



Carbon Nanotubes In Photovoltaics

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Abstract— Carbon nanotubes hold great potential for use in photovoltaic cells. Carbon molecules are long thin cylinders of carbon. Nanotubes have a broad range of electronics thermal and structural properties. They are molecules that can be manipulated chemically and physically in very useful ways. They open an incredible range of applications in material science, electronics, chemical processing, energy management and many other fields. Nanotubes are classified as single walled nanotubes and multi walled nanotubes. A SWCNT are ideal as thin film photovoltaic because they absorb light across wide range of wavelengths from visible to near infrared and possess charge carriers that move quickly. Organic photovoltaic devices are fabricated from thin films of organic semiconductors such as polymers and small molecule compounds and are typically on the order of 100 nm thick. Polymer based OPVs can be made using coating process such as spin coating or inkjet printing. A promising alternative to silicon conventional solar cells.

Keywords—solar cells; carbon nanotubes; CNTs; organophotovoltaics; OPVs; polymers

INTRODUCTION

Science is constantly searching for more efficient ways to collect free energy coming out of the sun efficiently. The conventional photovoltaic cell are expensive and hence not able to deliver the purpose in a techno economical manner. Most of the solar cells are based on silicon which is versatile but inexpensive. So there is a huge possibility to develop ways to collect other wavelengths without making any tremendous change to the basic design of solar panels. There is a threshold level for silicon voltaic cells defined. This material is only able to convert photons into energy only when the light intensity is higher than threshold bandgap. However silicon is only able to absorb radiations that are close to the infrared end of the spectrum. Recent advancements in the technology allows conversion of energy into a form where it can be absorbed. This includes a novel material consisting of an array of Multi Walled Carbon Nano Tubes(MWCNT) and photonic crystals. This absorber consists of MWCNT situated at the top of the cell. It is generally wider in surface area and hence provides good absorption. The principle of working involves the heating of absorber material and the transmission of heat energy into the photonic crystal layer that starts to glow at the peak intensity of radiation. It essentially occurs at the centre of bandgap.

Various organic materials finds their way into the Photovoltaic market. Different organic materials are : organic molecules, conjugated polymers and four conventional carbon material i.e. amorphous carbon, fullerenes, CNT's and graphene. Photovoltaic cells can be composed of organic material or they can be made by a combination of organic and inorganic material also called as hybrid cells. CNT materials is the primary component of both hybrid and organic cells. Organic materials possess conducting and semiconducting properties, lower cost and simple manufacturing methods. The absorption coefficient of organic materials is high.

Therefore they can be used in Photovoltaic applications. Most inorganic conventional solar cells become inefficient with temperature rise. On the other hand organic solar cells with the temperature rise become more efficient [1]. The optoelectronic, physical and chemical properties of CNT's is variable. CNT organic cells are still not manufactured at large scale but SWCNT were used in space technology.

Solar cells have undergone tremendous amount of development in past two decades. The overall development of solar cells is divided into generations. The first generation belongs to the silicon based solar cells. The second generation of solar cells is based on the applications of semiconductor based very thin films. The third generation involves Dye Synthesized Solar Cells (DSSC's). DSSC's may involve hybrid cells or organic semiconductor solar cells (also called OPV). The efficiency of photovoltaic cells have increased three times in the last couple of years [2]. Our focus is mainly on the area of recent development i.e. Carbon NanoTubes (CNT) and its application in photovoltaic cells. The efficiency increment is also the primary concern.

