Utilizing Carbon Nanotubes to Improve Efficiency of Organic Solar Cells

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Abstract

The weight, cost, and flexibility of organic photovoltaics have become increasingly applicable for use in bringing power to even the most remote locations. In order for these cells to be successful their efficiency, currently around 1-3% (compared to 20-30% for the traditional cells), needs to be on par with that produced by the traditional cells. Our research team worked in the experimental and theoretical settings to find ways to improve this efficiency. Through the introduction of functionalized carbon nanotubes as the donor and the hole carrier in a bulk heterojunction photovoltaic made with MEH-PPV-CN as the acceptor and electron carrier, we were able to create a theoretical model that illustrates mathematically and pictorially the ideal structure and size of a more efficient organic cell. An array of vertically-aligned, semiconducting nanotubes nearly spanning the two electrodes and surrounded by polymer matrix with spacing approximating the exciton diffusion length may provide optimal efficiency, provided such a device could be manufactured. We attempted many different fabrication processes, but were unable to create functional devices containing carbon nanotubes. While the time constraints of the project and the restrictions of our equipment allowed us to do only limited successful fabrication, we were able to fabricate devices that exhibit photoluminescence.
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I. Introduction
   A. Need

Finding alternative sources of power is a hot topic on the minds of many Americans right now, but imagine living in a society where finding any source of power is a daily issue. As third-world nations around the world continue to develop, there is a striking need to provide a source of electrical power to areas that have no access to the traditional power plants that Americans take for granted. A commonly proposed solution to this issue is to introduce solar cells to these remote areas. Solar cells produce relatively cheap and clean power, while their size and the maintenance requirements are small enough that they would suit locations that are inaccessible to other power sources. However, traditional solar cells have many drawbacks that make this proposal more of a dream than a reality.

While traditional solar cells may be a cheaper alternative to a full-blown power plant, they are still costly for these poor target areas and nations. Due to their fragility and installation they are also difficult to transport. Recently, there has been amazing progress in the field of organic solar cells. These devices seem ideal for poor and remote areas. The materials used in these cells are cheaper than their traditional counterparts, and they are much thinner and more flexible. These devices could be laid on roofs or almost any shape surface; therefore it would be much easier to find places where these devices could be setup. Organic solar cells are at a point where researchers can see their immense potential, yet there is still much work to be done before these devices can be successfully deployed. Currently, organic solar cells do not produce power with at an efficiency that makes them cost effective. There are many proposed resolutions to this issue currently in publication, and our research team decided to focus on the inclusion of multi-wall carbon nanotubes into the polymer matrix. The idea was that the carbon nanotubes (CNTs) will provide a more efficient path for the charges to travel along once they are generated within the device.

B. Scope

The polymer we studied was a matrix of MEH-PPV-CN. The original idea for using this product came from out partners at LPS. They had done previous work with this polymer and were looking to expand their research on its capabilities. The purpose of this experiment was to show that the efficiency of devices created with this polymer can be improved by adding carbon nanotubes to the matrix. We attempted to test this by synthesizing many different solutions of varying spin parameters as well as concentrations of nanotubes to polymer and then creating solar cells with the different mixtures. The IV characteristics of these devices were measured to see their photovoltaic effect.

As this is a design project, in addition to the lab fabrication and characterization endeavors were also undertaken to take a theoretical look at organic solar cells. We attempted to model a simple device, and design the ideal structure if we were able to build the devices atom by atom. Some design issues that could be optimized via a model is device thickness, ideal CNTs versus polymer concentration, and microstructure. The
research team worked both within the laboratory and in classroom settings to attempt to develop a more efficient organic solar cell.

II. Photovoltaic Cells

A. Traditional

While organic solar cells are currently en vogue in research circles their traditional predecessors have been around for decades. Consequently, the devices we studied operate through a similar process as the traditional cells. Conventional solar cells are usually made from silicon $pn$-junction. The $n$-type silicon has extra, loosely bound electrons that can be ionized by the absorption of a photon leaving behind a hole. If this event occurs sufficiently close to the junction, then the electric field across the junction will propel the hole to the $p$-side. When an electrical contact is made between the two sides of the junction, electrons will flow from the $n$-side to the $p$-side, generating a current.

However, the fact that the separated charges need to reach the junction before recombining severely limits these devices. Silicon is not the ideal material because it is a minority carrier. Meaning, the charge carriers are generated where they are outnumbered by opposite charges. Silicon was initially chosen only because it could build off the mature semiconductor industry. This problem has been mitigated by improving the purity and crystallinity of the silicon, which increases the distance traveled before recombination, and by creating multi-junction devices, which decreases the distance to the junction. Using these improvements, up to $\%35$ of the photons can be converted to electrons. Nevertheless, these improvements greatly increase the cost of the solar cells, and without fundamental breakthroughs, silicon will not meet the U.S. Department of Energy’s cost goal for solar energy$^1$.

