Organic Solar Cells
Enhanced by Cadmium Sulfide Nanoparticles
and a Carbon Buckyball Derivative (PCBM)

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Abstract

Organic solar cells (a.k.a. organic photovoltaic cells, OPVs, polymer solar cells) offer a promising approach to inexpensive, lightweight, flexible, and environmentally friendly devices that can convert sunlight into useable electrical power. Major challenges in developing organic cells at the current stage include low power conversion efficiency (standing laboratory record a maximum of 6% in literature compared to a typical 15% efficiency of commercial polycrystalline Silicon solar cells), polymer degradation especially in ambient air and humidity in the presence of light, and relatively low mechanical durability.

My research focuses on the fabrication and characterization of conjugated polymer solar cells incorporated with nanoscale structures, such as Carbon nanotubes, Cadmium Sulfdide nanoparticles and Carbon Buckyballs (e.g. PCBM). The incorporation of certain nanostructures has proven to enhance exciton dissociation and charge transport utilizing their high surface-area and unique electrical properties (i.e. high mobility, semiconductivity). Key factors including the type of nanomaterials, treatments, geometry, and concentration in the polymer matrix were studied. Relationships between these factors were established in terms of different facets of cell performance (e.g. power conversion efficiency, fill factor, Voc, Jsc, internal losses). Results showed that Cadmium Sulfdide nanoparticles independently enhance Voc, and PCBM nanoparticles enhance Jsc. It was also shown, however, that these two materials cannot work together to augment both values in tandem. They do, in fact, impede each other’s abilities to enhance organic solar cells.

I will be presenting background information on organic photovoltaics, current status of the field, and my research at the Hawaii Nanotechnology Laboratory and Hawaii Natural Energy Institute's (HNEI) Thin Films Lab on improving specific aspects of performance of bulk-heterojunction solar cells based on poly(3-hexylthiophene) (P3HT), a conjugated polymer, embedded with nanomaterials like Carbon nanotubes, Cadmium Sulfdide nanoparticles and Carbon Buckyballs.
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Abbreviations

η Efficiency
A Amps
AFM Atomic Force Microscopy
Al Aluminum
CdS Cadmium Sulfide
CdTe Cadmium Telluride
CNT Carbon Nanotube
CPV Concentrator Photovoltaic
E Irradiance
FF Fill Factor
HCL Hydrochloric Acid
HNEI Hawai’i Natural Energy Institute
HNL Hawai’i Nanotechnology Lab
I, J Current (in Amps)
Io Photoinduced Current
Is Saturation Current
ITO Indium Tin Oxide
I-V, J-V Current - Voltage
Jm Current at Pm
Jsc Short-Circuit Current
MWCNT Multi-Walled Carbon Nanotube
n Ideality Factor
ODA Octadecylamine
OPV Organic Photovoltaic
P Power
P3HT poly(3-hexylthiophene)
PCBM [6,6]-phenyl-C61-butyric acid methyl ester
PEC Photoelectrochemical Cell
PEDOT:PSS Poly(3,4-ethylenedioxythiophene) poly(styrene sulfonate)
Pm Maximum Power
Rp Parallel Resistance
rpm Rotations per Minute
Rs Series Resistance
SEM Scanning Electron Microscope
SMU Source Measuring Unit
SWCNT Single-Walled Carbon Nanotube
TCO Transparent Conductive Oxide
TFL Thin Films Lab
THF Tetrahydrofuran
V Voltage, Volts
Vd Voltage Across Diode
Vm Voltage at Pm
Voc Open-Circuit Voltage
Vt Thermal Voltage
W Watts
wt% Weight Percentage
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Chapter 1
Introduction

Organic solar cells (a.k.a. organic photovoltaic cells, OPVs, polymer solar cells) offer a promising approach to inexpensive, lightweight, flexible, and environmentally friendly devices that can convert sunlight into useable electrical power. Nanomaterials such as Carbon nanotubes, Cadmium Sulfide nanoparticles and Carbon Buckbyalls embedded in the active layers of these cells can increase performance of these polymer solar cells.

1.1 - Motivation

Currently, the solar power market is dominated by polycrystalline Silicon solar cells that are robust, well proven, durable and reliable. Silicon solar cells, however, suffer from high cost, bulk (requiring costly support), and potentially hazardous fabrication processes[1]. Silicon solar cells also have a theoretically thermodynamic maximum power conversion efficiency (for a single junction device) of 31%[2, 3, 4]; a ceiling that real solar cells are already approaching.

1.1.1 – Inequities of Current Commercial Technology

Silicon solar cells are not going to get much cheaper in the long run. While Silicon is abundant, high quality Silicon is expensive to produce, and the market for that quality is dominated by the computing industry. Novel crystal growth methods are currently producing and improving cheaper polycrystalline Silicon solar cells as well as amorphous Silicon solar cells that, while reducing cost, do not perform as well as their high-quality brothers. Silicon has an inherent problem in that it has low light absorption
which requires thicker layers in devices. This weakness is slightly balanced by the high
charge mobility in Silicon, but the problem limits the abilities of Silicon as an energy
converting material[5]. There is a demand for an alternative solar-to-electricity energy
conversion device.

1.1.2 – Advantages and Disadvantages of Organic Photovoltaics

Deposition methods used to produce polymer solar cells are cheap, simple, and
most importantly, scaleable. For example, there is the possibility that one day, polymer
solar cells can be produced reel-to-reel on flexible substrates, magnitudes faster and
representing fractions of the weight of an equal area of Silicon solar cells can be.
Polymer deposition techniques like spin casting, inkjet and screen printing are well
understood through other similar applications and can be almost directly applied to
semiconducting conjugated polymers[1].

Major challenges in developing organic cells at the current stage include low
power conversion efficiency (standing laboratory record a maximum of 5% in
literature[3] compared to a typical 15% efficiency of commercial polycrystalline Silicon
solar cells[2]) due mainly to low charge mobility[3], polymer degradation in ambient air
and humidity in the presence of light, and relatively low mechanical durability[6].

It has been proposed that while organic photovoltaics (OPVs) may not fill the
same need as traditional inorganic solar cells for large scale power, OPVs may be more
useful in smaller applications where lightweight, flexible solar cells are ideal. For
example, niche applications like solar cells built into clothing or bags[7]. OPVs can also
take advantage of the fact that heat can actually improve performance[8, 9], unlike
inorganic solar cells that react poorly to heat. This particular characteristic of OPVs
could find practical use in Concentrator Photovoltaic (CPV) systems where sunlight is concentrated with mirrors (usually in parabolic arrangements) onto a solar cell so that a cell can be illuminated by more than one sun. Because of the higher light intensity, the solar cell will heat up rapidly causing problems in inorganic cells, but can potentially be beneficial for OPVs[7].

1.1.3 – Incorporation of Nanotechnology

Power conversion efficiency has in the past been improved with the incorporation of nanomaterials, able to uniformly disperse in layers of polymer thinner than the diameter of a piece of dust[10]. These nanomaterials can provide percolation pathways for charges to more easily reach their desired electrode for practical output power. A unique problem nanomaterials pose, however, is their tendency to agglomerate due to high van der Waals forces between them[11].

Of immediate interests were Carbon nanotubes (CNTs); self assembling structures of Carbon atoms forming tubes resembling rolled graphite sheets. CNTs (while offering high theoretical strength, chemical stability and mechanical stability) exhibit very high conductance, high surface area, and sometimes even semiconductivity. Percolation paths of high-aspect ratio CNTs could remedy the low charge mobility inherent in conjugated polymers by providing more dissociation sites (due to high surface area) and better conduction once charges have been dissociated (due to high conductivity or tunable semiconductivity)[11, 12, 13, 14].

