**Title: Investigating the Properties of Organic Polymer Solar Cell incorporating Carbon Nanotubes**


## Abstract

Carbon nanotubes have exhibited excellent photovoltaic properties, including greater electrical conductivity, higher mechanical flexibility and extremely high surface areas. This makes it ideal for incorporation into the photoactive layer ordered bulk heterojunction polymer solar cell, the new generation solar energy device which could prove to be the answer to the emerging global energy problem.

The basis of the study is creating aligned, vertically structured nanotube system featuring an interpenetrating donor-acceptor bicontinuous network to increase power conversion efficiency. In the study, we have varied the post-fabrication thermal annealing time for comparisons. The composite material encompasses the PCBM:P3HT polymer blend coupled with high transport capability of CNTs. Multi-walled carbon nanotubes used are assumed to act as meso-scaffolds, where exciton dissociation takes place, and also as hopping centers for hole transport to provide better mobility for carrier transport as compared to conventional ITO electrodes.

We report that the low-cost, solution based method developed possesses great potential for improved device performance, with increase in conductivity after thermal annealing. Future studies would take the current concept of nano-scaffolds within polymer matrix a step further to expand the field of green technology for mankind.


## Introduction

With increasing need for energy conservation, increasing threat of running out of enough fossil fuel to sustain mankind's development, the need to develop renewable energy sources is the main impetus for creating low cost and high efficiency photovoltaic devices is apparent. Research has developed several types of solar cells to capture the sun's tremendous energy (89 PW), including organic polymer solar devices that are cheap and easy to produce. Organic semiconductors especially are gaining due attention because they can be easily processed in bulk and are flexible enough to be incorporated into smart-touch devices [1].

Organic polymers are characterized by having a delocalized π electron system that can absorb sunlight, create and transport photogenerated charge carriers, properties which determine their efficiency[2]. So far, interpenetrating conjugated polymer-fullerene networks (bulk heterojunctions), particularly the PCBM-P3HT model are the most efficient model, approaching almost 6% power conversion rate [3].

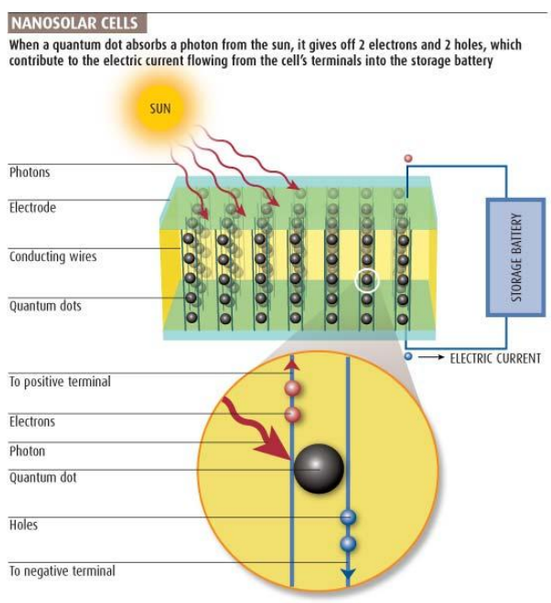


Figure 2. Diagram illustrating operational principle of polymer solar cell, including the propagation of charge carriers under illumination and transport to electrodes. The quantum dot in the figure would theoretically refer to some P3HT particles in this experimental, attached to carbon nanotubes. Ref [4]

Commercially most polymer solar cells are based on the silicon/ITO model which includes major limitations including rapid decomposition of

polymers under excessive heat. Hence they have to be processed at low temperatures using wet chemistry methods which might affect the aligned structure of ordered heterojunction cells. Broadly speaking bulk heterojunction devices have low mobility and low power conversion efficiencies, unsuitable for practical applications at most levels.

**Aims and Objectives**

The objective of this study is to report the effect of temperature change during annealing of organic polymer solar cells incorporating multiwall carbon nanotubes (MWCNTs). They function as interdigited hole extracting electrode within a polymer blend of poly(3-hexylthiophene): [6,6]-phenyl-C61-butyric acid methyl ester (P3HT/PCBM), between two metallic contacts.

