Efficiency Enhancement of Organic Solar Cell by Using Carbon nanotubes

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Abstract:

Even though organic solar cell is a significant alternative in the field of low cost power production, but the main disadvantage of this device is the low power conversion efficiency. The development of carbon nanotubes has played an important role in enhancing the efficiency of organic photovoltaic solar cell. A key step in achieving high efficiency with the utilization of carbon nanotubes is to enhance the charge separation and transport within the device. For these purpose, an organic photovoltaic (OPV) cell has been designed with a single-walled carbon nanotubes (SWCNTs) as transparent anode instead of In2O3:Sn (ITO), a small concentrations of (3 wt%) SWCNTs blending with the P3HT:PCBM active layer, and a metallic-carbon nanotubes (m-CNT) as cathode instead of Al (metal) electrode. Our theoretical calculation shows that the short circuit current (Isc), open circuit voltage (Voc) and fill factor (FF) are increased due to the doped SWCNTs which is responsible for increasing the efficiency of the device. For this theoretical model, the highest power conversion efficiency (PCE) is found up to 22% compared with the device without depositing CNTs.

Keywords: Organic solar cell, P3HT, PCBM, ITO, PCE, SWCNT

1. INTRODUCTION

The worldwide demand for energy has grown enormously over the recent years and it is likely to grow even more in the near future [1]. Because of the limited supply of our main energy sources (fossil fuels) [1], together with the growing concern about global warming and climate change, the development of renewable energy sources such as solar energy is a great priority. During the last few decades, several research considering inorganic and organic photovoltaic cells has been done to meet the demand of energy [2]. Among these, organic photovoltaic cell is a promising alternative to inorganic solar cells, because they are cheap, robust, and easy to make [3]. Even though organic solar cell is frequently used for its optimistic characteristics; one is frequently confronted with difficulties while designing organic photovoltaic devices due to their low power conversion efficiency.

The last few years have seen a remarkable increase of the power conversion efficiency (PCE) of laboratory-scale, solution-processed OPV devices, from the range of 2% [4] to present certified efficiencies in excess of 10% [5], a value widely considered a benchmark for commercialization. Organic solar cells are made by InO2:Sn (ITO) as anode electrode, poly-(3-hexylthiophene) (P3HT) with the C60 derivative [6,6]-phenyl-C61-butyricacid-methylester (PCBM) as active layer and Al as cathode electrode tend to be inefficient because the photogenerated excitons are usually not split by the formed electric field due to differences in the electrode work functions. Moreover, in the case that free carriers are created they have very low mobilities and the recombination process between electrons and holes is very favorable [6]. State-of-the-art bulk heterojunction (BHJ) OPVs currently achieve cell efficiencies up to ~13.6% under the standard solar spectrum AM1.5G [13]. However, significant improvements are still needed, with efficiencies >13.6% generally regarded as necessary for widespread commercial viability [13]. One of the alternatives to solve this handicap is the introduction of carbon nanotubes (CNTs) to fabricate photovoltaic devices to the aim of increasing the power conversion efficiency [1]. CNTs consist of one or more sheets of graphene wrapped around each other in concentric cylinders. Individually, they could be metallic or semiconducting depending on their chirality and diameter [7]. In the case of single-walled carbon nanotubes (SWCNT), the diameters typically range from 0.4 to 2 nm, and lengths up to 1.5 cm have been reported [8].

In a conventional organic solar cell, InO2:Sn (ITO) is the most popular material used for the transparent electrodes [9]. ITO is not ideal because it is expensive as well as being optically, electronically and chemically problematic [10]. Therefore, developing and commercializing a replacement for ITO is a major focus of OPV research and development. Recently a SWCNT networks film has the potentiality to use as the electrode in bulk-heterojunction (BHJ) organic solar cell. The work function of SWCNT networks is in the 4.8 to 5.0 eV range (compared to ITO which has a lower work function of 4.7 eV) leading to the expectation that the SWCNT work function should be
high enough to assure the efficient hole collection leading to better photovoltaic response [11]. SWCNT networks including their inherent flexibility, abundant materials, amenability to solution processing and preferential hole conduction which enable their use as a replacement for ITO in organic solar cell.