Also of interest is a Cadmium Sulfide (CdS) nanoparticles that is inherently n-type semiconducting. CdS films and particles have long been used as an n-type semiconductor in Cadmium Telluride-Cadmium Sulfide (or Cadmium Selenide) pn-
junctions for thin film solar cells [2, 12, 15]. Pn-junctions made with CdTe/CdS thin films have exceeded 15% conversion efficiency at AM1.5[4, 16, 17]. The conjugated polymer used in this study, poly(3-hexylthiophene) (P3HT), is inherently p-type semiconducting. The combination of the two produces what’s called a bulk-heterojunction solar cell; meaning the two different materials are mixed together to make a bulk composite containing dispersed junctions throughout the active layer (compared to a Silicon-Silicon homojunction structure). Bulk heterojunctions can also be created using polymer/polymer blends in which each polymer has different characteristics to create numerous junctions throughout the bulk of the material[1, 18].

One of the most interesting and widely used nanostructure in organic photovoltaics is a Carbon Buckyball derivative called “[6,6]-phenyl-C$_{61}$-butyric acid methyl ester”; or PCBM or Methanofullerene for short. PCBM is a functionalized Carbon Buckyball, meaning it’s been altered to include a side chain in place of one of its carbon atoms. This side chain allows PCBM to be easily dispersed in solvents like Chloroform, used here in this project. PCBM has very interesting electrical properties that, when paired with its high surface area, allow it to very strongly separate bound exitons in a polymer solar cell allowing more useable power to be extracted [19, 20, 21, 22, 23].

1.2 - Thesis Scope

This particular project focuses on the fabrication and characterization of conjugated polymer solar cells incorporated with nanoscale structures, such as Carbon
nanotubes, Cadmium Sulfide nanoparticles and Carbon Buckyballs. The incorporation of these types of nanostructures has proven to enhance exciton dissociation and charge transport utilizing their high surface-area and unique electrical properties (e.g. high mobility, semiconductivity). Key factors including the type of nanomaterials, concentration, and dispersion in the polymer matrix will be discussed.

Relationships between these factors and cell performance (e.g. power conversion efficiency, stability) will be established based on an equivalent circuit revealing sources of power conversion, power output, and power loss. The results should help clarify the role of each nanomaterial in developing organic solar cells.

I will be presenting research done at the Hawaii Nanotechnology Laboratory and Hawaii Natural Energy Institute’s (HNEI) Thin Films Lab on exploring power conversion and internal losses of bulk-heterojunction solar cells based on poly(3-hexylthiophene) (P3HT), a conjugated polymer, embedded with nanomaterials like Carbon nanotubes, Cadmium Sulfide nanoparticles and Carbon Buckyballs.
Chapter 2
Cell Fabrication and Testing

The fabrication of each solar cell is accomplished by successive depositions of polymers AND metal (Aluminum) on glass slides coated with Indium Tin Oxide (ITO), a transparent conducting oxide (TCO). Each deposited layer is on the order of 100 nm, so care must be taken in cleaning bare slides and keeping slides clean between each deposition. The estimated size of just coal dust (typically one of the smaller diameter particles possibly encountered) is 1-100 μm [10], meaning even the smallest of these are already as thick as some of the layers deposited. The consequences of such contaminations are visible to the naked eye during different deposition steps. Figure 2.0.1 shows the final cross section. This figure will be referenced often.

Figure 2.0.1: Cross Section of complete cell. ITO coated glass is purchased as is (besides etched portion on left edge). The glass provides a mechanical substrate and the ITO layer serves as the transparent positive electrode through which light is shown. The Poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate), or PEDOT:PSS, is an electron blocking layer that absorbs a negligible amount of light and also improves adhesion of the Active Layer[25]. The Active Layer is the light absorbing layer where photons excite excitons. The Aluminum layer serves as the negative electrode.
Each step presented itself with numerous problems and many solutions were explored throughout the process of developing the final procedure. These problem areas will be noted as each step is discussed.

2.1 – Substrate Preparation

The first step in the fabrication of each cell is preparing the as bought substrates, ITO coated glass slides (1x3 inch, 15-25 Ω/sq, Sigma-Aldrich #636916). The 3 inch slides are cut into 3 1x1 inch slides for two reasons. First, the spin coating process (for PEDOT:PSS and Active Layers) works best with symmetrical substrates (preferably circular, but that was not an option). Second, the masks that were available to me for the deposition of Aluminum are 1x1 inch square.

Next is the etching of the ITO to provide a nonconductive surface on which one of the electrodes could be placed onto the final cell without shunting through the entire device. The left side of Figure 2.0.1 shows the area where the ITO has been etched off. The final films are so thin and fragile that even the touch of a flexible tip electrode on a spring loaded micropositioner would pierce all the layers and contact the ITO. It was necessary to provide a surface to contact only the Aluminum and NOT the ITO at the same time.

To etch only a strip of each substrate, masks were made with typical off the shelf clear box tape (anything that can resist Hydrochloric Acid for 1 hour) to expose only an approximately 3/8 inch strip along one edge to protect most of the ITO film from the acid. The exact width of the strip is unimportant because active areas later used in the calculation of current densities were measured individually for each cell. Through trial and error it was discovered that the best way to accomplish this masking was to tape the
entire surface, gently using a razor blade to cut across the tape 3/8 inch from an edge (the ITO can be scratched by a razor blade, leading to problems later), and removing the 3/8 inch strip to expose only that area of the substrate. Through this entire process an ohm meter was used to test after at least 2 different steps to make sure the conductive side (ITO) was being masked (instead of bare glass).

Finally, each substrate is scribed (batch # and substrate letter) for identification and placed in ~8M Hydrochloric Acid for approximately 1 hour. It is visibly apparent whether or not ITO still exists so after 1 hour, a visual inspection would determine whether more time was needed. The 8M HCL was continuously recycled with periodic tests with pH indicators, but sometimes it got weak between tests and so a little more time was needed (and concentrated acid added to my recycled volume to strengthen it). Whenever there was doubt, the ohm meter could be used to determine if the ITO had been completely etched. The etched substrate will then look like Figure 2.1.1.

![Figure 2.1.1: Top view of etched substrate.](image)

After the etching process, substrates are doused in copious amounts of dissolved baking soda to neutralize acid, and then copious amounts of tap water, followed by a few
rinses in de-ionized water. The tape was removed, making sure no sticky residue remained (blotting with clean tape worked great to remove these residues), and each substrate was rinsed again in de-ionized water to thoroughly remove any acid that may have been left.

Substrate cleaning is of the utmost importance and great care was taken with each. First each substrate was hand scrubbed on both sides with an Alconox soap solution and a Kimwipe followed by a thorough rinse in water then de-ionized water. Then the substrates were sonicated in acetone under a hood (to keep acetone fumes out of the lab breathing space), followed by a clean acetone rinse. Subsequent sonication in ethanol and a clean ethanol rinse removed the acetone residue. Finally a sonication in de-ionized water completed the cleaning process. From this point forward as many precautions were taken to keep the substrates free from any dust, oil, or any other contaminant. A dropped substrate must go through the entire cleaning process again or spin coating will result in an uneven film with the possibility of bare spots which will render a solar cell completely useless.

### 2.2 - Spin coating

After substrate preparation, the deposition of the polymer films is accomplished by spin coating. The spin coater I used is a Headway Research Model PWM32 (shown in figure 2.2.1) which uses a vacuum chuck to hold a substrate in place while it spins the substrate up to 8,000 rpm. The controller accepts "recipes" that control the acceleration rate, final speed, and duration of any held speed with the flexibility to implement many steps.
The polymers are dissolved in solvent (water, Chloroform, and in earlier trials, toluene), dripped onto the stationary substrate completely wetting the entire surface (failure to do so results in spider web spreading of the solution and very uneven films), and then the substrate is spun according to the recipe. When the substrate begins accelerating, the fluid will spread from the center out spinning excess solution off and the fluid layer will reach an equilibrium thickness based on the speed of the substrate and viscosity and evaporation rate of the solution. Because the film reaches thicknesses on the order of 100 nm, the solvent evaporates very quickly.