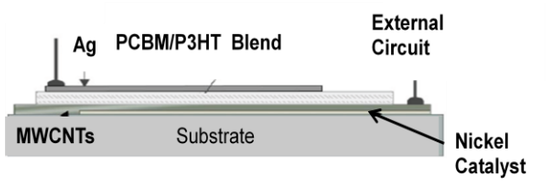


Figure 1. Schematic layout of fabricated organic polymer (PCBM-P3HT) solar cell incorporating carbon nanotubes and silver metal as electrodes. Ref [5]

The purpose of incorporating carbon nanotubes is to ensure an interdigited, aligned structure such that the domain sizes of donor and acceptor is small, allowing minimal distance for excitons to reach an interface with the electron acceptor before decay (<10NM). [6] Results are expected to enhance the absorption spectrum of illuminated light, increasing carrier mobility through its ballistic conductivity and transports electrons or holes more efficiently to respective electrodes. [6a]

In this study, MWCNTs are grown on substrates before in-situ dispersion and slight functionalization with SDS, an electron withdrawing functionality to increase compatibility and distribution within polymer matrix. Previous studies have shown that the fluorinated alkanes covalently bonded to electrode surfaces can help enhance the work function by increasing surface potential [7]. For comparison purposes, we have varied the parameters of the solar including growing the CNTs on 2 types of substrates (silicon wafers / quartz wafers) as well as the post fabrication annealing conditions of the devices to study the effect on surface morphology of the photoactive layer. This implies that contact resistance between the metal contact, carbon nanotubes and polymer composite will be directly affected; hence circuit current density (Jsc) and resistance values are the main focus of the study.

Reference devices are fabricated with the corresponding parameters, but without any carbon nanotubes. All other procedures and structures, including the photoactive layer CNT-PCBM/P3HT remain identical for all samples including thermal annealing duration and concentration of carbon nantoubes. For more details on the methodology of the experimental, please see behind under appendix.

**Results & Discussions**

Study of the surface morphology of the photoactive layer was conducted under the scanning electron microscope (SEM). Results revealed that CNTs were mainly uniformly deposited onto substrates with a relatively high density and height of ~30nm for each nanotube.

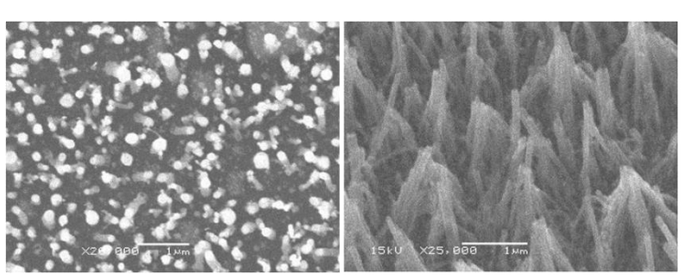

Figure 3. SEM images of carbon nanotubes a) before and b) after the functionaliztion and deposition of P3HT:PCBM layer. The clump aggregates may imply the attachment of polymer particles to oxidized tips of CNTs via van der waal's.

Most of the nanorods were aligned in the direction for electron transport and that a thin film of polymer can be made out slightly by the darker regions as indicated when spin-cast of polymer, forming a relatively even solution of P3HT-PCBM between the gaps of carbon nanotubes. However due to the low conductivity of the polymer, SEM images are unable to distinguish the exact thickness or composition of the polymer. From figure 3b, the tips of the nanotubes are clumped together in aggregates which could also lead to low contact area at the polymer-CNT interface than was previously expected.

