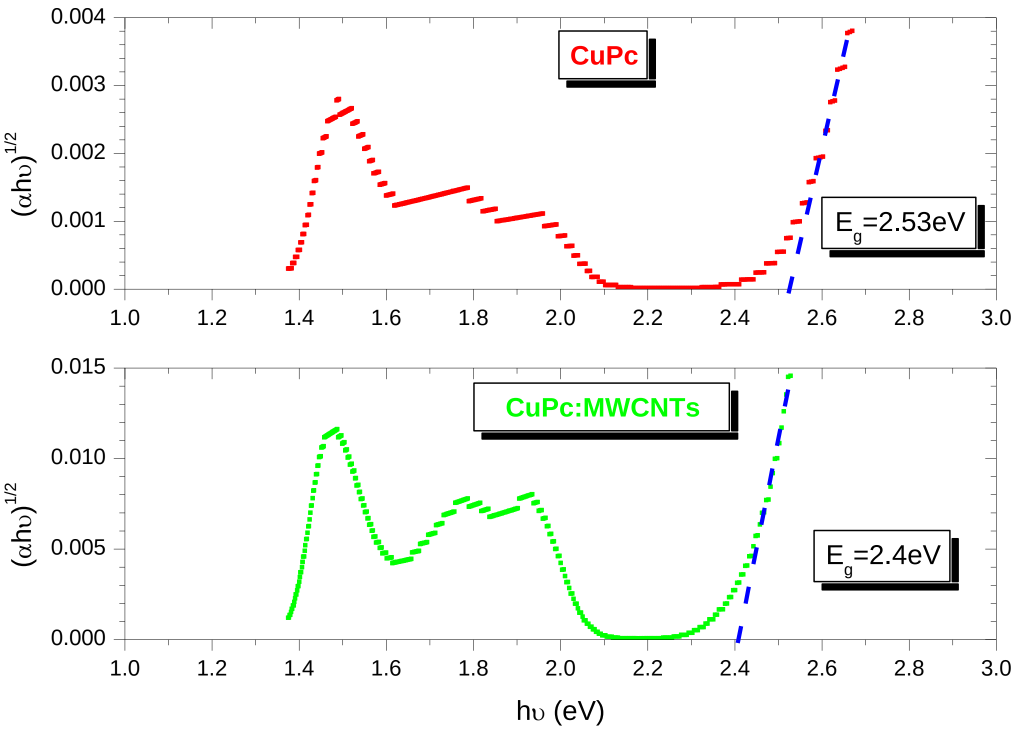

Figure 2- Tauc model to determine the band gap of the studied CuPc-based thin films

The optical band gap is determined by drawing a graph between $(\alpha h\nu)^n$ vs. hν (see Figure 2) where n=1/2 or 2 for direct or indirect transition, respectively. From the graphs shown in Figure 2, the intersection point with the photon energy axis (x-axis) corresponds to the band gap. CuPc has exhibited E_g of 2.53eV which changed to 2.4eV on adding MWCNTs. This insignificant change is due to the small amount of MWCNTs.

3.2. Morphological, structural and electrical properties

The morphological and structural properties of the studied thin films were carried out to give information about the electrical mechanisms inside the thin films as the morphology and the structure plays an important role in the electrical properties of organic thin films [3,23]. Figure 3(A) shows the XRD patterns of the CuPc-based thin films and CuPc:MWCNTs composite. It is clear that the thin films under study have exhibited a single peak around 2-theta = 7^o, which is related to the phase (200) of the Pc molecules[20]. Recently, Jain et al. have demonstrated that the charge carrier mobility is induced by the structure of the CuPc

[28]. Moreover, the AFM images showed that surface morphology displayed small ribbons in the CuPc:MWCNTs composite thin film, whereas the CuPc thin film exhibited a rough surface with some aggregates. Such ribbons suggested the creation of the on-plane orientation of CuPc molecules as detected by the XRD, and this is very important in the field of electrical applications. The electrical properties were examined using interdigitated electrodes (IDEs) purchased from DropSens (Spain) (see Figure 4 (A) and (B)).