B. Organic

Organic photovoltaics function in a similar manner to their classical predecessors. There are essentially four steps to photon to electron conversion: photon absorption, exciton diffusion to a $pn$-junction, charge separation, and charge transport to their respective electrodes. The cost of these devices will be much lower than traditional solar cells because they employ cheaper materials, such as conductive polymers, and processing techniques, such as spin casting and evaporation. There are generally three components in an organic solar cell: the active layer, band alignment layers and the electrodes. The active layer is the most important component. It composed of an electron donor and an electron acceptor and is responsible for photon absorption, charge separation and conduction to the electrode. The band alignment layers are placed between the active layer and the electrodes. Their role is to minimize the band bending that arises from the Schottky barrier between the semiconducting active layer and the metallic electrodes. Commonly, LiF is used on the Al electrode and PEDOT is used on the ITO electrode. The purpose of the electrodes is to serve as efficient charge collectors and to create an electric field throughout the active layer through the difference in their work functions. Usually ITO is chosen because it is transparent and has a high work function (4.7 eV). It
usually paired with Al (4.28 eV) because they have a large difference in work function (0.4 eV). A common device structure can be seen in Figure 1.

![Figure 1: Common device structure for an organic solar cell](image)

### 1. Photon Absorption

For the material system we designed, the photon absorption usually occurs in the electron donor, although both donor and acceptor can absorb. The key material property related to photon absorption is absorption coefficient. While conductive polymers can have very high absorption coefficients, they tend to be only for low wavelengths (300-400 nm) which do not match the solar spectrum very well. This means that for adequate photon absorption to occur, the thickness of the active layer needs to be increased. This is undesirable because it increases the distance that separated charges need to be transported and lowers the amount of charges that reach their electrodes. We hope that by using CNTs as the electron donor, we can increase the absorption efficiency of the cell.

### 2. Exciton Diffusion to Junction

Photon absorption creates excitons which are electron-hole pairs that are bound to each other via Coulombic attraction. In order to generate charges, these electron-hole pairs must be separated at a *pn*-junction (or a donor/acceptor junction) before they recombine. Unfortunately, due to short exciton lifetimes and poor mobility conductive polymers have very low exciton diffusion lengths, between 10 and 20 nanometers. This means that in a bilayer junction, only excitons created within the diffusion distance of the interface contribute to the current flow. Excitons generated farther than diffusion length from an interface recombine before they have a chance to separate. The need to have a junction very close to the exciton generation sites, yet still have a device thick enough to absorb significant amounts of light, led to the development of another junction structure: the bulk heterojunction.

In a bulk heterojunction, the same effect is used, but with nanoscale mixing of the donor and acceptor. Instead of having only a junction layer, there are junctions throughout the entire active layer. By placing a junction within the diffusion length of almost every exciton creation point, the efficiency of the device can be radically improved. Figure 2
shows a schematic diagram of a bulk heterojunction. It is important to note that while a bulk heterojunction improves charge separation, it does it at the cost of increasing the distance and complexity of the path that charges must travel. Furthermore, it places difficult morphological requirements on the active layer being as the donor and acceptor must not only be mixed on the nanoscale but also bicontinuous. It is our hope that replacing the donor with CNTs whose exciton diffusion length is greater than conductive polymers this strict morphological requirement can be relaxed without decreasing efficiency.

![Schematic diagram of a bulk heterojunction](image)

**Fig 2:** Schematic diagram of a bulk heterojunction. The red represents the electron donor while the blue represents the electron acceptor.

### 3. Charge Separation

Charge separation occurs at a donor/acceptor junction when the local electric field generated by the difference in band gaps of the donor and the acceptor is large enough to overcome the Coulombic attraction of the exciton. The absorbance of a photon in the donor material promotes an electron to its LUMO, and leaves a hole in its HOMO. At the junction, the electron will jump from the donor’s LUMO to the acceptor’s LUMO because it is a lower energy state. The electrons will then travel “downhill” to the lower workfunction electrode, while the holes travel “uphill” to the high workfunction electrode. Figure 3 illustrates this process.

![Band diagram of organic solar cell showing charge separation and transport](image)

**Fig 3:** Band diagram of organic solar cell showing charge separation and transport.
4. Charge Transport

The final step for current generation is charge transport to their respective electrodes. Charge transport is guided by the electric field generated throughout the active layer by the difference in workfunctions of the electrodes. This can be seen in Figure 3 as the band bending that creates the “uphill” and “downhill” for the charges to travel. However, despite having a guiding electric field, charges can be lost as they travel to the electrode. Thus, it is important to minimize the distance and the complexity of the path that the charges must travel. It is our hope that replacing the electron donor with CNTs which have a much better charge mobility, the amount of holes reaching the ITO electrode can be increased.

III. Materials Used

For our solar cells, we used multi-walled carbon nanotubes as the electron donor and MEH-PPV-CN as electron acceptor. The CNTs were supplied by Zyvex and their diameter was 5-15 nm, their length was 0.5-5 µm, and were 60% metallic and 40% semiconducting. The CNTs were functionalized to improve their solubility.