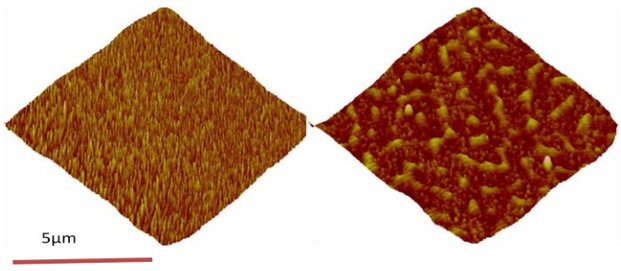


Figure 4. AFM height images of polymer composite (PCBM:P3HT concentration= 1:1)surface morphology before (left) and after (right) thermal annealing. A more regular and rougher surface is obtained after heat treatment, indicating greater blending with carbon nanotubes. Captured surface area is 5 µm×5 µm.

Figure 2 shows the effect of different polymer concentration and thickness on surface topography of the photoactive layer. Atomic Force Microscopy (AFM) images reveal that without annealing the surface is even with indistinct peak-valleys showing the protrusion of CNT layer and uneven polymer distribution. After annealing for 10 and 20 mins, the surface becomes rougher than that of the unannealed film, which may decrease the charge transport distance and reduce recombination of excitons through light scattering. A rougher surface also indicates self organization of the P3HT blend, which further implies formation of an ordered structure.

Generally results show that the thicker the Polymer layer, the longer time needed to anneal it. As indicated in table 1, the quartz substrate showed a higher current reading since it is more transparent than silicon, which allow more photons with sufficient energy to dissociate electron-hole pair to pass through to photoactive layer. In device 2, the current density increased from 0.0502A to 0.055694A for quartz substrate than silicon substrate of similar annealing time. In all fabricated cells with CNTs, there are enhanced current readings than non-CNT cells, as expected, but the resistance is much higher for quartz than normal silicon, which could probably be due to its non-conductive nature. Although silicon substrates are more functional due to their semi-conductivity nature that improves the multi-electric field model, we believe that metal-backed quartz substrates could be more ideal in terms of generating a higher bandgap excitation for both holes and electrons.

| **Test Structure** | **Device No.** | **Annealing Time (mins)** | **Peak current density (A)** | **Resistance ( Ω)** |
|---|---|---|---|---|
| **Silicon Oxide/ CNT-PCBM/ P3HT/ Ag** | 1 | Unannealed, dry in open petri dish | 0.01289 | 90.3 |
| | 2 | 5 mins | 0.05029 | 65.4 |
| | 3 | 10 mins | 0.06487 | 71.8 |
| | 4 | 20 mins | 0.06189 | 78.2 |
| | 5 (reference) | 5 mins | 0.04642 | - |
| **Quartz/ CNT-PCBM/P 3HT/Ag** | 6 | 5 mins | 0.05569 | - |
| | 7 (reference) | 5 mins | 0.02471 | - |

Table 1. Performance of various fabricated P3HT/PCBM solar cells at different annealing conditions. Quartz samples have also been fabricated together with non-CNT devices for reference. Devices 5, 6 and 7 exhibit a very high resistance as denoted by (-)

I-V characterization results demonstrate that the longer the post-annealing time, the better the cell efficiency, albeit by a small factor. In figure 5, comparing device 1 which was not annealed and device 2 which was annealed at a temperature of 110°C for 5 mins, Jsc readings increased relatively significantly. After annealing for 10 mins (device no.3), the current increases slightly to 0.0648782A which is the best out of all the solar cells fabricated.