2.2.1 - PEDOT:PSS Deposition

The first step on the spin coater is actually for further cleaning of the substrate. To remove any dust particles that may have fallen onto the substrate since the full
cleaning, I spun a substrate at 5000rpm and sprayed it with ethanol from a bottle. When the ethanol was spun off and evaporated (the colors were an indication of this), it was sprayed with de-ionized water and left spinning until the water was spun off and evaporated.

At this point the substrate was removed from the spin coater and a small strip of ordinary scotch tape was placed inside the etched area of the substrate (covering most of the bare glass, but leaving as small a strip of it as possible exposed) which will preserve the non-conductive area (remember, PEDOT:PSS is a conductive polymer). Then the masked substrate is placed back into the spin coater and coated with two depositions of PEDOT:PSS diluted by an equal volume of de-ionized water at 3000rpm (accelerated at 1000rpm/s) for 60s.

The as-bought PEDOT:PSS proved to be a little too viscous to spin coat an even layer and the dilution made it work wonderfully. At first, only one layer of PEDOT:PSS (as will be discussed, one layer of P3HT as well) but found that adding a second layer greatly improved the repeatability of successful cells (this fabrication process produces many non-functioning cells). Contrary to what might be expected, adding a second layer to an already existing layer did not result in a doubling of the thickness of the film, but instead the thickness remained the same because the solvent in the second deposition would dissolve the first layer and the remainder would recombine into a more uniform layer of the same thickness. Deposition speed and duration were chosen from common procedures in literature [10, 20, 24].

After removal of the scotch tape mask, the samples are then vacuum annealed at 120°C at <25mmHg vacuum in a vacuum oven (shown in figure 2.2.2) for 10 minutes, as
suggested by literature [10, 20, 24], to drive off any remaining water. This is an
important step because P3HT (deposited later on top of PEDOT:PSS) readily degrades in
the presence of water vapor [3].

Figure 2.2.2: Vacuum Oven used to anneal polymer layers.

2.2.2 – Active Layer Deposition

Deposition of the active layer (P3HT combined with a variety of enhancements
like Carbon nanotubes, Cadmium Sulfide nanoparticles, PCBM) is accomplished in much
the same manner as the PEDOT:PSS layer, except without the scotch tape mask. P3HT
has such a low carrier diffusion length that a layer under the Aluminum pad will not
affect the operation of the cell (the active area is only where the active layer is
sandwiched between two conductors). In previous experiments the active layer was
masked as well, but the Chloroform in my solution would partially dissolve the tape
making for an unnecessary mess; the step was eliminated.
The basic P3HT (comes in solid pellets) is dissolved in Chloroform with a 10mg:1mL (P3HT:Chloroform) ratio [12, 14]. Care should be taken in doing this as quickly as possible to avoid exposure of P3HT stock to ambient air. After opening a bottle only four times (even followed by an Argon “wash” to try and fill the bottle with an inert atmosphere), the remainder of the bottle was oxidized and did not function. The poor stability of conjugated polymers (i.e. P3HT) resulted in difficulties with handling and storage for experimentation. One of the downfalls of studying such an exotic substance is that its properties are largely uncharacterized and I had to learn them the hard way, by trial and error. Because of the exposure limitations, larger batches were made at a time because the P3HT seemed to last longer in solution. The color of the solution would change from a brilliant translucent and fluorescent orange to a dull opaque brown shortly before samples made with it became unresponsive to light (these samples would still show diode behavior).

After weighing out and mixing the parts of the solution (P3HT, Chloroform and any enhancement), the solution was ultra-sonicated for at least 30 minutes. Bottles with plastic chemical resistant seals in the caps must be used because the Chloroform vapor will dissolve the glue in the cardboard seal in cheaper caps and the vapor will leak out. This is detrimental to both storage safety issues and the valuable contents of the bottle (dry P3HT will be exposed to ambient air).

After sonication, the solution was spin coated onto the annealed and cooled substrates (now with a thin layer of PEDOT:PSS), again with two layers, for 20s at 1000rpm with a 1000rpm/s acceleration rate[11]. The duration was shortened (compared to the PEDOT:PSS deposition) because Chloroform is much more volatile than water and
evaporates much quicker. The color change is quite dramatic and happens within about 3 seconds turning from the translucent fluorescent orange of the solution to a solid, dark reddish purple. From this point on, every sample is kept in the dark as much as possible and no more than 6 samples at a time were spin coated before the batch was transferred to a glass vacuum vessel for any further storage before annealing. I developed these procedures to try and eliminate as many variables as I could by exposing the active layers to not just as little light and ambient air as possible, but exposing each sample to the same amount for proper comparison.

2.2.3 – Vacuum Annealing

After both films were spin coated (usually in batches of 12 substrates), all the samples were vacuum annealed at 120°C at <25mmHg vacuum in a vacuum oven for 5 minutes [10, 20, 24]. The samples were then transferred to a glass vacuum vessel (figure 2.2.3) for storage overnight. Previous tests had been done making samples the night before final Aluminum deposition and testing compared to making samples immediately before final Aluminum deposition. It was obvious that cells performed better when stored under vacuum (always in the dark) overnight. It is possible that there are still trace amounts of water or Chloroform left from the spin coating processes, however vacuum annealing for longer than the times I settled on to attempt to remove these trace amounts resulted in decreased cell performance.

The vacuum oven, a recent addition to our lab, drastically improved the repeatability of this fabrication process. It has been shown that different annealing procedures change the morphology of the polymers, and can be tuned accordingly for
desirable results[26]. It has also been shown by AFM that thermal annealing improves the bonding of PEDOT:PSS to the active layer (in my case P3HT)[27]. Prior to the use of the vacuum oven, experiments with inferior annealing techniques including inert air (Argon) and vacuum annealing in glassware resulted in a lot of variability and only some sporadic improvements. I did have some success with a “vapor annealing” procedure in which the substrates are suspended in a Chloroform vapor for a period of time[22, 28]. The process was being used in an attempt to reduce cost, complexity and temperature of device fabrication (temperature because it could allow the use of some flexible substrates with low melting points). The process usually improved performance, but repeatability was difficult. The process was very hard to control (the entire process had to be in an Argon atmosphere), and also rather dangerous (Chloroform is an inhalation and extreme fire hazard). The vacuum oven became an indispensable piece of equipment in this fabrication process.

Figure 2.2.3: Glass vacuum vessel in cabinet for storage of samples overnight. Ambient air and light both contribute to degradation of the active layer.
2.3 – Aluminum Deposition

The final fabrication step is the thermal evaporation of Aluminum onto the cell, creating the negative electrode (the ITO is to positive electrode). This process is carried out at the Hawai`i Natural Energy Institute’s (HNEI) Thin Films Lab on a machine called a thermal evaporator (figure 2.3.1). A thermal evaporator is used to thermally melt various source metals (Aluminum in my case) in a high vacuum \((-1 \times 10^{-7} \text{ torr})\). Under such high vacuum, when the Aluminum evaporates it has a very high mean free path, meaning it can go a long way before colliding with anything (like ambient air particles) and losing its energy. By putting the substrates in this path, the hot, vaporized Aluminum will condense onto the substrates forming a thin film. A metal mask blocks the Aluminum from coating the areas under it. The specific masks used were designed to deposit 4 separate pads onto each substrate resulting in 4 separate devices on one 1 inch square substrate.