In this research, we try out the feasibility of incorporating single-walled carbon nanotubes in organic bulk heterojunction solar cells to improve their photovoltaic performance by enhancing their charge collection efficiency and thereby increasing the optimal active blend layer thickness. Here, we designed a theoretical model where a critical concentrations value of 3 wt% [11] of SWCNTs are added to blends of poly(3-hexylthiophene): [6,6]-phenyl-C$_{61}$-butyric acid methyl ester in order to create networks of efficient hole conduction pathways in the device active layer without affecting the light absorption. The nanotube addition leads to a 22% increase in the optimal blend layer thickness from 90 nm to 110 nm [14], enhancing the short circuit current density and photovoltaic device efficiency by as much as ~10% [14]. The associated incident photon-to-current conversion efficiency for the given thickness also increases by ~10% uniformly across the device optical absorption spectrum, corroborating the enhanced charge carrier collection by nanostructured electrodes. Though a higher thickness can generate more photo-current, because of the limited charge transport ability of the organic semiconductors used, most of the photo-generated carries recombine inside the bulk of the device [13]. Again, the nanostructured molecules protrude into the blend layer and shorten the travel distance for dissociated free charge carriers within the low mobility semiconductor blend, thereby reducing recombination loss in thicker active layers [14]. Using this approaches, higher efficiencies can be achieved. Regardless of the approach used, it would be of advantage to improve the charge transport to increase the device efficiency.

Several difficulties, such as, low stability in air, lack of optical transparency, and the requirement of ultra-high vacuum processing were processed when designing a solar cell with conventional Al electrode [15]. Conventional Al electrode also suffer another drawback i.e., Al electrode contains calcium and lithium fluoride which limit the performance of OPV. This leads to the demand for transparent low work function materials for cathodes in OPV cell. In order to overcome these difficulties, we have incorporated carbon nanotube as a cathode instead of conventional Al electrode while designing a solar cell. In this regard transparent carbon nanotubes sheet on top of the active layer has been demonstrated as a cathode in our proposed model. Power conversion efficiency can be increased by an amount of ~3% [15] by applying a bias voltage to the electrode replaced with CNT because photo-generated electrons are effectively and efficiently collected by CNT. As a result, a collective power conversion efficiency of around 22% can be obtained by properly incorporating CNTs on the OPV devices.

2. MATERIALS AND METHOD

A typical bulk heterojunction (BHJ) organic solar cell consists of a pre-patterned transparent contact (TC) on glass, a hole transparent layer (HTL), the BHJ active layer, and metallic back contact. The best organic solar cell use In$_2$O$_3$:Sn (ITO) as anode functionalized with a layer of poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate) (PEDOT:PSS) and an active layer consisting of a blend of poly(3-hexylthiophene) (P3HT) with the C$_{60}$ derivative [6,6]-phenyl-C$_{61}$-butyricacid-methylester (PCBM) [16].

2.1 Sample Preparation

Conductive CNT coatings have recently become a prospective substitute based on wide range of methods including spraying, spin coating, casting, layer-by-layer, and Langmuir–Blodgett deposition [17,18,19,20]. The transfer from a filter membrane to the transparent support using a solvent or in the form of an adhesive film is another method for attaining flexible and optically transparent CNT films [21]. Commercially available single-walled carbon nanotubes, produced by arc discharge, were dissolved in solution with surfactants and then sonicated. The transparent electrodes were fabricated by coating microscope slides with purified, arc-produced SWCNTs. These were purified by a process consisting of acid reflux, washing and centrifugation to remove metal catalyst and non-tubular forms of carbon. The purified SWCNTs were then dispersed in water and alcohol. The well dispersed and stable solutions were vacuum filtered over a porous alumina membrane. Following drying, the SWNT films were transferred to a flexible glass substrate by printing. The density of this network (nanotubes/area) can be controlled with high precision by simply controlling the volume of dilute suspension filtered through the membrane [22]. This method also has the benefit that the speed of the vacuum filtering process does not allow for tube flocculation, creating homogeneous films, and the transfer-printing method produces relatively smooth films [22]. Furthermore, the method is inexpensive, scalable to large areas, and allows for the transfer of the film to a variety of surfaces. The SWCNT used for solar cell applications is usually selected in order to keep the contact resistance low and ensure efficient collection of the photogenerated charge carriers. The SWCNT coated glass substrates were ultrasonically cleaned in acetone and isopropyl alcohol [23]. Silver contact pads and collection lines were vapor deposited outside the active areas of the devices. Prior to depositing the active layer, a layer of PEDOT:PSS was spin cast on the SWNTs at 4000 rpm and then placed directly on a 110°C hot plate and annealed.
for 20 min [22]. Consistent results were obtained when either the PEDOT:PSS solution was applied on the surface and let free to diffuse several minutes before the spin-coating operation in order to fill in the open porosity of the SWNT film or when a PEDOT:PSS/1:1 mix was used to improve the wetting.