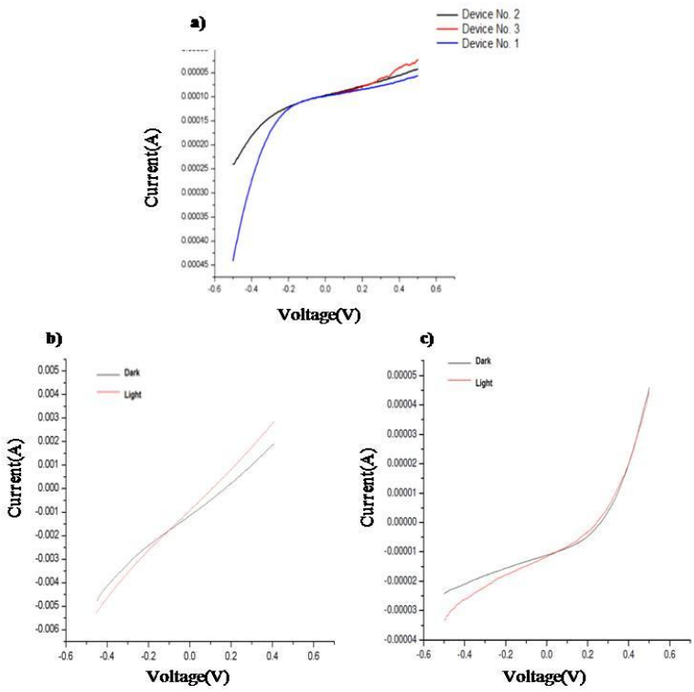


Figure 5. a) I–V characteristic curves of devices measured under illumination . The conditions are: Device 2 (5 mins), Device 3 (10 mins) at 110°C and Device 1 (unannealed). b) Device 6 and c) Device 7 under illumination respectively.

The values are supported by the I-V curves of figure 5a. Diode effect is greater in device 2 and 3 compared to 1, as can be seen by the improved current density induced by enhanced electric field. In devices without carbon nanotubes, there is a linear characteristic implying resistor effect without significant diode properties (fig 5b) However, for those incorporating carbon nanotubes, a gradual increase towards greater potential was observed, with a steeper curve as annealing time increases (fig. 5c).

Measurements indicate that after thermal annealing, P3HT shows greater reformed crystalline self-assembled structure involving enhanced conjugation length and greater contact with carbon nanotubes. We propose improved charge carrier mobilities along the long axis of fibrils along π–π stacking as reported by [8] As a result, the formation of interpenetrating, optimal polymer phase segregation crucial for higher efficiency is achieved. However excessive annealing (high temperatures) may have slightly adverse effect (as in device 4; 20 mins) [9] and we conjecture that it may lead to expansion and wrapping of P3HT molecules around the carbon nanotubes, although it is not a significant factor.

According to results obtained higher temperatures did not seem to change the metal cathode layer work function, contrary to what assadi et al. proposed of a decrease in conductivity at higher temperature due to the disruption to quasiplanar structure of the polymer chain by small twists of the monomer units. [10]

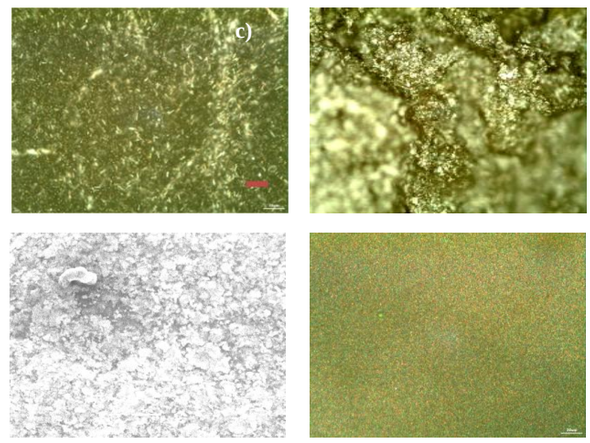


Figure 6. Microscope Images (Nikon camscope) of device surface morphology. Voids can be clearly seen in a) annealed polymer layer as well as b) annealed silver layer. c) The rough texture of the silver with polymer contact in contrast with d) unannealed polymer surface in

## Limitations

Although we have effectively compared the effect of thermal annealing on the ordering and alignment of polymer within the CNT structure, it is yet to determine if thermal annealing in various stages have any definitive effect on the efficiency of the solar cells. The metal cathode layer was applied manually by painting the silver paste on top of the polymer composite; hence the contact resistance may also affect the conduction of electrons (fig. 6c). The presence of empty spaces between the carbon nanotubes would mean that the polymer molecules have infiltrated through the layer on top of and between the carbon nanotubes to be in direct contact with the substrate below. (fig. 6a,b). Due to its high conductivity and electrical field generated at the interface, shorting may occur due to the formation of a singular unobstructed pathway for flow of

electrons from the carbon nanotubes with the metal cathode above.