Figure 2.3.1: Thermal Evaporator at HNEI Thin Films Lab (TFL)
Aluminum behaves very uniquely in this scheme. Unlike most metals, the deposition rate (and therefore the final film thickness) is difficult to control, but final thickness can be measured later with a profilometer (figure 2.3.2). Typical metals will melt into a puddle in a Tungsten boat and deposition can be controlled down to a few angstroms/second for a deposition lasting a many minutes, depending on the desired thickness. Aluminum, on the other hand, doesn’t like to puddle (it spatters). Instead, a twisted Tungsten wire coil is used to melt the Aluminum and the molten metal is drawn into the twists by capillary action where it will stay for only a matter of seconds before dripping off the heating element (and uselessly cooling and solidifying). What must be done to get a good sized film then is to watch very closely as the element heats up and the moment the metal melts (the filament will go dark as it instantly cools from the liquid), the power must be pumped way up to achieve a flash evaporation. Typical deposition rates rise quickly to a maximum of around 200 angstroms/second and then quickly drop (as the Aluminum is either flash evaporated or drips off the coil) for a deposition time of around 20-30 seconds.

Figure 2.3.2: Profilometer used to measure thicknesses after depositions.

After the deposition of Aluminum, the solar cell is complete and ready for testing, shown in figure 2.3.3.
Figure 2.3.3: Two finished solar cells. Dark polygons are Aluminum pads defining 4 devices on each substrate.

2.4 – Testing

Testing is accomplished through the use of a Keithley 238 High-Current Source-Measure Unit (SMU) and an Oriel Solar Simulator (at AM1.5, 100mW/cm², figure 2.4.1). SMUs are devices capable of sourcing or measuring current and voltage simultaneously. The solar simulator consists of a housed Xenon lamp with mirrors and lenses that columnnate the light to illuminate an 8x8 inch area uniformly. Filters are used to tune the beam to as close to the typical spectrum natural sunlight as possible. The equipment for testing is also at HNEI’s Thin Films Lab.

The geometry of the cells requires that they be bottom illuminated (with reference to fabrication orientation), meaning light is shown through the clear glass substrate which has negligible absorption. For testing the cells are inverted so that the bottom is facing up, and contacts are connected underneath the cell (to ITO and Al electrodes, as shown in figure 2.4.2). Cell performance is given by the SMU (controlled by a computer running LabView), used to measure current output for a given voltage.
Figure 2.4.1: Oriel Solar Simulator (at AM1.5, 100mW/cm²), 8"x8" area of columnated light.

Figure 2.4.2: Testing setup illustrating bottom illumination (inverted cell with respect to fabrication orientation). Simulated light is shown from above through the clear glass substrate and the response to a given voltage (source) is measured in the form of output current (measure) by the SMU (Source Measuring Unit). Electrical Connections are made to the (+) and (-) terminals via micropositioners with flexible 2-probe tips. The SMU is controlled by a computer running LabView.
The results are plotted on an I-V curve (amps-volts). The area of each individual device is measured after testing so that current densities can be plotted and the normalized curves can be compared. Power curves are also plotted by multiplying the current and voltage, plotted against voltage. Figure 2.4.3 shows a typical family of IV curves with different light intensities.

![IV Curve Diagram](image.png)

Figure 2.4.3: Typical shape of IV curves tested under different light intensities. Note the \( J_{SC} \) (short circuit current where curve crosses y-axis) and \( V_{OC} \) (open circuit voltage where curve crosses x-axis). The flatness of the curve before \( V_{OC} \) and the steepness of the slope through \( V_{OC} \) are indications of a good solar cell.

The maximum power point occurs in the elbow of the curve where rising voltage and dropping current will reach a maximum. It'll rise as voltage goes up and current stays relatively constant, and then hit a peak before \( V_{OC} \) and eventually drop to zero. The sharper the elbow (resulting from a flat curve before \( V_{OC} \) and a steep curve through \( V_{OC} \),
the less internal losses there are within a cell. A more complete discussion of these properties will come later in section 2.5 – Analysis.

As mentioned before, each substrate has a total of 4 devices. Before testing, an ohmmeter is used to quickly determine if any of the devices have shunted, rendering them useless. A resistance of up to about 1kΩ indicates a shunt. Resistances above 1kΩ are sometimes still shunts, but an I-V curve is needed to determine this. Resistances on the order of 1MΩ usually perform very well.

Each device is measured in both dark and illuminated (AM1.5, 100mW/cm²). Typical voltage sweeps ran from -0.5V to 0.8V for pristine cells in 0.02V increments. Voltage sweeps for CdS samples were run from -0.5V to 1.5V because of the increased Voc. The dark curves show degree of diode behavior, the turn on voltage (open circuit voltage, Voc) and amount of rectification. The short circuit current of a good cell in the dark will be on the order of $10^7$ to $10^9$ A. A pristine cell (no enhancements) has a Voc between 0.1V and 0.7V, but varies a lot from bottle to bottle and from batch to batch. Samples containing CdS, on the other hand, have reached a Voc as high as 1.1V.

The electrodes are contacted with 2-point probes mounted on Signatone micropositioners which allow very fine movements and a gentle contact. The use of 2-point probes is useful because the resistance between the two points can be measured to ensure that good contact is made with the electrode surface. A small area of polymer must be scratched off to expose the ITO for contact.

More sophisticated tests on organic photovoltaics are usually carried out in inert atmospheres to minimize the effect of oxidation. A glove box with some sort of light exposure port (that will not further filter the incident light) is best for this procedure, but
this apparatus could not be incorporated into these tests. Successive tests on a single device showed steady losses in power conversion ability and tests done the following day on cells left in ambient air showed little to no photoresponse. The losses in performance are attributed to rapid degradation of the polymer in ambient air. However, even in a glove box, a loss of performance can be observed even within a few hours indicating other means of degradation (like light)[25]. Old cells do, however, maintain their rectifying (diode) behavior for a longer period of time.

2.5 - Analysis

Understanding of solar cell performance is greatly facilitated by its equivalent circuit [5], an analog circuit whose components each describe a certain aspect of charge transfer inside a solar cell. The simplest of equivalent circuits for a solar cell is the ideal case shown in Figure 2.5.1.

Figure 2.5.1: Ideal Equivalent Circuit for a solar cell
### 2.5.1 – Dark Current

In the dark, the current source will provide no current and the cell is simply a diode which "turns on" at a certain voltage. A simple analogy to help visualize a diode is a water valve that opens when a certain pressure (analogous to voltage) is reached in one direction, but prevents the flow completely (in the ideal case) in the opposite direction. The typical equation to describe this process is given by the exponential shown in equation 2.5.1 and the I-V curve of this equation (which is the dark response of figure 2.5.1) is shown in figure 2.5.2.

\[
I = I_s (e^{V/nV_t} - 1)
\]

**Equation 2.5.1**

- \( I \): output current
- \( I_s \): saturation current (typically \(10^{-10}\))
- \( V \): output voltage
- \( n \): ideality factor (often assumed to be 1)
- \( V_t \): Thermal voltage (material property)

---

![Ideal Dark Curve](image)

**Figure 2.5.2**: I-V curve representing equation 2.5.1 with \(I_s=10^{-10} \text{A}\) and \(1/nV_t=25 \text{V}^{-1}\)
2.5.2 - Light Current

When the solar cell is illuminated, the current source in figure 2.5.1 is activated and the response becomes equation 2.5.2 and figure 2.5.3:

\[
I = -I_o + I_s(e^{V/nV_t} - 1)
\]

Equation 2.5.2: Output Current of Ideal Solar Cell. \(I_o\) = photoinduced current from current source in figure 2.5.1

![Comparison of dark vs. illuminated ideal curves](image)

Figure 2.5.3: Comparison of dark and illuminated curves with \(I_o = 30\text{mA}\). Also shows the power generated (P=VI) with the maximum occurring around 0.68V.

2.5.3 - Power and Efficiency

From the ideal illuminated curve it is easy to see that power rises linearly as voltage rises because the current response before the turn on voltage is nearly constant.
This in turn puts the maximum power point very near the elbow of the ideal illuminated curve and almost all the useable current and voltage can be utilized. If the irradiance on this idealized cell is $E$ (and the responses are assumed to be current and power densities), the efficiency of the cell is given by equation 2.5.3[2, 5, 29].

$$\eta = \frac{P_m}{E} = \frac{(FF)V_{oc} J_{sc}}{E}$$

Equation 2.5.3: Efficiency where $P_m$= maximum power density (W/cm$^2$), $E$= Irradiance (W/cm$^2$), $J_{sc}$= short circuit current (A) and FF= Fill Factor (discussed in next section).