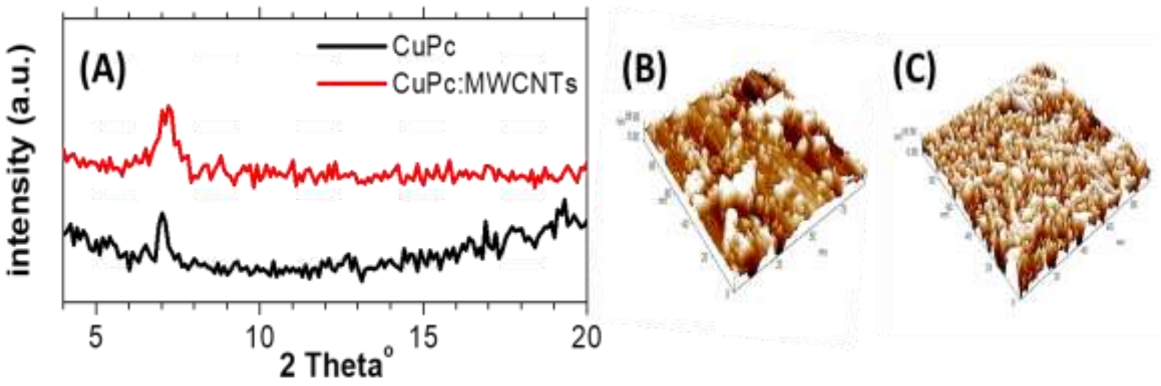

Figure 2-(A) XRD patterns CuPc and CuPc:MWCNTs thin films (B) AFM (3D image) of CuPc thin film and (C) AFM (3D image) of CuPc:MWCNTs thin film

IDE is employed to measure the electrical conductivity (σ) using the following equation [29]:

$$\sigma = \frac{I}{V}\left(\frac{n}{WtL}\right) \quad (3)$$

where: t is the thickness of the film (~200 nm), W is the distance between the fingers (6.67mm), n is the number of fingers (500), and (L) is the distance between electrodes (5µm).

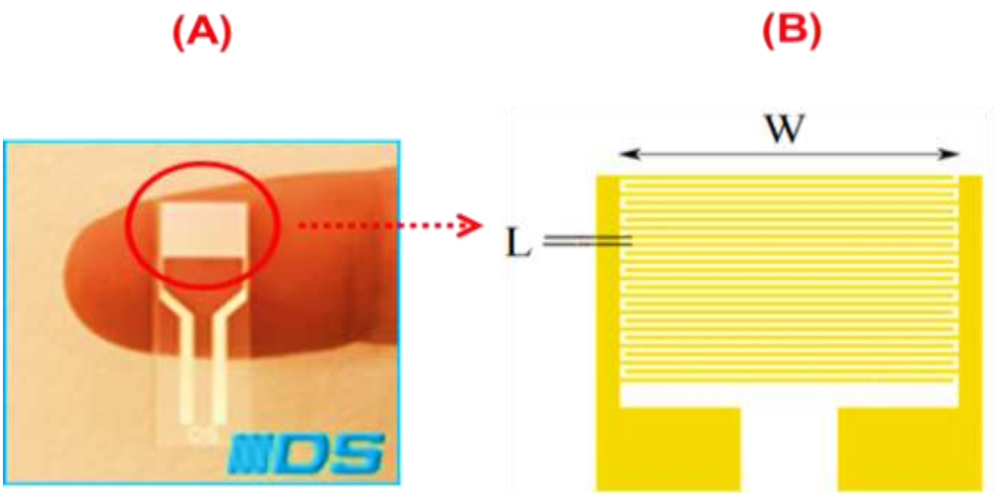

Figure 3- (A) Interdigitated electrodes (IDE) and (B) Sketch diagram of IDE

I-V characteristics of the CuPc based thin films are used to determine the resistance of the thin films. The current through the CuPc thin film has significantly increased(about 15 times) by the addition of MWCNTs, as displayed in Figure 5 (A). This increase is due to the increase of the electrical conductivity of the thin films from 0.0115S/m in CuPc thin film to 0.167S/m after adding MWCNTs to CuPc. This increase is attributed to the enhancement in the surface morphology by creating pathways for the electrical charges through the MWCNTs network [30].