### 2.2 Fabrication of Photovoltaic Cell

For devices preparation, after depositing PEDOT/PSS hole transporting layer onto the SWCNT anode, active layers consisting of P3HT:PCBM:SWCNT and, for comparison, a mixture of P3HT:PCBM:SWCNT were spin-cast from solution in ambient air at speed ranging from 500 to 1000 rpm in order to form layers with different thicknesses. And this was followed by a post-fabrication vacuum thermal anneal (150°C for 10 min) to promote blend phase separation and reduce oxygen charge traps resulting from the ambient device processing [14]. Fig. 1 shows the schematic of the proposed organic solar cell using CNTs.

![Fig.1: Schematic of the proposed device structure used in this work.](image1)

![Fig.2: Energy level diagram of the proposed organic solar cell.](image2)

Single wall carbon nanotubes were functionalized using the following method. Raw HiPCO single wall carbon nanotubes (Unidym) were further purified by heating in air at 300°C for 4 h, followed by bath sonication in concentrated HCl to remove the remaining metal catalysts [14]. A suspension of purified nanotubes (100 mg) in an acetone/water solution (20 ml/20 ml) was sonicated for 2 min using an ultrasonic probe. N-methylmorpholine-N-oxide (1 g) was added into the suspension, and the solution was stirred for 5 min. We then added 250 mg osmium tetroxide, after which the solution was stirred for 3 days at room temperature. The resulting mixture was filtered through a 0.45 lm Nylon 66 membrane (Supelco Analytical) and washed with a copious amount of water and then acetone. The sample was dried under vacuum at room temperature overnight. We suspended 40 mg of dried sample in tetrahydrofuran, and 4-dimethylaminopyridine (24 mg) and pyridine (1 ml) were added. Then palmitoyl chloride was dripped in slowly under N₂ gas. The solution was stirred at room temperature for 1.5 days, and then water was added. The solution was filtered through 0.45 µm Nylon 66 membrane and washed with water thoroughly and then with acetone. The sample was dried under vacuum at room temperature overnight. Highly oriented CNT sheets approximately 3mm wide were dry-pulled from a CNT forest synthesized at UTD, and laid on top of the P3HT:PCBM layer [24]. After five layers were laid, the carbon nanotubes were densified with 3M™ Novec™ 7100 Engineered Fluid, methoxy-nonfluorobutane (C₄F₉OCH₃). Contacts were created using silver paint.

### 2.3 Measurements

Energy level diagram of the device used in this work is shown in figure 2. For the active layer, highest occupied molecular orbital (HOMO) of P3HT and the lowest unoccupied molecular orbital (LUMO) of PCBM are shown since these are the transport levels for holes and electrons in the device respectively. The light intensity was calibrated for a condition of 100 mW/cm² (1 SUN) [8].

One of the key solar cell parameters affecting the cell power conversion efficiency (PCE or η) is the series resistance, or internal resistance, Rs. The series resistance represents the total resistance of the cell and is a composite of: 1) the active and interfacial layer resistances, 2) electrode resistances, and 3) the various contact and interconnect resistances [12]. It is known that Rs can have a pronounced effect on the solar cell fill factor (FF), which is defined as [12]:

\[
FF = \frac{V_{\text{max}} \times I_{\text{max}}}{V_{\text{oc}} \times I_{\text{sc}}} \quad (1)
\]

Where \(I_{\text{max}}\) and \(V_{\text{max}}\) are the current density and voltage, respectively, at the maximum power output of the solar cell, \(I_{\text{sc}}\) is the cell short circuit current density, and \(V_{\text{oc}}\) is the cell open circuit voltage. The fill factor is one of three primary factors in determining \(\eta\) [12]:
\[ \eta = \frac{V_{OC} \times I_{SC} \times FF}{P_{in}} \times 100\% \] (2)