If the irradiance in this particular idealized simulation is assumed to be the typical intensity of sunlight on earth at air mass 1.5 (a common standard average), $E=100\text{mW/cm}^2$. If $P_m=18.8\text{mW/cm}^2$ (from equation 2.5.2 and figure 2.5.3), the efficiency of this cell $\eta=18.8\%$, which is higher than the efficiency of a commercial polycrystalline solar cell (~15%)[2].

2.5.4 – Fill Factor (FF)

While efficiency is a very good indication of the quality, another very important property is the fill factor (FF) of a solar cell [2, 5, 29]. The fill factor is the ratio of the maximum power to the ratio of the product of the open circuit voltage ($V_{oc}$) and the short circuit current ($J_{sc}$), as shown in equation 2.5.4. These two quantities can be much better understood through a graphical representation shown in figure 2.5.4.

$$FF = \frac{P_m}{V_{oc} J_{sc}} = \frac{V_m J_m}{V_{oc} J_{sc}}$$

Equation 2.5.4: Fill Factor (FF) where $V_m$ and $J_m$ are voltage and current and maximum power.
Figure 2.5.4: Comparison of the rectangular areas representing $P_w$ (maximum power) represented by the striped rectangle and the product of $V_{oc}$ and $J_{sc}$ represented by the gray rectangle. The ratio of these two areas represents the fill factor is a good indication of internal losses in a solar cell.

The term “fill factor” makes much more sense visually because it is an indication of how much the maximum power point utilizes the available current and voltage in a cell. The short circuit current is the most current a cell is able to generate with a given light intensity and the open circuit voltage is the maximum voltage the device materials can provide. Anything less than those values are internal losses; even the small amounts lost in the curved elbow (instead of a sharp corner) while the diode turns on. In the ideal case, shown in figure 2.5.4, the fill factor is very high ($\approx 80\%$) and there aren’t many more improvements that could be made to this cell. When a more realistic case with internal losses is considered next, however, the FF becomes a very valuable comparison between different solar cells and sometimes a more definitive measure of quality than just efficiency.
2.5.5 – Internal Losses (Series and Parallel resistances)

A more realistic equivalent circuit (than figure 2.5.1) contains internal resistances as shown in figure 2.5.5. There are of course better, more complex circuits but this is the most complicated we'll consider here for our purposes because it describes a lot about what ails many organic photovoltaic cells. The addition of a series resistance (Rs) and a parallel resistance (Rp) models two different types of internal losses in a solar cell. Rs, like the name suggests, represents series resistances like contact resistances between layers, lateral collection resistances across the ITO film, and even the contact resistances to the electrodes (although the 4-probe setup will eliminate most of this resistance during testing, a practical setup would include that contact resistance).

![Figure 2.5.5: A more realistic circuit (than 2.5.1) with Rs= series resistance and Rp= parallel resistance. For calculations the term Vd has been added which represents the voltage across the diode (and in turn, Rp).](image)
Rp, on the other hand, represents shunt currents and any sort of bypassing or parasitic currents that go directly to ground across Rp (according to Vd) instead of making it to our external circuit (labeled V in figure 2.5.5).

Through some circuit analysis, equation 2.5.2 becomes equation 2.5.4, which includes Rp. The only difference in the equation is the current lost to Rp represented by V/Rp which will shunt some of Io to ground. Equation 2.5.5 shows what happens when Rp is added to the circuit. It divides the voltage in the circuit so that only Vd, a portion of V, is seen at the diode affecting the exponential quantity. Combining equations 2.2.4 and 2.2.5 results in equation 2.5.6.

$$I = -I_o + \frac{V}{R_p} + I_s(e^{V/nV_t} - 1)$$

Equation 2.5.4: I-V response incorporating Rp

$$I = -I_o + I_s(e^{V_d/nV_t} - 1) = -I_o + I_s(e^{(V - IR_s)/nV_t} - 1)$$

Equation 2.5.5: I-V response incorporating Rs. Vd in the first equation corresponds to Vd in figure 2.5.5 across the diode.

$$I = -I_o + \frac{V_d}{R_p} + I_s(e^{(V - IR_s)/nV_t} - 1) = -I_o + \frac{(V - IR_s)}{R_p} + I_s(e^{(V - IR_s)/nV_t} - 1)$$

Equation 2.5.6: I-V response incorporating both Rs and Rp.

Of course, equations are often better represented visually to understand what is happening. Figure 2.5.6 shows the three equations above as well as the original ideal case, and figure 2.5.7 shows the corresponding power curves.
Figure 2.5.6: Overlays of I-V responses of equations 2.5.2, 2.5.4, 2.5.5 and 2.5.6

Figure 2.5.7: Overlays of the power curves of figure 2.5.6
It is apparent how internal resistances rob a solar cell of output power. The addition of both a series resistance (in these models, Rs = 5Ω) and a parallel resistance (here Rp = 100Ω) consumes about one-third of the power of an ideal solar cell. Visualize the maximum power rectangles like in figure 2.5.6 (the quantity V_{oc} x J_{sc} remains relatively constant in each calculation) and imagine how the FF will decrease as well.

2.6 - Conclusions

The entire fabrication process of each batch usually happened across three days. The materials required for a complete cell were ITO coated glass slides, PEDOT:PSS, P3HT, any enhancement materials (CNTs or CdS), Aluminum, and Chloroform. Other important materials needed for preparation were various cleaning and etching chemicals (Acetone, Ethanol, Hydrochloric Acid), and typical chemical lab materials like safety gloves and plastic/glassware.

The processing of the cells required a pretty small but vital set of equipment. First was the ultra-sonicator for mixing solutions thoroughly. Mechanical mixing is usually insufficient for nanomaterials. Next was the spin-coater for polymer deposition. There are other methods available like spray coating, inkjet printing, and sputter deposition, but the spin-coater was available, easy to use, and produced great results. Between spin-coating steps, the vacuum oven was an indispensable step to anneal the samples without exposing them to ambient air. It provided a much higher degree of repeatability in these experiments. Equipment I had to borrow time on at HNEI’s Thin Films Lab were the thermal evaporator, to deposit the Aluminum electrode, and the solar simulator connect to the SMU to test and analyze my cells.
Cleanliness was always the most important consideration at every step. The extremely small thickness of each layer required absolutely no dust, oil, residues (like tape), or even water droplets. Any one of those could potentially create a shunt through such thin and delicate layers. The smallest scratch would render most cells useless.

The next most important aspect was exposure. Too long in ambient air, most importantly in the presence of light, degrades the active layer polymer whether it be in a storage, in solution, or deposited on a substrate. Proper comparisons therefore required that every cell be exposed to as little light and ambient air as possible and that they all experienced relatively the same amount of each. Of course, the best way to deal with all of this would be to carry out the entire process in an inert atmosphere, but that was not an option here.
Chapter 3
Results

This chapter will show how the solar cells performed in terms of the equations, graphs, and equivalent circuits explained in Chapter 2. The immediate difference you'll find with my organic photovoltaic cells (compared to the simulations, based on polycrystalline silicon solar cells, in the previous chapter) is that the voltages are comparable, but the currents are magnitudes lower. This means the power outputs of these cells are nowhere near impressive, but these analysis tools identify aspects of the cells that can afford room for improvement. By taking small steps to try and improve specific aspects of the cells, it was established what types of enhancements affected what aspects of the solar cells in terms of the equivalent circuits and accompanying equations.