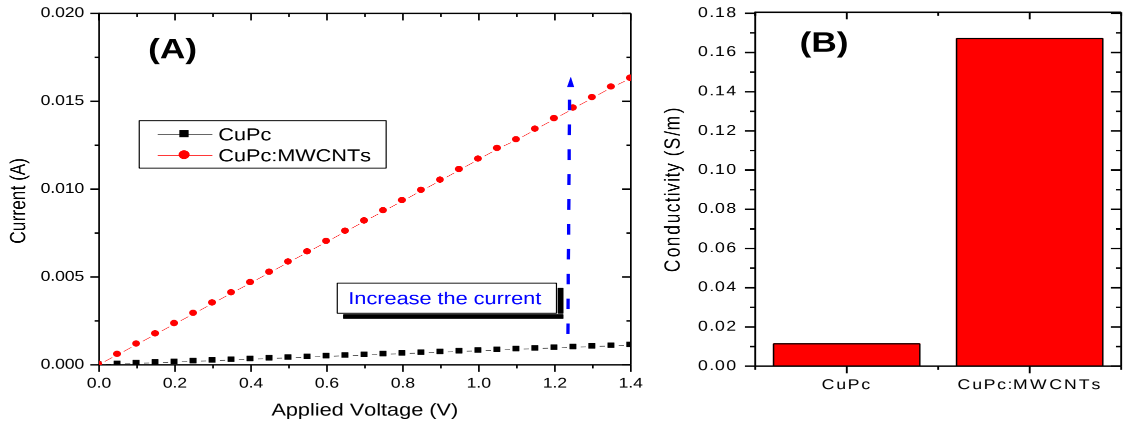

Figure 4-(A) I-V characteristics and (B) Electrical conductivity of the CuPc-based thin films

3.3. Application of CuPc thin films in sensor and solar cells

The Pc thin film sensor properties were investigated using ammonia gas. A setup made of Keithley 2400 source-meter, and Teflon based chamber with external and internal connections was used to determine the gas sensing properties. The latter thin films were deposited on IDEs. The thin films were subjected to a fixed concentration of ammonia gas inside the chamber. Figure 6 shows the response of the Pc thin film sensor, with and without MWCNTs, to the ammonia gas. It is clear that the resistance of the sensor changed after the exposure to the gas; however, the sensor with MWCNTs revealed lower resistance due to its high conductivity. The change in surface resistance can be due to the adsorption of ammonia substances on the surface of the thin layer. The CuPc thin film sensor showed a rapid response and recovery times, as demonstrated in Figure 6.

In order to investigate the CuPc thin films in solar cell applications, CuPc layer was used as a complementary layer to increase the absorption ability (more carries' generation), and on the other hand, it plays an essential role in the charge carries separation and transportation.

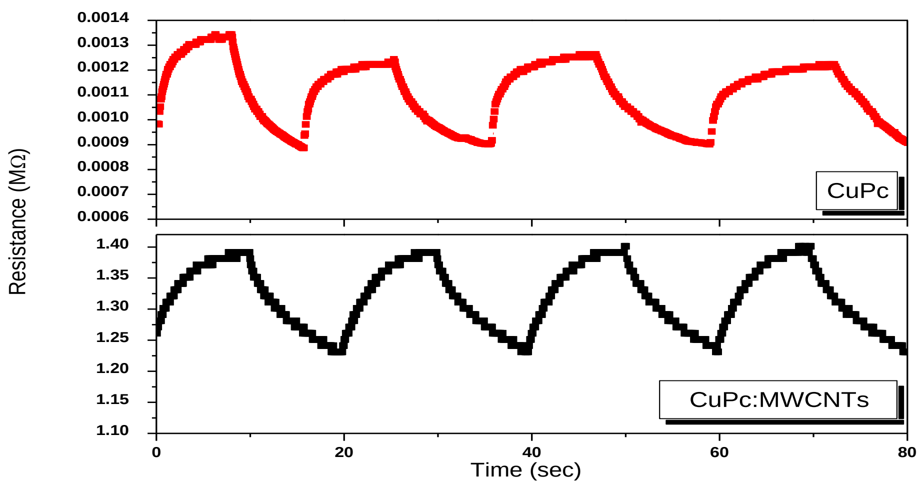

Figure 5-Application of ammonia sensor for thin films based on CuPc.