The values of the fabricated samples are lower than previous published results, possibly because these devices are as yet unoptimized in terms of concentration of PCBM:P3HT loading rates or CNT concentration, neither was PEDOT:PSS (a smoothening conductive layer) included as it was not in the scope of the experiment.

**Applications**

The development of these ordered bulk heterojunction solar cells using the structured organization of MWCNTs could potentially be used to replace the larger, less flexible ITO/silicon solar cells in the mass market, such as instant rechargeable handphone batteries or heat warmers in cold countries. Particularly, the development of these new generation solar cells could be used as convenient electricity-producing devices for households in developing countries which face lack of sufficient energy due to inadequate electricity provision. They can be used as small stick-on, adhesive solar batteries without any dye leakages or chemical solution spillage which is currently a concern among poorer countries. The method also boasts an easy-to-produce process which can even be made DIY given the high stability of CNTs and high aspect ratio which only requires a small surface area to provide sufficient power.

**Conclusion**

In conclusion, promising results demonstrate a new approach to fabricating nanotube-polymer solar cells and suggest that MWNTS would serve as highly suitable alternatives to conventional ITO contacts which are more expensive, less flexible and has comparatively lower aspect ratio for conduction, as as demonstrated by Ago et al [11]. MWCNTs will serve to enhance device performance by manifold factor through the introduction interpenetrating donor-acceptor networks with photoactive composites, which has been much emphasized but without significant breakthroughs. Moreover, annealing at high temperatures increases cathode contact in terms of surface morphology, resulting in smoother surfaces and better absorption. These results will help to better current understanding of the applications of carbon nanotubes and hopefully expand the field of large scale, low cost and high efficient solar power devices that is convenient for use in household devices in developing countries without convenient energy sources.

Future applications of carbon nantoubes in ordered organic polymer solar cells could be the use as meso-scaffolds for nanoparticles of polymer such as P3HT or MEH-PPV. One of the major challenges is to achieve good adhesion between CNTs and the matrix through covalent coupling; hence future research may include finding optimum concentration of functional groups to have adequate connectivity to the matrix without compromising the stability of the nanotubes or perfect $sp^2$ hybridized graphene sheet.

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**Equipment & Software:**

All text and images are edited using Microsoft Word/Powerpoint.

SEM images are obtained using the model JSM -590LV

AFM images are obtained using the Scanning Probe Microscope Nanoscope IIIA

I-V graphs are plotted using OriginPro7

**Appendices**

Experimental Methodology:

CNTs are grown locally using the PECVD method on silicon oxide/quartz wafers coated with thin layers of chromium and nickel catalyst. The wafers were cleaned and dried with methanol followed by compressed nitrogen air before deposition. Dimensions of the wafers are 2.0cm by 2.0cm, with a square of 0.3cm by 0.3cm on the CNT samples marked out using permanent black markers as electrode contact. The fabricated samples were washed and functionalized with 2.00g of Sodium Dodecyl Sulphate (SDS) mixed with 200mL of de-ionised water, then dried under room temperature. After which the structures were submerged in chloroform solution (~10mL, 0.5M) and dispersed by ultrasonicating for 20 mins. P3HT solution (reported region-regularity of >99%) (~6mg/mol) dissolved in toluene solution is then prepared, and with the CNT samples ultrasonicated at ($30^0$C) for 15 mins. PCBM powder was dissolved into toluene solution and mixed homogenously on a stirrer with P3HT solution to form photoactive blend. The fabricated structure undergoes spin-coating with the PCBM:P3HT mixture at rates of 600 r.p.m for 60s each.After which, thin strips of silver conductive paint is painted across the surface of the polymer as reflective electrodes. The entire device is then thermally annealed on a hotplate at a fixed temperature of 110 °C.

For comparison purposes, we have fabricated solar cells on two different types of substrates, silicon wafers as well as quartz coated with catalyst to grow the CNTs. We have also changed the annealing time and duration for the devices. Reference devices are fabricated with the corresponding parameters, but without any carbon nanotubes. All other conditions and procedures are identical in all samples.