CLASSIFICATION OF NANOTUBES AND ITS GROWTH MECHANISM

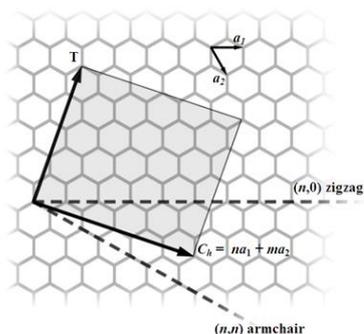
Carbon nanotubes are hexagonally oriented and cylindrical nanostructures having length to diameter ratio of 132,000,000:1 . Carbon nanotubes are generally strong and stiff. The tensile strength of CNT's is sixteen times that of stainless steel. They are members of fullerene family. The bonding structure of sp² orientation which is responsible for all its properties. Its length varies from nanometers to micrometres. The high aspect ratio is responsible for the excellent thermal and electrical properties of CNT's. The thermal capacity of CNT is five times that of copper [3]. Classification of carbon



nanotubes depends on the number the graphene layers. The CNT's consisting of single round rolled are called Single Walled CNT (SWCNT) while when there are number of rolled layers then it is called Multi Walled CNT's (MWCNT).

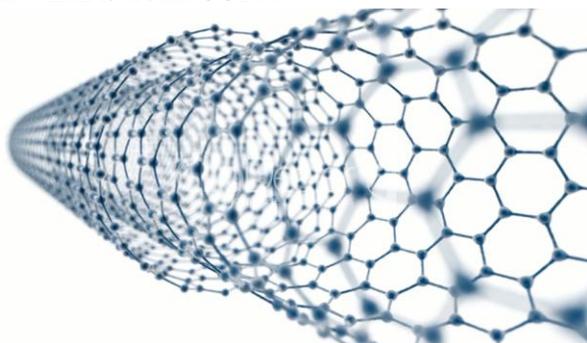
A. Single Walled Carbon Nanotubes (SWCNT)

The structure of SWCNT is similar to one atom thick layer of graphite called "graphene" into a cylinder. It is represented by (n,m). Here n,m are the unit vectors in the two directions of the hexagonal lattice of graphene [4]. Its approximate diameter can be determined from the values of n and m integers. These integers are responsible for the electronic characteristics of SWCNT. Its band gap varies from zero to approximately two eV depending upon its structure. Its electrical conductivity depends upon the band gap. It is more widely used as compared to MWCNT's. It also has metallic and semiconductor properties.



B. Multi Walled Carbon Nanotubes (MWCNT)

Multiwalled Carbon Nanotubes (MWCNT) have structure similar to sheets of graphites arranged in concentric cylinders [4]. There are two models for understanding of MWCNT i.e. Parchment model and Russian doll model. The Russian doll model is preferred over the Parchment model. For example SWCNT having (0,8) unit vectors is placed within (0,17) SWCNT. In Parchment model one sheet of graphite is rolled around itself. The distance between interlayers is similar to distance between graphite layer which is around 3.52 Å.



CARBON NANOTUBE IN PHOTOVOLTAICS

CNT's have small diameter and high aspect ratio. Active molecules are of the order of few nanometers. Therefore ready charge transfer across nanotubes and polymer based units takes place. Diameter of SWCNT is in the range of 2 to 10 nm while that of MWCNT is in the range of 5 to 10

nm i.e. well within the range of diameter upto 20 nm suggested for Organic Photovoltaic devices [5]. Both carbon nanotubes and polymers have π - conjugated system which supports electron transfer from one π - orbital to another π - orbital. The corresponding materials for CNT comes in a wide range namely oligomers , polymers , quantum dots and semiconductors. Semiconductors may have bulk or nano structure. There are two approaches that make CNT's compatible with polymer solar cells. They are CNT and small molecule combination and the other is CNT and polymer combination. The CNT complimentary element serves the function of absorption of light [6]. CNT is utilized to accept the electrons i.e. as electron acceptor (with some exceptions). Geometry of solar polymer cell is as shown in fig. CNT is applied to every possible element considering all permutations.