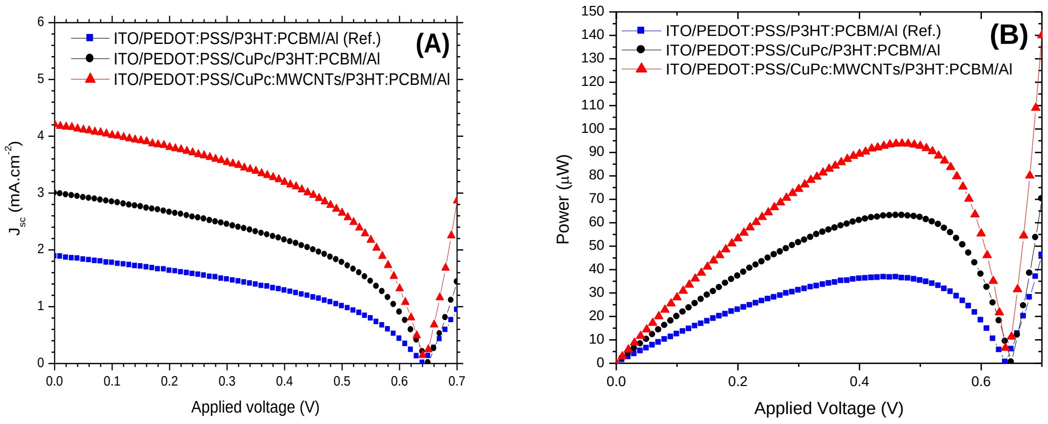

Figure 6-(A) J-V characteristics under light condition (solar cell application) and (B) Output power of the solar cells

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P3HT:PCBM is a well-known standard organic active layer. Therefore, it has been selected to investigate the Pc layer within the organic solar cell. P3HT:PCBM based active layer was used and prepared according to our previous work [3]. Figure 7(A) shows the solar cell characteristics; it is clear that using an internal layer enhanced the performance of the solar cell. Using CuPc increased the Power Conversion Efficiency (PCE) from 0.72% in the reference device to 1.22%, whereas using CuPc:MWCNTs has resulted in a higher PCE of 1.79%. Such an increase might be due to the increase in the charge carries' generation and separation by the internal layer, which assists the charge carries' transportation inside the device and reduces the charge carries' recombination. Moreover, reducing the recombination has resulted in increasing the Fill Factor(FF) from 43% to 47% and 48% as demonstrated in Table 1**.** Figure 7 (B) shows the internal power of the solar cells. The output power of the solar cell with CuPc:MWCNTs is higher than the others at a maximum point close to the open circuit voltage (V_{oc}).

Table 1- Solar cell parameters of the studied devices based on P3HT:PCBM active layer

Sample	I_{SC}(mA/cm^2)	V_{OC}(V)	FF(%)	PCE (%)
ITO/PEDOT:PSS/P3HT:PCBM/Al	2.64	0.65	43	0.72
ITO/PEDOT:PSS/CuPc/P3HT:PCBM/Al	4.194	0.64	48	1.22
ITO/PEDOT:PSS/CuPc:MWCNTs/P3HT:PCBM/Al	5.894	0.64	47	1.79

4. Conclusion:

Copper Pc with and without MWCNTs was prepared and studied for the application of sensors and solar cells. A small change in the optical band gap from 2.5eV to 2.4eV was observed; this small change is due to the small amount MWCNTs added. Morphological, structural and electrical properties suggest the creation of charge carries pathways due to the nanostructure of thin films. CuPc thin films showed a good response to ammonia gas. The solar cell performance of P3HT:PCBM based solar cells using CuPc:MWCNTs layer was enhanced with an efficiency increase from 0.71% to 1.79%.

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