A. Carbon Nanotubes

The major design issue we investigated was the utilization of functionalized carbon nanotubes as our donor material. In the past the polymer acted as the donor and “bucky” balls were used as the acceptor. Theoretically, CNTs will help improve the efficiency of the cells due to their high optical absorbance (needed to produce excitons) and extremely high conductivity (needed to move the charges to the electrodes). Specifically, we used mulit-wall nanotubes because they were superior to their single-wall counterparts with respect to the key properties of conductivity and absorbance.

When carbon nanotubes are processed, the chirality of the tube will affect many of the properties. The chirality of the nanotube will determine whether the tube is metallic or semi-conducting. For our purpose the carbon nanotubes will consist of a mixture of semi-conducting and metallic tubes. Furthermore, the chirality of the carbon nanotubes will determine the overall optoelectronic properties, along with the diameter. The diameter of the carbon nanotube is an important property as it has a direct correlation with the optical bandgap. Carbon nanotubes have the unique electrical characteristic of utilizing a diffusive process resulting in electron scattering. Due to the hexagonal array of atoms on the tube, nanotubes prohibit electrons from diffusing through the wall. This characteristic forces the electrons to travel down the axis of the tube, generating a very rapid and efficient charge transport system. Carbon nanotubes also exhibit faster phonon transport than any other material. Furthermore, carbon nanotubes allow a current capacity 4 times larger than the next best material. These properties make carbon nanotubes very useful in numerous applications.

There are essentially two types of carbon nanotubes that can be produced, differentiated by the amount of layers of the nanotube. Single walled nanotubes (SWNT) can be made
that resemble a rolled piece of graphene. SWNT have diameters ranging from 0.4 to 2 nanometers and lengths reported up to 1.5 cm. MWNT have been found to have diameters of roughly 10 to 200 nanometers with lengths on the order of hundreds of microns. These dimensions lead to extremely high aspect ratios which aid in their extraordinary conductivity. Figure 4 shows two SEM micrographs of SWNT and MWNT. One can see the obvious difference in structure and diameter between the two images.

![Figure 4: SEM micrographs of SWCNT (left) and MWCNT (right)](image)

The optical properties of carbon nanotubes are important characteristics to understand for fabrication of our organic solar cells. The optical absorbance of carbon nanotubes are affected by both structure and dimension of the nanotube. Metallic and semiconducting nanotubes will have relatively different absorbance spectras. Furthermore, there will be differences in the spectra for MWNT and SWNT. Absorbance spectras are also dependent on the diameter of the nanotubes being analyzed.

The chirality of the nanotube will affect whether a nanotube will be a metallic or semiconducting. Since it is often difficult to distinguish between metallic and semiconducting nanotubes, optical absorption can be used to distinguish between the two. A problem exists, however, that absorbance spectras vary significantly when the tubes are bundled with metallic and semiconducting tubes. Also, the surroundings of carbon nanotubes have a significant effect on its absorbance. These factors need to be taken into consideration given the possibility of uneven dispersion of carbon nanotubes in the polymer blend. Figure 5 compares metallic nanotubes to semiconducting tubes. It is evident that metallic nanotubes will peak at a much lower wavelength that semiconducting nanotubes.

Optical absorbance can also be affected by the structure of the nanotube. For MWNT and SWNT, the optical absorbance spectras vary a great deal. Figure 6 compares the absorbance of MWNT and SWNT. As can be seen in the image, SWNT have much higher absorbance spectras peaks than in MWNT. Often, measurements of optical absorption of MWNT can be difficult and yield inaccurate results.
Lastly, diameter has a very large effect on the optical absorbance of the nanotube. Often optical absorption can be used in order to characterize the diameter distribution of carbon nanotubes. However, the optical absorbance of nanotubes can be affected by the superposition of diameters in bundled nanotubes. Dispersive chemicals can be used to avoid this problem and optical absorbance can be accurately calculated. For MWNT, optical absorbance does not allow diameter distribution analysis. SWNT can be made with varying diameters through the use of different growth catalysts. Figure 6 compares optical absorbance for 4 different diameter sizes of SWCNT. From the image, it can be concluded that larger diameters produce higher optical absorption. Also, from the peaks,
diameter distributions and difference in gap energies for varying chirality’s can be calculated. Diameter and chirality distribution can be related to the photon energy by the equation

$$E = 2n\alpha \gamma /d$$

where \(n\) is an integer, having values of 1, 2, 4, 5, or 7 for semiconducting SWNTs and \(n = 3\) or 6 for metallic SWNTs, \(\alpha\) is the carbon-carbon bond distance with a value of 0.142 nm, and \(d\) is the SWNT diameter. The carbon-carbon overlap integral for SWNTs, \(\gamma\), has been reported to range from 2.45 to 3.0 eV.