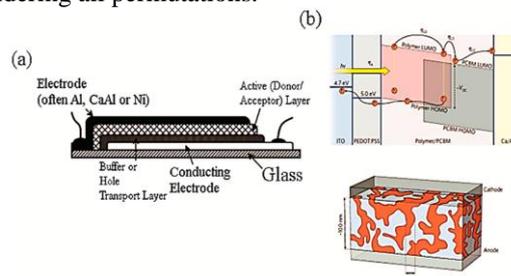


Figure 1. (a) Typical structure of a polymer based solar cell. Adapted from [7]

Reproduced with permission; (b) The operating mechanism of an OPV with a model often presented for the network of the polymer and the acceptor. Adapted from [8]

ADVANCEMENT IN CNT TECHNOLOGY FOR PV APPLICATION

The solar cell electrode must be transparent and highly conductive. The two commonly used materials are Indium Tin Oxide (ITO) and Fluorine Tin Oxide (FTO). Indium Tin Oxide is generally preferred due to its inherent properties. Indium is a rare earth metal which involves the application of other metals for its metallurgical processes. Hence it will be unable to fulfil the demands of the world at one end if required to do so. Also the process of formation of ITO in high quality is very expensive. Hence it is generally of a low quality. Solar ITO and FTO are not stable when applied to slightly acidic or basic environment. They are likely to diffuse electrolyte which results in loss of efficiency[9].

The replacement of ITO is seen in CNT's. CNT's possess many properties that make them more suitable for the photovoltaic applications and primarily in solar cell electrodes. They have low resistivity which means large amount of charge can effectively flow over the same cross sectional area and axial length. They have high specular transmittance. They can form 3D sheets in crystal lattice called Bucky papers. 3D topology of mesh like CNT allows more surface area for charge accumulation unlike



ITO electrodes. They also have high thermal conductivity and are good in heat dissipation. Unlike ITO and FTO they are stable on the incident of light. They have high electron mobility which supports its application in hole extraction layer [10]. They also have high work function which helps in hole transportation via CNT's.

APPLICATIONS OF CNT IN PHOTOVOLTAICS

A. Carbon Nanotube Composites In Photoactive Layer

Combination of conjugated polymer along the tube axis of carbon nanotubes is used in some OPV's. Under this process a Bi continuous network is formed resulting in a interpenetrating bulk donor – acceptor hetero junction which facilitates charge separation and collection. The introduction of internal polymer – nanotubes junctions in the polymer matrix results in the efficiency increment. Generally poly(3-hexylthiophene)(P3HT) or poly(3-octylthiophene)(P3OT) are used.

These polymers are spill coated on a conductive electrode having thickness in the range of 60 to 120 nm. In polymer and SWCNT power conversion efficiency is generally very low and less than 0.04% under 100mW/cm² [12]. With the increase in percentage of SWCNT the chances of short circuit in the solar cells increases. A different combination of polymer and CNT can also be used. Both SWCNT and MWCNT are capable of combining with the polymer or by themselves. A physical combination of functional MWCNT and P3HT polymer is synthesized to create a P3HT MWCNT with fullerene C₆₀ double layered device [13]. The power efficiency is low at 0.01% under 100mW/cm².

B. CNT's In Dye-Synthesized Solar Cells

The outstanding chemical stability of carbon nano materials i.e. CNT ensures environmental safety compared to other photo voltaics that may be a consideration under the agenda to reduce degradation. Dye-Synthesized Solar Cells (DSSC) have simple fabrication, process minimal production cost and high efficiency. Titanium dioxide nano material are widely used as electrodes for the DSSC. *The key problem in achieving higher photo conversion efficiency in nanostructures is due to the problems with the transport of electrons across the particle networks.*

The highest conversion efficiency below air mass (AM) is 1.5 (100mW/cm²) irradiation reported for this device till date is 11% [14]. Therefore despite its initial success the efforts to increase the efficiency has not been successful. In recent times CNT based nano composites and nanostructures can be used to let the flow of photo generative electrons in charge injection and extraction. [15]CdS quantum dots are applied on SWCNT's. Other varieties include CdSe and CdTe attached to CNT's. DSSC are also fabricated using sol gel method to produce titanium dioxide over the MWCNT tubes to act as electrode [16].