3.1 - Pure P3HT (Pristine) Solar Cells

Pristine solar cells (no enhancements) showed varying performance based on many factors. Efforts to stabilize these factors still resulted in a $V_{oc}$ ranging from 0.1V to 0.6V. $J_{sc}$ varied a lot but was always on the order of 1μA. Individual devices on a common substrate performed very similarly, as did devices made from the same batch of solution. Different bottles of P3HT (each bottle holds 1g of polymer) and different batches of solution (differing in age after a new bottle is opened) produced variations. Figure 3.1.1 shows how the I-V responses can vary with the same bottle of P3HT used two weeks apart. Interestingly enough, the voltage rises with age while the current drops. The combination, however, yields an overall decrease in both power efficiency and FF showing the importance of protecting the supply from light, oxygen and water vapor.
Unfortunately, upon starting the systematic study to finalize this project (discussed later in this chapter), the new bottle of P3HT I used performed at the low end of the spectrum. There was no alternative, regrettably because of material constraints, but the important part of the experiment was comparison. So despite the fact that it performed under par, it was consistently under par. It does, however, make a very good example of how different bottles perform differently as shown in figure 3.1.2.

After successfully fabricating working cells and developing a reliable procedure that produced repeatable results, the central part of this project began. As mentioned in the motivation section, nanoparticles are ideal candidates for organic photovoltaic enhancements because they have the potential to solve one of the largest drawbacks of these cells, low carrier mobility in conjugated polymers. The inherent scale of the cells,
usually using thicknesses on the order of 100nm, necessitates that any addition to the polymers either dissolve or have dimensions with the same order of magnitude.

![Graph: IV Curves - Pristine (2 different bottles of P3HT)](image)

Figure 3.1.2: Comparison of devices made with two different bottles of P3HT. Similar fabrication processes.

### 3.2 – P3HT-Carbon Nanotube Solar Cells

The first candidates for cell enhancements were carbon nanotubes (CNTs). The reason these were chosen was because work had already been done with them previously in other experiments (exploring both mechanical and electrical properties), and we could grow them at the Hawaii Nanotechnology Laboratory (HNL). The first problem with CNTs is the inherent difficulty of dispersion. They’re so small and have such a large surface area that they tend to aggregate together because of van der Waals forces between
them. The hopes were that the viscosity of the polymer (P3HT) might help to at least partially counteract these forces and allow dispersion. Also, unlike many other applications, a stable dispersion for only a short amount of time (on the order of 10 seconds would’ve been enough) was needed because the spin coating process would solidify them almost instantly after deposition.

3.2.1 – Typical Approaches

Attempts to wash our as-grown CNTs first with Hydrofluoric acid, to release them from the Silicon Dioxide wafers they were grown on, then with Nitric and/or Hydrochloric acid to further remove impurities proved fruitless. The as-grown loaves of CNTs would only fray at the edges releasing very few individual clusters. Ultrasonication between all combinations of steps in a variety of different solvents (Acetone, Ethanol, Chloroform, Xylene, and Toluene) could not break them apart so the as-grown CNTs were abandoned as candidates.

A second attempt was made with as-bought multi-walled CNTs (MWCNTs) from Sigma-Aldrich (#636487, >95% pure). They employ a growth method that doesn’t involve a substrate so they are already separated, but they will still aggregate. In solvent these MWCNTs would disperse in sonication, but quickly begin to aggregate once removed from agitation. Even with the smallest weight percentages I could use (limited by the sensitivity of our scale down to ~5mg), the MWCNTs produced fissures, pinholes and clumps in the spin coating process. Subsequent testing showed that every cell would shunt and show no photoresponse.
One of two things presumably happened, the first being that the CNTs are producing a percolation path as shown in figure 3.2.1. CNTs are very good conductors, and MWCNTs especially are all metallic in nature. They are also very robust so even a few percolation paths would probably be enough to sustain conductance at the low voltages I test at (<1.5V). Percolation is possible at a very low weight percentage (on the order of 0.02 to 0.1wt%) of CNTs in nanocomposites. The other possibility is that the aggregates created a cluster big enough to actually disrupt the surface such that spin coating didn’t completely cover the ITO/PEDOT:PSS surface and subsequent deposition of Aluminum created a shunt through a pinhole. Despite the cause, no solution to the shunting could be found.

![Figure 3.2.1: Creation of a percolation path through a network of Carbon nanotubes that electronically connecting the Aluminum (top) electrode to the ITO/PEDOT:PSS (bottom) electrode.](image)

Next on the list (both in availability and material cost) were single-walled CNTs (SWCNTs) (Carbon Solutions, AP-SWNT Batch #AP-204) of higher purity. Testing produced the same results as before. Although there was visibly less aggregation, every cell would shunt even with the smallest amount of CNTs added.
For another test, a sample of Octadecylamine (ODA) functionalized MWCNTs in Chloroform was used. The purpose of the functionalization was to allow the CNTs to uniformly disperse in solvent instead of agglomerate like untreated CNTs inherently do. If agglomerates could be avoided, perhaps this would solve the shunting problem. SEM imaging, however, showed that the MWCNTs were mostly destroyed in the process. These samples did not shunt, but did not perform well either (worse than pristine samples). It was after this point that more unorthodox procedures were delved into. Further tests in this direction would have required the use of more costly materials in a contradictory effort to produce cheaper solar cells.

3.2.2 – Novel Approaches

Consulting literature, success with CNTs dispersed in polymer resulted from ultra-high pure CNT samples and meticulous functionalizations. Both of which were appearing to be out of my reach so other avenues of deposition were pursued. The first try involved coating a pristine cell with an Acetone/CNT solution because Acetone dissolves P3HT very slowly (needs heat/sonication usually) so it was thought that maybe the pristine P3HT could act as a buffer layer preventing percolation. The Acetone would partially dissolve the P3HT to coat the top surface with CNTs. The process did not work, however, and the percolation theory was confirmed (because there was no way for there to be pinholes resulting from aggregation with a solid active layer in place). It can only be assumed that the Acetone still dissolved the P3HT just enough for a few CNTs to poke through and contact the bottom electrode.
The next and last attempt made with CNTs was an aerosol deposition. It was an attempt to use mechanical agitation (turbulent airflow) to separate the CNTs so that they were agitated until the moment they were deposited on a heated pristine cell. The heat was to make the P3HT tacky so that the CNTs would be partially embedded. The apparatus consisted of glassware and tubing, and the agitation was provided by compressed Argon. The cell was placed in a flask on a hot plate and different temperatures were attempted to find the lowest temperature that would allow the CNTs to stick to the surface. The exhaust of the process was bubbled through a large amount of water to prevent the release of the CNT aerosol. Further documenting this process is unnecessary because even at the lowest temperatures, getting the CNTs to just stick to the P3HT allowed them to penetrate through and shunt every cell.

While in theory, the addition of CNTs makes a lot of sense, mechanically they are extremely hard to incorporate into such a thin film. The dispersion problem of CNTs is quite possibly one of the largest reasons CNTs rarely perform up to their theoretical expectancies. A lot of research goes into functionalizing them overcome this problem, and as of yet all those processes are time consuming and expensive. If, perhaps, a process is discovered which enables cheap, simple and uniform dispersion of CNTs, organic photovoltaics would finally take their first steps towards commercialization because even now, the record 5% efficiency in organic photovoltaics incorporates a lot of cost. If the cost were driven down, 5% efficiency might be acceptable because it’s pretty rare that there isn’t enough roof space for a solar array. Area is not the limiting factor, it is cost.
3.3 – P3HT-Cadmium Sulfide Nanoparticle Solar Cells

A small sample of Cadmium Sulfide (CdS) nanoparticles was then tested as an enhancement. The sample was received dispersed in Tetrahydrofuran (THF), another solvent capable of dissolving P3HT. Initial qualitative experiments showed that the addition of CdS consistently increased the Voc almost twofold. While pristine cells would have a $V_{oc}$ between 0.1 and 0.6V, cells with CdS could reach 1.1V at open circuit and rarely dropped below 0.7V. It has been shown that unlike in pristine cells, where the $V_{oc}$ is usually dependant on the work function differential between the two electrodes, bulk heterojunctions get their $V_{oc}$ from the difference in work functions between the donor and acceptor materials[30]. In this case, P3HT donates electrons and CdS accepts them, indicating that the difference in work functions between P3HT and CdS is higher than the difference between ITO and Al.