![Figure 7: Comparison of the optical absorbance spectrums for SWCNTs of varying diameter.](image)

**B. MEH-PPV-CN**

The polymer being used in the active layer of the solar cell is Poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-(1-cyanovinyl-enephylene)], which is abbreviated MEH-PPV-CN. Figure 8 depicts the molecular structure of the mer. The polymer is a variation of one of the most commonly used polymers in polymer/fullerene photocell research, MEH-PPV. The conjugated bonds along the backbone of the polymer provide a path for conducting charges. The addition of a cyano side group to helps increase the electron affinity of the polymer and produces better band alignment with the carbon nanotubes, allowing the polymer to act as an electron acceptor. According to the manufacturer\(^7\), American Dye Source, MEH-PPV-CN is a light emitting polymer with peak emission wavelength of 558nm and peak absorption at 405nm. The measured absorbance spectrum for the polymer can be seen in Figure 13. It absorbs in a relatively small region at the shorter wavelengths of the solar spectrum, meaning that a lot of the energy present in the longer wavelength will pass through the polymer layer. This is acceptable because the carbon nanotubes will absorb in the longer wavelength region and capture the energy from a larger portion of the solar spectrum. Combining these two materials successfully may produce an organic solar cell capable of higher efficiencies than current technology.
IV. Modeling

In an effort to look at our project from a theoretical design standpoint we broke the current generation process down into four phases: photogeneration of excitons, exciton transport to the junctions, electron-hole separation, and charge transport to the electrode. The team looked at each of these steps from a conceptual and mathematical perspective and worked to develop a strong understanding of what steps (i.e. device thickness, material location/structure/concentration) we should take to optimize our device’s output. It may turn out that one process is much slower than the others and the model for that “rate limiting step” becomes more important than the rest. However, we do not know if this is the case. In general, modeling bulk heterojunction organic solar cells requires the use of extremely complex mathematical treatments that extend well beyond the capabilities of a one semester senior design project. Our approach to the problem must be simplified to focus on understanding the physics of polymer/nanotube solar cells on a basic level and applying this knowledge to our design. We will begin with a preliminary model of a simple bilayer heterojunction, for which models can be developed, and we will extend the relevant results towards understanding the bulk heterojunction.

A. Model Device Geometry

The simplest model to look at initially is a bilayer device, with only one, flat interface between the electron donor and acceptor. Figure 9 shows a schematic of the device geometry. The top layer represents the ITO electrode, followed by a layer of carbon nanotubes (CNT), a layer of polymer, and finally the Al electrode on the bottom. A coordinate system is also defined such that x is the dimension in which the light is penetrating into the device, and x=0 is defined to be at the CNT/ITO interface while x=L is defined to be at the CNT/polymer interface (see the inset of Figure 9).

B. Photogeneration of Excitons

The process of generating excitons essentially depends on the optical absorption characteristics of the system. As photons are absorbed, electrons are excited to higher energy states, leaving holes in the lower energy states. These electron-hole pairs experience a Coulombic attraction and are referred to as excitons. Figure 10 shows a schematic illustration of what happens in the solar cell during this step.
Previous research has shown that carbon nanotubes have a relatively high work function, so they are likely to act as the electron donor in the solar cell\textsuperscript{8,9}. Since the excitons from the electron donor are typically found to contribute most to the photocurrent, we can simplify the problem by neglecting contributions from the polymer layer and only focusing on the excitons created in the carbon nanotube layer where \( x \) ranges from 0 to \( L \). Furthermore, we will assume that one exciton is created for every photon absorbed, neglecting the effects of any other absorption mechanisms within the materials. The final assumption will be to approximate the solar spectrum as though the sun were a perfect black body radiator of temperature 5630K. This matches the peak maximum and peak width to the ASTM Air Mass 1.5 standard, and is a good approximation of the solar spectrum\textsuperscript{10}. If more accurate information is needed, then the procedure below can be
repeated using a table of solar irradiance data along with numerical integration techniques instead of the black body expression.

Given these assumptions, one can start with an expression for the black body solar spectrum irradiance:

$$S_{\text{Inc}}(\lambda) = \frac{2hc^2}{\lambda^5} \frac{1}{e^{\frac{hc}{\lambda kT}} - 1}$$

If the absorption coefficient for the carbon nanotubes is known as a function of wavelength, then the absorbed power per unit area as a function of depth can be determined:

$$S(x, \lambda)[W / m^2] = S_{\text{Inc}}(\lambda)e^{-\alpha(\lambda)x}$$

$$I(x, \lambda) = \int_0^x \frac{S_{\text{Inc}}(\lambda)\lambda}{hc} e^{-\alpha(\lambda)\xi} d\xi$$

$$I(x) = \int_{\lambda_1}^{\lambda_2} \frac{S_{\text{Inc}}(\lambda)\lambda}{hc} e^{-\alpha(\lambda)\xi} d\xi d\lambda$$

In the final expression, the irradiance has been divided by the photon energy and integrated over the relevant range of wavelengths to give an expression for the number of photons absorbed per unit area as a function of depth in the material. Using the assumption that there is one exciton created for every photon absorbed, this function will also be equivalent to the number of excitons generated at a given depth. Note that the expression is not entirely correct since the incident energy will need to be corrected by factoring in the absorbance and scattering effects of each of the layers in between the outside of the device and the beginning of the nanotube layer (the ITO layer for this particular model).