Where, \( P_{in} \) is the incident light per unit area of the cell. We proceed here from an established relationship describing I-V behavior in solar cells and directly accounting for resistance (Rs) effects on cell performance [12]:

\[ I = I_{ph} - I_{0} \left\{ \exp \left[ \frac{q(V + IR_s)}{nKT} \right] - 1 \right\} - \frac{V + IR_s}{R_{sh}} \] (3)

Where \( n \) is the diode ideality factor, \( K \) is the Boltzmann constant, \( T \) is the temperature of the device and \( V \) is the externally applied bias voltage, \( I_0 \) is the reverse saturation current, \( q \) is the elementary charge, \( I \) is the current density, \( R_s \) is the equivalent circuit shunt or parallel resistance, and \( I_{ph} \) is the photocurrent generated by the cell before recombination losses. In the ideal case, \( R_s = 0, R_{sh} = \infty \) and equation (3) can easily be solved.

3. RESULTS AND DISCUSSIONS

In this research, the characteristics and also the permance of OPV devices have been investigated theoretically by using MATLAB simulink. To enhance the photovoltaic characteristics of organic solar cell, a photocurrent of 0.0224 A/cm² [12] has been considered as the basis for this theoretical calculation. Carbon nanotubes have excellent electrical properties along the longitudinal axis, and their previous successful application as efficient hole conductors in organic solar cells stems from their work functions’ (~4.7-4.9 eV, regardless of tube species) being well aligned with the highest occupied molecular orbital of P3HT (~5.1 eV) [14]. Spontaneous helical wrapping of P3HT chains along the carbon nanotubes might further improve the selective collection of hole carriers from P3HT [14]. Importantly, the nanotube networks have been dispersed within the P3HT:PCBM active blend layer in a manner that permits precise control of the active layer thickness which does not influence the blend optical absorption as shown in Fig. 3 (this Figure is taken from the ref. 14). Figure 4 depicts \( V_{oc} \) dependence on M concentration in a wide range of compositions for a clearer observation. A maximum \( V_{oc} \) value is obtained for 3 wt% of M and lower values for higher M compositions. The open circuit voltage the device was found to be up to 1.04 V (this Figure is taken from the ref. 13).

The theoretical calculated results can be summarized as of two different dimensions: first, we demonstrated the current-voltage (IV) sweeps of the OPV and then we showed the extracted power measurement as a function of voltage. Hence, the combination of these two measurements gives the picture of device characteristics and the highest power conversion efficiency. Figure 5 shows the I-V characteristics of the device designed with considering the different layer structures. It is clear from this figure that the short-circuit current is found to increase with the introduction of SCNT on the modeled structure. The increase of \( I_{sc} \) with SWCNTs can be explained reasonably by considering the following reasons: increased charge generation, increased carrier mobility, increased built-in voltage \( V_{bi} \), increased charge collection efficiency at the electrodes and improved charge extraction. It is proposed that the enhancement in the photovoltaic properties of the composite device is due to the introduction of CNTs as electrodes and internal polymers/s junctions within the polymer matrix. These junctions act as dissociation centers, which are able to split up the excitons and also create a continuous pathway for the electrons to be efficiently transported to the negative electrode. As a consequence, electron mobility is enhanced which balance the charge carrier transport to the electrodes.

![Fig.3: Optical absorbance of ~90 nm thick (solid black line) and nanotubes containing (red dashed line) P3HT:PCBM blend film, showing that the addition of nanotubes does not affect](image1)

![Fig.4: Comparison of the experimental values of the open-circuit voltage (red curve) and a fit based on a biased diode (green curve) [13].](image2)
Next, we show the important comparison of voltage versus power for different layer structure which also called

![Graph of I-V characteristics curve for the optimized device.](image1)

the relative device performance picture. Figure 6 shows the bias voltage dependent extracted output power from the devices with different layer structures. It is found from the Fig. 6 (a) that the extracted powers become increased while gradually incorporating the SWCNTs on the proposed layer structure, and the maximum power was found to extract when we design the layer of the device for the composition of SWCNT/PEDOT:PSS/P3HT:PCBM:SWCNTs/CNT. The corresponding power conversion efficiency also enhanced due to the increased output power as shown in Fig. 6 (b). A key step in achieving this high efficiency is the utilization of SWCNTs coated with an ordered P3HT layer to enhance the charge separation and transport in the device active layer.