For comparative purposes, I evaporated the THF and dispersed the CdS in my usual Chloroform/P3HT solution to rule out the influence of THF. The results supported the rise in $V_{oc}$ due to the addition of CdS.

3.3.1 – Cadmium Sulfide Supply

At this point, a systematic study on the effect of wt% of CdS in an organic photovoltaic cell was begun. Because of the variations between batches and between bottles, much larger batches were prepared at a time for comparison of many distinct variables at a time. These larger batches consisted of polymer used from the same bottle and solutions made all at the same time. From figures 3.1.1 and 3.1.2 showing performance differences with age and between bottles, it was obvious that these two
requirements must be met for a viable comparison of any sort. These requirements also required that all my CdS came from the same source.

A colleague at HNEI had a lot of leftover CdS from a chemical thin film deposition of CdS onto TCO/glass slides for photoelectrochemical (PEC) devices which are used to convert the energy from incident photons to split water into Hydrogen and Oxygen gas instead of to create electricity. CdS is a very toxic compound, and the fact that it tends towards forming extremely small crystals capable of being absorbed through human skin makes it even more dangerous. Instead of making more of the compound, obviously it would be a great idea to recycle the waste to be used for this project.

3.3.2 – Proof of enhancing capabilities of Cadmium Sulfide

As with any new material, proof of the enhancing properties of this new supply of CdS was required. Preliminary tests unfortunately did not look very good. Evident in figure 3.3.1 is that the unwashed CdS (as received) is not enhancing performance but diminishing it. Upon washing just once with water, however, the $V_{oc}$ rises as expected with very little detraction from $J_{sc}$.

![Figure 3.3.1: Effect of washing CdS before dispersion into P3HT solution. 15-A-2 is a pristine cell, 15-C-2 is a cell with unwashed CdS and 16-C-2 is a cell with CdS that has been washed once in water.](image-url)
3.3.3 - CdS Preparation

With this verification that the CdS was indeed enhancing the \( V_{oc} \), further washing of the samples once more in water and twice in ethanol in an attempt to remove any salts that may still be present in the solution. Each wash cycle consisted of dilution of solution to \(~500\text{mL}\) (of either water or ethanol) in a decanting funnel and letting it sit at least overnight for the solids (CdS) to settle.

Upon settling, the solid was purged through a valve at the bottom of the funnel into a jar. In the jar the solution was diluted to \(~250\text{mL}\) with whatever solvent was to be used next and ultra-sonicated for at least 30 minutes and the decanting process was repeated. It became evident that with each wash, the particles remained suspended for longer periods of time and the overnight settling was not sufficient. The last decanting sat for around 4 days before no more CdS would settle.

3.3.4 - Effect of different wt\% of CdS on performance (OPV18)

With the CdS proven and washed, I moved on to exploring the effects of different wt\% of CdS on device performance in sample set OPV18. Qualitative tests from section 3.2.2 used a 1:1 ratio of CdS:P3HT. In solution, it looked like far too much CdS and upon spin casting it was clear that it was because there were aggregates and sometimes the surface would become uneven. However, even with that weight percentage and the high degree of non-uniformities, you can see in figure 3.3.1 that the cell still functioned and that the CdS did have an influence on operation.

Regardless, the amount of CdS used was decreased in order to achieve cleaner spin coated surfaces. 50\%, 25\% and 10\% CdS:P3HT ratios were chosen for comparison.
The sample set was increased to 12 substrates (vs. previous batches of 6) to incorporate the comparison of pristine solution to the three CdS solutions (3 substrates per solution). All four solutions were made at the same time, in the same amounts, in the same conditions. Furthermore, this enlarged sample set ensured that all 12 substrates would be treated exactly the same except for the contents of the active layer. 3 substrates of each solution containing 4 devices each (after Aluminum evaporation) provided 12 devices of each solution to provide enough data to calculate reliable average responses.

The results of sample set OPV18, shown in figure 3.3.2, were very interesting indeed because the increasing weight percentages presented a tradeoff of different indications of performance. The solution that produced the highest $V_{oc}$ produced the lowest $J_{sc}$ (10wt%) and the solution that produced the lowest $V_{oc}$ produced the highest $J_{sc}$ (disregarding the pristine cell that is). Of course, notice how the pristine cell is only providing just over 0.1V on average at open circuit. This is an indication that something about this particular bottle of P3HT is not ideal (refer back to figures 3.1.1 and 3.1.2), but since all solutions were made from the same bottle at the same time, the relative performances are viable. With a typically responsive batch of P3HT, much improved responses from the CdS samples are expected.

A look at the average power curves of the devices, in figure 3.3.3, shows that the only cell to produce more power than the pristine cell was the 50% CdS sample. Despite that fact, however, the 25% and 10% CdS samples were very close to the pristine sample in terms of maximum power output and the did so at a higher voltage. This means that in a practical application, the CdS samples, regardless of the drop in current, can produce about the same amount of power at a higher voltage than pristine cells.
Figure 3.3.2: Average current densities of samples with different wt% (labeled) of CdS:P3HT in OPV18.

Figure 3.3.3: Average power densities of samples with different wt% (labeled) of CdS:P3HT in OPV18.
To understand the practicality of this, it must be understood that for a solar cell array to be used in a real life situation, stacks of cells must be connected in series to create a useable voltage. This creates a few problems in that in series, the current through the stack will be that of the lowest current in the stack, meaning all the cells will only perform as well as the weakest cell (or a cell with a shadow cast on it, or debris, or a damaged cell). This would also mean that if one of the cells stopped functioning for any reason, it would stop the entire stack from functioning. Higher voltage cells means less cells in series in a stack, and the impacts described above are lessened.

It should be noted, however, that the CdS curves exhibit severe Rs and Rp internal losses. The Rp loss is evident from the rather large slope in the curve before $V_{oc}$ (in this region, flat is ideal). The Rs loss is evident in the slope of the curve after $V_{oc}$ when the diode turns on (here, an infinite slope is ideal). The FFs of the CdS curves are also very low as well, and despite the low voltage of the pristine cell, it has the best FF. This is why an understanding of the different aspects of I-V curves becomes important; seemingly similar cells based on numbers like efficiency and FF alone are often misleading.

What OPV18 showed, however, is that if there was a way to increase the current of a cell while CdS acts to increase the voltage, the benefits of the two working together could improve the efficiency many times over. The key would be using specific enhancements to develop specific aspects of a solar cell (i.e. $V_{oc}$, $J_{sc}$, Rs, or Rp) to enhance the cell through multiple additive improvements. It just so happens that the $J_{sc}$ can be increased by magnitudes with the addition of a functionalized Carbon Buckyball
called "[6,6]-phenyl-C₆₁-butyric acid methyl ester", or PCBM or Methanofullerene for short. The functionalization allows the material to be solvent-soluble.

3.4 – P3HT-CdS-PCBM Solar Cells (Tandem Enhancement)

While PCBM is a very well established and documented enhancement for organic photovoltaics capable of increasing currents by magnitudes [5, 19, 20], inclusion of this material into this project was for the possibility that it could work with CdS to improve the function of a solar cell in tandem through two separate and specific enhancements.

In my previous experiments it was proven that CdS could improve the open circuit voltage of a cell and (interestingly enough) it was the lowest percentage (10%) of CdS that I tried that provided the largest gain in $V_{oc}$. Despite the higher $V_{oc}$, however, this solution actually provided less power than a pristine cell. My hypothesis was that if the currents of these cells could be increased to counteract the lessening of currents with the addition CdS, the overall power could be increased significantly.