**C. Exciton Transport to Junction**

Once an exciton is created it must reach an interface for the charges to separate and contribute to the photocurrent, otherwise it will decay through some other pathway that will not lead to current generation. The exciton will not be biased by any electrical fields present in the material since it is charge neutral. However, it will preferentially travel along certain directions of the molecule to which it is bound. Excitons can travel along the axis of a carbon nanotube or along the conjugated backbone of a conducting polymer much more easily compared to other directions. On a microscopic scale this presents another challenging problem. However, if we assume that on a macroscopic scale the nanotubes and polymer chains are distributed in random orientations then the excitons will proceed to move randomly through the material until it reaches an interface or decays. This process is a form of diffusion, and it hints at the typical diffusion equation:

$$\frac{du}{dt} = D \frac{d^2u}{dx^2}$$

where $u$ represents the volume concentration of excitons in the material. The equation still needs to be modified to account for the processes of exciton decay and
photogeneration of excitons. If we assume that the decay is proportional to the concentration of excitons present by some rate factor R, it will lead to a negative term on the right side of the equation. Equation 3 derived in the previous section is already an expression for the photogeneration of excitons in terms of the number of excitons generated per unit area per unit time, and will become an additive term on the right side of the equation. Overall, this results in the equation:

$$\frac{du(x,t)}{dt} = D \frac{d^2 u(x,t)}{dx^2} - R \cdot u(x,t) + A \cdot I(x)$$

(5)

The next step is to impose boundary conditions and initial conditions, and this can be achieved by making some assumptions about how the process will occur. At the CNT/Polymer interface the exciton will separate into two charges, therefore excitons are destroyed. If we assume that this process is 100% efficient, it will lead to the condition that $u(L,t) = 0$. Similarly, at the polymer/electrode interface the exciton will most likely separate, and the charges will be lost in the metallic free electron gas. This leads to $u(0,t) = 0$. Finally, we can assume that at $t=0$, the material begins in the ground state and that there are no excitons anywhere in the material, or that $u(x,0) = 0$. These three conditions lead to a solvable PDE, which is in general very complex. Solutions will be in the form of a summation of sine terms in a Fourier series that depends on the Fourier decomposition of the non-homogeneous term $I(x)$.

The quantity of interest out of all of this would be to look at the flux of excitons across the interface, $du/dx$ at $x=L$. Ultimately, this could be related to the photocurrent produced by the solar cell. Due to the complexity of modeling these solutions, computer approximations would be necessary, and this is too complex to explore in the timeframe of this project. On the other hand, the approach is still valid and partial differential equations of this nature are being used to study exciton diffusion in conjugated polymer system in current research\textsuperscript{11,12}.

**D. Electron Hole Separation**

Electron-hole separation in bulk heterojunctions occurs almost exclusively at the junction because in the bulk material in the active layer there is not enough of an energy difference to separate the electron and the hole. However, at the junction, the difference in the energies of the two materials is many orders of magnitude greater than that exhibited within the bulk, and the Coulombic forces binding the exciton can be overcome.

In previous work with organic polymers, the polymer was the donor and the fullerenes were the acceptor. For this geometry, the bulk of the current excitons are generated in the polymer, and must migrate to the junction formed by the polymer/fullerene interface. In MEH-PPV, excitons have a mean path length of between ten and twenty nanometers, so the only “useful” polymer is that within that distance of a junction.

For the nanotube mixture, the nanotubes are the donor and the polymer is the acceptor. In this case, the bulk of the photoexcited electrons originate in the nanotube. Exciton lifetimes have been measured to range from 10-100 ns in single-walled CNT. Since the
radiative lifetime is 120 ns\textsuperscript{14}, it is unlikely that excitons will decay by recombining to form a photon. However, this does not guarantee good charge separation being as there are other ways the exciton can decay, such as phonon interactions. None-the-less, CNT would seem to be much better charge separators than conductive polymers. This may mean that the need for nanoscale mixing is relaxed.

### E. Charge Transport to Electrode

While in previous organic photocells the polymers conducted holes and the acceptor conducted electrons, the roles are reversed in this photocell. This means the heavier charge is transported along the fastest pathway. For MEH-PPV, the fastest transport path is along the polymer backbone, with cross-chain transport being orders of magnitude slower. Ideally, polymers and nanotubes would be aligned perpendicular to the electrodes to provide the most rapid transport path possible. The key factors for determining how efficient our devices will be are the electron mobility within our polymer and the hole mobility within the CNTs. The highest recorded electron mobility for MEH-PPV at room temperature is $3.3 \times 10^{-7}$ cm\textsuperscript{2}/Vs while the average hole mobility for CNT’s at room temperature is around 3000 cm\textsuperscript{2}/Vs. Note the latter value is 10 orders of magnitude above the best polymer mobility indicating it would be unlikely to be a rate limiting step\textsuperscript{15-19}.