Pristine MWCNT's have hydrophobic surface and poor dispersion. To overcome this problem H₂O₂ treatment is used to generate carboxylic acid groups on oxidation with MWCNT. This reaction releases gases including CO₂ and H₂O which are non toxic to the solar cell and hence can be released. The benefit of using SWCNT's over MWCNT in photoactive layer of photovoltaic devices is the mixed purity when synthesized. It consists of 1/3rd metallic and remaining 2/3rd semiconducting material. Mettalics SWCNT's (m-SWCNT) is designed for excition of recombination of electron and hole pairs. at the junction of metallic and semiconducting SWCNT's a schottky barrier is formed that helps in minimizing the hole transmission probability [17].The poly chiral s-SWCNT enable a wide absorption from visible to near-infrared rays(NIR)light. This increases photo current than using a single chiral nanotube. Cells made with this architecture are highly stable and have higher power conversion efficiencies but still it is very less than PE(10%) of polymer-fullerene hetero-junction [18].

C. Carbon Nano Tubes As Transparent Electrodes

CNTs posses several properties like low resistivity, high specular transmittance broad range from UV to MIR .It has superior flexibility .They can exist in sheets i.e. Bucky paper. The 3-D topology mesh like circuit allows charge flow across large area and not to planner interface only. They have high thermal conductivity that helps in heat dissipation .they are also stable on application of light to their surface. They posses high electron mobility which suggests its application in hole extraction layer. [19] They have high work function(4.8 to 4.9eV) that make them suitable for hole transportation unlike ITO which are unstable in presence of acids and bases.

SWCNT films exhibits a high optical transparency in broad spectral range from visible to near infrared range [20]. However the electric sheet resistance of ITO is lower than that of SWCNTs. But the efficiency of SWCNT is of order 1% to 2.5% that is comparable to ITO based devices. Hence, the advancements may help in developing CNT-based transparent electrodes exceeds the results obtained from ITO materials.

CONCLUSION

It is a brief review of CNT applications in photovoltaics and the design development of future generations solar cells. CNTs support better sunlight absorption and they also generate photo carriers. It involves transfer of electrons and holes which is a good property in the case of photovoltaics. They have low cost of manufacturing. But the efficiency of CNT based solar cells is far behind that of conventional cells, *problems lies with the donor-accepter material otherwise CNT-conducting based polymer hybrid solar cells would be cheaper.* On the other hand electrode CNTs are very promising due to good conducting property and low resistivity. They also posses high flexibility.