Finally, a summary of our calculated results is provided here. Table 1 shows the comparison among different devices with their photovoltaic characteristics. It is clear from this table that both the open circuit voltage and short circuit current density are seen to increase with nanotubes loading. In the absence of SWCNT in the device composed of ITO/PEDOT:PSS/P3HT:PCBM/Al, the measured $V_{oc}$ is 0.82V and $I_{sc}$ is 0.0224A/cm². When nanotubes are introduced and a network is established, the picture changes dramatically, giving rise to the $V_{oc}$ and $I_{sc}$. The increasing value of $V_{oc}$ is 0.84V and $I_{sc}$ is 0.023A/cm² for the layer structure of SWCNT/PEDOT:PSS/P3HT:PCBM/Al where SWCNT is used as an anode electrode instead of ITO. Accordingly, the table gives a picture of efficiency enhancement with the increased value of the sort-circuit current, open-circuit voltage and fill factor. Comparatively highest power conversion efficiency of 21.8% is found for the device structure SWCNT/PEDOT:PSS/P3HT:PCBM:SWCNTs/CNT due to the increased value of sort-circuit current, open-circuit voltage and fill factor. It is concluded from the tabulated result that the SWCNT/PEDOT:PSS/P3HT:PCBM:SWCNTs/CNT device structure gives the highest power conversion efficiency as it draws the highest extracted power. The photovoltaic behavior becomes stronger and the device efficiency becomes high. The effects of SWCNTs will be manifested mainly by the enhanced fill factor (FF) over planar electrical contacts, because the FF is more strongly affected by charge recombination. Therefore, the doping

![Comparison of a) voltage versus extracted output power and b) voltage versus power conversion efficiency.](image2)

<table>
<thead>
<tr>
<th>Device structure</th>
<th>$I_{sc}$ (A/cm²)</th>
<th>$V_{oc}$ (V)</th>
<th>FF</th>
<th>Efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ITO/PEDOT:PSS/P3HT:PCBM/Al</td>
<td>0.0224</td>
<td>0.82</td>
<td>0.74</td>
<td>13.6</td>
</tr>
<tr>
<td>SWCNT/PEDOT:PSS/P3HT:PCBM/Al</td>
<td>0.023</td>
<td>0.84</td>
<td>0.75</td>
<td>14.5</td>
</tr>
<tr>
<td>SWCNT/PEDOT:PSS/P3HT:PCBM:SWCNTs/Al</td>
<td>0.0253</td>
<td>1.04</td>
<td>0.778</td>
<td>20.5</td>
</tr>
<tr>
<td>SWCNT/PEDOT:PSS/P3HT:PCBM:SWCNTs/CNT</td>
<td>0.0261</td>
<td>1.07</td>
<td>0.779</td>
<td>21.8</td>
</tr>
</tbody>
</table>

Table 1: Comparison of the Photovoltaic characteristics of the different device structures.
of carbon nanotubes in each layer of organic solar cell gives an optimized device structure which is compatible with any condition of device behavior and shows the highest efficiency than any other organic solar cell.

4. CONCLUSION

SWCNT films are an alternative to enhance the efficiency as a hole-collecting electrode for organic excitonic solar cells. Our theoretical simulation demonstrated that the efficiency up to 21.8% has been obtained for a non-optimized device with the structure SWCNT/PEDOT:PSS/P3HT:PCBM:SWCNTs/CNT. This is the highest value reported so far for employing carbon nanotubes than other excitonic devices. Additionally, the devices are highly rectifying and show relatively large values of $I_{sc}$, Improved charge separation and collection efficiency was evidenced by the large difference between light and dark conductivities as well as the increased in open-circuit voltage, short-circuit current, and fill factor. A critical concentration value of 3 wt. % of CNT is found to achieve the highest $V_{oc}$ for the majority of the CNTs studied. The results show that the CNT electrodes and conjugated polymer-CNTs composite represent an alternative way to manufacture organic photovoltaic cells with improved performance. Further improvements in device performance can confidently be expected with more controlled film preparation and polymer doping.

REFERENCES