Numerous papers have shown the electron mobility in MEH-PPV can be equated by\textsuperscript{13}:

$$\mu = \mu_0 e^{0.89\gamma \sqrt{E}}$$

(6)

Where $\mu_0$ is the zero field mobility (for MEH-PPV this value has been determined to be $(1 \pm .5) \times 10^{-7}$ cm\textsuperscript{2}/Vs) and $\gamma$ is the electric field coefficient (for MEH-PPV this value is given by $(4.8 \pm 3) \times 10^{-4}$ (m/V)$^5$). $E$ is the electric field applied to the device by the differing work functions of our electrodes. From this equation we can use that mobility to find the current density within the polymer\textsuperscript{13}:

$$J = \frac{9\varepsilon \mu E^2}{L}$$

(7)

Where $\varepsilon$ is a constant equal to $3.1 \times 10^{-11}$ C\textsuperscript{2}/(Nm\textsuperscript{2}) and $L$ is the thickness of the polymer. From this equation it is simple to predict that reducing the thickness of the device will produce more current.

### F. Ideal Structure

There are essentially two tradeoffs in the structure of the solar cell that need to be optimized. There is a tradeoff between minimizing the distance to a junction and the complexity of the path separated charges need to travel. There is also a tradeoff between the amount of photons absorbed, and the distance the charges need to travel (i.e. device thickness). Figure 11 depicts what we believe the ideal structure to be. Its ordered layers
minimize the distance to the junction without increasing the complexity of the charge’s path. The optimum thickness for the device can be determined with the correct material constants from the model above. Note that there is a relatively thick layer of polymer coating the Aluminum electrode. This is to prevent the cell from shorting.

Figure 11: Schematic drawing of the ideal device structure.

V. Fabrication Process

A. Substrate Fabrication

Devices were prepared by etching ITO substrates, evaporating Al on part of the ITO as contacts, spin coating first the PEDOT layer then the active layer, evaporating LiF on the entire substrate, and finally evaporating Al with a mask to form the contacts.

The ITO (Indium-tin-oxide) etched substrates were prepared through photolithography and etching. Photolithography was preformed in a clean room. Positive resist was spun onto a substrate of ITO (210nm) on glass. A contact mask was placed on top of the resist and then the sample was exposed to UV light. After the mask was removed, the developed resist was dissolved and the sample was removed from the clean room.

The ITO was etched in a fume hood by submerging the substrate in 50% Hydrochloric acid and 50% DI water for 15 min. Resistive measurements were taken at the etched parts of the substrate to insure that all the ITO was removed. The substrates were dipped in acetone to remove the remaining photoresist. All remaining organic material was removed by submerging the substrates in boiling 1,1,1 Trichloroethane for 2 minutes and then dipping the substrates in acetone followed by methanol.

The etched ITO substrates were placed inside the glove box. Individually, the substrates were placed into a mask similar to the shape of the ITO, but without overlapping with what would later be the active areas. The chamber was pumped down to \( \sim 2 \times 10^{-6} \) Torr and 600 angstroms of aluminum were evaporated onto the device to improve electrical contact to the ITO electrode.
B. Active Layer Fabrication

Devices were prepared by etching ITO substrates, evaporating Al on part of the ITO as contacts, spin coating first the P-DOT layer then the active layer, and finally evaporating LiF on the entire substrate and then evaporating Al last with a mask to form the contacts.

The ITO (Indium-tin-oxide) etched substrates were prepared through photolithography and etching. Photolithography was performed in a clean room. Positive resist was spun onto a substrate of ITO (thickness) on glass. A contact mask was placed on top of the resist and then the sample was exposed to UV light. After the mask was removed the developed resist was removed and the sample was removed from the clean room.

The ITO was etched in a fume hood by submerging the substrate in 50% Hydrochloric acid and 50% DI water for 15 min. Resistive measurements were taken at the etched parts of the substrate to insure that all the ITO was removed. The substrates were then dipped in acetone to remove the remaining proto-resist. All remaining organic material was removed by submerging the substrates in boiling 1,1,1 Trichloroethane for 2 minutes and then dipping the substrates in acetone then methanol.

The etched ITO substrates were then placed inside the glove box because the polymer active layer is sensitive to degradation when it is exposed to oxygen, the glove box maintains a nitrogen atmosphere. Individually, the substrates were placed into a mask similar to the shape of the ITO, but without overlapping with what would later be the active areas. The chamber was then pumped down to ~2x10^-6 Torr. Six hundred angstroms of aluminum were then evaporated onto the device. PEDOT-PSS was then spun onto the substrate to make up for the Schottky barrier between the ITO, our high work function material, and the active layer. The PEDOT-PSS was spun onto every device with the following parameters:

<table>
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<th>Stage</th>
<th>Speed (RPM)</th>
<th>Ramp time (sec)</th>
<th>Stay time (sec)</th>
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<td>60</td>
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</tbody>
</table>

Stage 1 is to insure uniformity, stage 2 determines the thickness, stage 3 is the drying stage. The solution was deposited into the substrate prior to the spinning, so it’s a little different from the spin coating we’ve been talking about. Ramp is how long it takes to get to the RPMs, and time is how long the spinner stays at the RPM value.