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REFERENCES

- [1]. Katz, E.A.; Faiman, D.; Tuladhar, S.M. Temperature dependence for the photovoltaic device parameters of polymer-fullerene solar cells under operating conditions. *J. Appl. Phys.* **2011**, *90*, 5343–5350.
- [2]. Li, G.; Zhu, R.; Yang, Y. Polymer solar cells. *Nat. Photon* **2012**, *6*, 153–161
- [3]. See, C.H.; Harris, A.T. A review of carbon nanotube synthesis via fluidized-bed chemical vapour deposition. *Ind. Eng. Chem. Res.* **2007**, *46*, 997–1012.
- [4]. Reich, S.; Thomsen, C.; Maultzsch, J. *Carbon Nanotubes: Basic Concepts and Physical Properties*; Wiley-VCH Verlag GmbH & Co. KGaA: Weinheim, Germany, 2004.
- [5]. Hatton, R.A.; Miller, A.J.; Silva, S.R.P. Carbon nanotubes: A multi-functional material for organic optoelectronics. *J. Mater. Chem.* **2008**, *18*, 1183–1192.
- [6]. Schuettfort, T.; Snaith, H.J.; Nish, A.; Nicholas, R.J. Synthesis and spectroscopic characterization of solution processable highly ordered polythiophene-carbon nanotube nanohybrid structures. *Nanotechnology* **2010**, *21*, 025201–025206.
- [7]. Patyk, R.L.; Lomba, B.S.; Nogueira, A.F.; Furtado, C.A.; Santos, A.P.; Mello, R.M.Q.; Micaroni, L.; Hummelgen, I.A. Carbon nanotube-polybithiophene photovoltaic devices with high open-circuit voltage. *Phys. Status Solidi* **2007**, *1*, R43–R45.
- [8]. Li, G.; Zhu, R.; Yang, Y. Polymer solar cells. *Nat. Photon* **2012**, *6*, 153–161
- [9]. Sharma, A.; Andersson, G.; Lewis, D.A. Role of humidity on indium and tin migration in organic photovoltaic devices. *Phys. Chem. Chem. Phys.* **2011**, *13*, 4381–4387.
- [10]. Kymakis, E.; Amaratunga, G.A.J. Single-wall carbon nanotube/conjugated polymer photovoltaic devices. *Appl. Phys. Lett.* **2002**, *80*, 112–114.
- [11]. Gabor, N.M.; Zhong, Z.; Bosnick, K.; Park, J.; McEuen, P.L. Extremely Efficient Multiple Electron-Hole Pair Generation in Carbon Nanotube Photodiodes. *Science* **2009**, *325*, 1367–1371.
- [12]. Kymakis, E.; Klapsis, G.; Koudoumas, E.; Stratakis, E.; Kornilios, N.; Vidakis, N.; Franghiadakis, Y. Carbon nanotube/PEDOT: PSS electrodes for organic photovoltaics. *Eur. Phys. J. Appl. Phys.* **2006**, *36*, 257–259.
- [13]. Ulbricht, R.; Lee, S.B.; Jiang, X.; Inoue, K.; Zhang, M.; Fang, S.; Baughman, R.H.; Zakhidov, A.A. Transparent carbon nanotube sheets as 3-d charge collectors in organic solar cells. *Sol. Energy Mater. Sol. Cells* **2007**, *91*, 416–419.
- [14]. Zhipan, Zhang; Ito, S.; O'Regan, B.; Daibin Kuang; Zakeeruddin, S.M.; Liska, P.; Charvet, R.; Comte, P.; Nazeeruddin, M.K.; Pechy, P.; Humphry-Baker, R.; Koyanagi, T.; Mizuno, T.; Gratzel, M., (2007). "The electronic role of the TiO₂ light-scattering layer in dye-sensitized solar cells". *Zeitschrift für Physikalische Chemie* **221** (3): 319–327. doi:10.1524/zpch.2007.221.3.319
- [15]. Robel, Istvan; Bunker, Bruce A.; Kamat, Prashant V., (2005). "Single-walled carbon nanotube-CdS nanocomposites as light-harvesting assemblies: Photoinduced charge-transfer interactions". *Advanced Materials* **17** (20): 2458–2463. doi:10.1002/adma.200500418
- [16] Lee, Tae Young; Alegaonkar, P.S.; Yoo, Ji-Beom, (2007). "Fabrication of dye sensitized solar cell using TiO₂ coated carbon nanotubes". *Thin Solid Films* **515** (12):51315135. Bibcode:2007TSF...515.5131L. doi:10.1016/j.tsf.2006.10.056
- [17] Fuhrer, M. S.; Nygård, J.; Shih, L.; Forero, M.; Yoon, Y.-G.; Mazzoni, M. S. C.; Choi, H. J.; Ihm, J.; Louie, S. G.; Zettl, A.; McEuen, P. L., Crossed Nanotube Junctions. *Science* **2000**, *288* (5465), 494–497.
- [18] Li, G.; Zhu, R.; Yang, Y., Polymer solar cells. *Nat Photon* **2012**, *6* (3), 153–161.
- [19] van de Lagemaat, J.; Barnes, T.M.; Rumbles, G.; Shaheen, S.E.; Coutts, T.J.; Weeks, C.; Levitsky, I.; Peltola, J.; Glatkowski, P., (2006). "Organic solar cells with carbon nanotubes replacing In₂O₃:Sn as the transparent electrode". *Applied Physics Letters* **88**(23): 233503–1–3.
- [20] Wu, Zhuangchun; Chen, Zhihong; Du, Xu; Logan, Jonathan M.; Sippel, Jennifer; Nikolou, Maria; Kamaras, Katalin; Reynolds, John R.; Tanner, David B.; Hebard, Arthur F.; Rinzler, Andrew G., (2004). "Transparent, conductive carbon nanotube films". *Science* **305**(5688):12731276. Bibcode:2004Sci...305.1273 W. doi:10.1126/science.1101243.PMID 15333836