The substrates were then heated for 10 min at 200°C on a hot plate.

For the devices on which the active layer was spun (all but the last), the active layer was then spun on using the following parameters:

<table>
<thead>
<tr>
<th>Stage</th>
<th>Speed (RPM)</th>
<th>Ramp time (sec)</th>
<th>Stay time (sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
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<tr>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>1</td>
<td>1000</td>
<td>10</td>
<td>20</td>
</tr>
<tr>
<td>2</td>
<td>2000</td>
<td>10</td>
<td>60</td>
</tr>
<tr>
<td>3</td>
<td>6000</td>
<td>10</td>
<td>20</td>
</tr>
</tbody>
</table>

No heating was necessary for this layer.

The different active layers used included:

- Pure CNT, stirred via magnetic stirrer in chlorobenzene
- Pure polymer in chlorobenzene
- Sonicated CNT in chlorobenzene
- Mixtures of sonicated CNT and polymer in chlorobenzene
- Sonicated CNT in Methyl-Ethyl-Ketone (MEK)

After the active layer was spun on, the device was placed on a blank mask so as to cover the entire device with LiF, which makes up for the Schottky barrier between the active layer and the Al contacts, our low work function contact. The device was placed in the evaporation chamber and then the chamber was pumped down to \( \sim 2 \times 10^{-6} \) Torr. Twenty angstroms of LiF were then evaporated onto the device. After the chamber was pressured back up, the device was placed in a new mask, so as to overlap four squares of ITO. The chamber was then pumped back down to \( \sim 2 \times 10^{-6} \) Torr. Six hundred angstroms of aluminum were then evaporated onto the device. The finished devices were placed in a cryostat in order to remove them from the glove box to test them without exposing them to an oxygen atmosphere.

Most active layers showed definite signs of agglomerates breaking through the polymer layer which lead to the devices acting as resistors, however all the active layer that had CNT in them, even the layers that did not appear to have a large amount of agglomerates turned out to be resistors. For the last device, a solution of MEK and CNT was sprayed onto the substrate with an atomizer and then a pure polymer in chlorobenzene was spun to make a heterojunction. This device also turned out to be a resistor, but this method showed the best promise for depositing a uniform thin film of CNT onto the substrate.

**C. Aluminum Electrode Fabrication**

After the active layer was spun on, the device was placed in a blank mask so as to cover the entire device with LiF. The device was placed in the evaporation chamber, pumped down to \( \sim 2 \times 10^{-6} \) Torr, and 20 angstroms of LiF were evaporated onto the device. After the chamber was brought back to atmospheric pressure, the device was placed in a new mask, so as to overlap four squares of ITO. The chamber was pumped back down to \( \sim 2 \times 10^{-6} \) Torr and 600 angstroms of aluminum were evaporated onto the device.
VI. Characterization

Three techniques were used to characterize the structure and behavior of our solar cells: atomic force microscopy, absorption spectroscopy, and IV measurements of the completed devices. AFM was used in determining the properties of our carbon nanotube film. The images provided information on the morphology of the nanotube layer and gave a rough idea of the average nanotube dimensions. The absorption behavior of the polymer and the nanotubes were analyzed using absorption spectroscopy over wavelengths ranging from 200nm to 3000nm. Finally, the IV characteristics of the fabricated devices were measured in darkness and under illumination with a source that simulates the solar spectrum. The response of the devices under illumination ultimately allows for the determination of the short circuit current, open circuit voltage, and the efficiency.

A. AFM

Carbon nanotube films were prepared for AFM characterization by spin coating a nanotube suspension onto glass substrates using a series of spin parameters that match those used in device fabrication. The spin parameters appeared to have little effect on the spatial distribution of the nanotubes, and large agglomerates were frequently observed on all samples. Figure 12 shows two images that are representative of the film.

![AFM images of the spun carbon nanotube film. Images are 5um x 5um.](image)

The agglomeration presents a major problem because it is believed that they are responsible for short-circuiting the solar cell. This behavior may be a result of the solvent used to suspend the nanotubes. In addition to the agglomerates, a fine network of nanotubes is visible across the surface of the substrate, which would be beneficial for charge transport in a real device. If the nanotubes form a percolation path that can quickly transport separated charges to an electrode, the solar cell will be more efficient.

B. Absorption Spectroscopy

Absorption spectroscopy was performed on films of pure polymer, pure carbon nanotubes, and a mixture of the two on quartz substrates. Measurements were taken over
an interval of wavelengths between 200nm and 3000nm, and the spectra were normalized by dividing out the response of a blank quartz substrate. Any abrupt discontinuities in the graphs are most likely due to switching between various light sources and photodetectors, since no single light source or photodetector functions over the entire range of wavelengths measured. Figure 13 shows the results of the absorption spectroscopy.

Note that the polymer only absorbs in a relatively small region with a peak value near 400nm. At longer wavelengths, absorption is negligible within the polymer. The results for the pure nanotube film and the mixture are difficult to interpret. The nanotube films tend to form very rough surfaces, which can cause light to scatter. Scattered light will not reach the photodetector, and it will appear as though the film is absorbing more light than it actually is. The nanotubes do absorb light at longer wavelengths although it is difficult to quantify\textsuperscript{20}. The results for the mixture are similar to the pure carbon nanotubes in that scattering is most likely causing elevated absorption measurements. Note that the absorption peak of the polymer is present at the mixture at lower wavelengths and it closely matches the results of the pure polymer.

![Normalized absorption spectra](image)

**Figure 13:** Normalized absorption spectra for the polymer, nanotubes, and mixture.

### C. IV Measurements

A characteristic IV curve for a pure polymer devices can be seen in Figure 14. Note that the device functions as a light emitting diode, allowing high currents under forward bias, and little to no current for reverse bias. At around 0.8 mA or greater light emission,
caused by electrons and holes recombining, was observed from the diode. The slightly different IV curves for the four devices are likely caused by the differing active area for the devices with the higher currents corresponding to the devices with larger areas. While both light and dark currents were measured, there was not a noticeable difference between them. This is to be expected since almost all excitons that are created radiatively recombine due to the lack of a junction.

A pure CNT device was also fabricated and its IV characteristics can be seen in Figure 15. The device acted as a resistor with a resistance <350Ω. This is to be expected since CNTs form a direct contact between the two electrodes, essentially shorting the device. The resistance seen likely comes from the LiF and PEDOT resistive layers. While light and dark measurements were taken, they were essentially identical, because no interfaces were present to dissociate the excitons into free charges which could be separated and collected at the electrodes.

Several CNT polymer blend devices were constructed. However, all of the devices were short-circuited and behaved like resistors. This problem is believed to be caused by the agglomeration of CNT. Several techniques were tried to solve this problem and are discussed elsewhere in this paper.

![Pure Polymer #3 IV Curves](image)

**Figure 14**: Pure polymer device IV curve. Light emission was observed at currents of 0.8 mA.
VII. Conclusion

The design of these components came from background knowledge that we spent a considerable amount of time collecting. Previous literature on the topic of organic solar cells provided helpful information and directions for our project. We looked to extend the well studied trend of using C60 “bucky” balls in the polymer to using carbon nanotubes. We developed a basic model that we felt would produce the best possible efficiency if we were able to place the materials in exact locations within the device. This model is simply a theoretical proposal; there is still work to be done mathematically and experimentally to verify if even our basic modeling assumptions were accurate. While we were designing an essentially optimal device, we were also working to create an operational device in the lab. Many devices were created using everything from pure polymer to pure nanotubes and many mixtures of the materials. While we were unable to produce a non-shorting device we feel reducing the concentration of nanotubes and restricting nanotube agglomeration will lead to fewer shorts. Overall, we were able to theoretically design a device, apply some of our theories within the lab, develop a recipe for fabrication, characterize a series of devices, and develop some theories for how we could improve the process in the future.
VIII. Future Work

Due to time constraints, we were not able to accomplish all that we would have wished. We would try to change the CNTs that we are using. First, we would switch to single-walled CNTs of varying small diameters (0.8 – 2 nm) to get high absorbance coefficients that match the solar spectrum. These CNTs should also be functionalized to improve their solubility. Ideally, they should be functionalized with the monomer of MEH-PPV-CN to allow them to be fully dissolved and dispersed in the polymer matrix. Good dispersion is key being as we believe our solar cells did not work because CNT agglomerates were shorting the device. Finally, if possible, we would pattern our substrate in such a way that would cause the CNTs to vertically align with the correct spacing to achieve our ideal device structure. Several techniques to vertically align CNTs have been published\textsuperscript{14}, but they appear to be beyond the capabilities of the available facilities.

Once we have a working device, there are a number of other design considerations that will need to be addressed. They included upscaling the process to make large sheets of cells and packaging issues such as anti-reflective coatings and encapsulation to protect the sensitive organics from the environment. These can largely be accomplished by well-understood industrial processes that are currently available.

There exist some experiments that still need to be run. The first of which would be to optimize the device thicknesses to get the maximum amount of photon absorption in order to promote exciton generation. Compartmentalization will also be a key issue with the final device. It will be important to have the cells physically separated so that exposure of one cell to the atmosphere does not jeopardize adjacent cells, and the appropriate size of those individual, discrete cells would need to be determined. It might also be worthwhile to take a closer look at methods for layer generation. While we looked primarily at spin coating, other methods of applying the polymer/CNT layer exist, such as atomization and wet processing (e.g. Lanmuir-Blodgett or similar deposition).

IX: Acknowledgements:

Laboratory for Physical Sciences
Zyvex Corporation
Erin Flanagan and Dr. Ray Phaneuf
References