3.4.1 – Solutions with PCBM (OPV19)

To ensure consistency in my comparisons again, solutions for this batch were made by taking measured volumes of my previous solutions (4 total), calculating the mass of P3HT in each, and adding an equal mass of PCBM. So all four solutions had a PCBM:P3HT ratio of 1:1, each with a different percentage of CdS (0, 10, 25 and 50%). Literature about optimal PCBM wt% suggests between 75% and 100% PCBM:P3HT, but most commonly a 100% ratio is employed. The mixture was then ultra-sonicated for at least 30 minutes. The PCBM is very interesting material indeed; it looks like soot dry but

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even a quick swirl in the Chloroform/P3HT solution and all particulates disappear. The solution does get darker but there are no agglomerations whatsoever; a very rare thing to see in nanotechnology.

3.4.2 – Proof of Technique

Upon testing the first samples out of this batch (which were the non-CdS), currents up to a few milliamps (vs. typical microamps) were obtained and for the first time efficiencies could be expressed without the use of scientific notation (~0.8% vs. previous efficiencies on the order of 1x10^-4%)! Of course, that is consistent with the function of PCBM according to literature, offering confidence in this fabrication technique. Also of note, as can be seen in figure 3.4.1, the voltage is higher than it was without the PCBM but still relatively low compared to CdS samples.

![Average J and Power density of Pristine-PCBM cells](image)

**Figure 3.4.1: Average current and power densities of pristine-PCBM cells in OPV19. Note scale (mA, mW) and compare to figures 3.3.2 and 3.3.3 (OPV18 - μA, μW).**
3.4.3 – Failure of Tandem Enhancement

Sadly, upon testing the PCBM+CdS samples, the currents were nowhere near the levels of the pristine-PCBM performance. In fact, as can be seen in figure 3.4.2, the addition of PCBM actually degraded the current and voltage. It seems the two materials do not work together at all, and the PCBM even diminishes the capabilities of CdS functioning as a voltage enhancement.

Figure 3.4.2: Comparison of average current densities from OPV18 (open curve markers, CdS only) and OPV19 (filled curve markers, CdS+PCBM). Pristine curves are not included because they can only be represented on a log scale since Pristine+PCBM cells performed at 1000 times the current. A power comparison is presented later in figure 2.4.4.

What is interesting, however, is that the curves reversed their relative productivity. The power curves seen in figure 3.4.3 show that in OPV18, the higher the CdS content, the higher the maximum power point. In OPV19, the maximum power of the solution with the highest CdS content performed horribly and the lower the CdS
content, the higher the power. It seems the CdS is actually a poison to PCBM and somehow tries to dominate the transfer of charges within the solar cell. The cells with 25% and 10% CdS exemplify the high open circuit voltages expected of the CdS enhancement. It cannot be explained, however, why the $V_{oc}$ of the OPV19 cells with 50% CdS were so low. Even the pristine-PCBM sample had a higher average $V_{oc}$ at around 0.4V (from figure 3.4.1).

![Graph](image)

**Figure 3.4.3:** Power comparison of OPV18 (CdS only) to OPV19 (CdS+PCBM). Pristine curves can only be compared on a log scale, as shown in figure 2.4.4.

The trend of OPV19 suggests that perhaps there is a level between 0% and 10% CdS that might allow the PCBM to become active again. However, it is not expected that when that happens the CdS will influence the reaction. It can be seen already in figure
3.4.3 that although the samples in the 19-10% set had the highest average power density in OPV19, the $V_{oc}$ is lower than that in 19-25%. Lowering the CdS content is expected to also lower the $V_{oc}$ and instead of the two materials (CdS and PCBM) working together, they would simply trade off domination of charge transfer.

3.4.4 – Trace CdS in a Pristine-PCBM Device

Enough PCBM was available for only about 2 more substrates, so to make final devices including PCBM, only trace amounts of CdS added. Drops of a solution containing P3HT and CdS were added to the solution containing P3HT and PCBM in a 1:1 ratio (the last ~mL left) with a pipette. The total volume of the drops could only be estimated, and 10 drops made for ~0.1mL of solution containing 10% CdS:P3HT. With these estimations, the ratio of CdS:P3HT in the final solution is estimated to be 0.1wt%.

As was projected, the two enhancements (CdS and PCBM) did not work together and in this scheme the PCBM dominated, but was still poisoned by the CdS and achieved less current than the pristine-PCBM cell and no improvement of the open circuit voltage. In fact, the pristine-PCBM and PCBM-0.1wt%CdS cells both achieved maximum power at the exact same $V_{oc}$=0.22V.

Comparing the power output of the entire PCBM set (pristine, 50%, 25%, 10% and 0.1%) required the use a logarithmic scale in figure 3.4.4. The trend between higher voltages w/ increasing CdS and higher currents with less CdS is readily visible. However, while CdS does increase the voltages, it is detrimental to the ability of PCBM to increase operation currents. From a strict power output point of view, the best performance came from the pristine-PCBM cell with no CdS.
3.4.5 – Conclusions

The results of preliminary tests with pristine solar cells (only P3HT) confirmed most typical literature results. Storage life and exposure limitations were discovered, taken account for and, as much as possible, controlled.

The addition of CNTs of any sort proved to be beyond the scope of this project. Every test resulted in shunted or inconclusive cells and the material was abandoned as a source of polymer solar cell enhancement. Published results of solar cells incorporating CNTs could not be reproduced, presumably because of purity and functionalization limitations.
Cadmium Sulfide (CdS) nanoparticles produced repeatable trends and consistently improved $V_{oc}$ levels. Batch OPV18 (summarized in table 3.4.1) shows a clear rise in $V_{oc}$ as a higher CdS wt% is used. It does, however, also show a drop in current as a higher CdS wt% is used.

In an effort to raise operating currents while raising operating voltages, a tandem enhancement scheme was attempted using CdS nanoparticles to increase $V_{oc}$, and PCBM nanoparticles to increase $J_{sc}$ in batch OPV19. Separate tests with only one of these nanoparticles resulted in the indicated increase, but combining the two did not yield additive enhancement. Table 3.4.1, figure 3.4.5, figure 3.4.6 and figure 3.4.7 show this fact that while CdS tries to dominate the cell (evident from higher than pristine $V_{oc}$), the PCBM seems to diminish the ability of CdS increase voltage. The two nanoparticles tend to compete for domination of charge transport and even then, the enhancement ability of the dominant species is diminished in the presence of the other. In this batch (OPV19), the CdS always dominated and the presence of PCBM reduced the ability of CdS to enhance $V_{oc}$.

A final test with only a trace amount (0.1% in OPV20) of CdS was done to explore whether there was a point where PCBM would dominate instead of the CdS. Material constraints offered only one level of CdS concentration to be tested. The results showed that the PCBM did indeed begin to dominate with a small enough wt% of CdS. $V_{oc}$ of a P3HT-PCBM cell and a similar cell with a trace amount of CdS added were comparable showing that the CdS was not dominating the reaction (as shown in figure 3.4.6), but the drastic drop in current (figure 3.4.4) shows that the CdS is impeding on the enhancing properties of PCBM in this polymer solar cell.
Table 3.4.1: Summary of average performances accomplished by CdS, PCBM and the combination of the two materials.

<table>
<thead>
<tr>
<th>Batch</th>
<th>OPV18 (no PCBM)</th>
<th>OPV19 (with PCBM)</th>
<th>OPV20 (with PCBM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CdS wt%</td>
<td>Max Power (W/cm²)</td>
<td>Efficiency (%)</td>
<td>FF</td>
</tr>
<tr>
<td></td>
<td>50%</td>
<td>25%</td>
<td>10%</td>
</tr>
<tr>
<td>Max Power</td>
<td>4.49E-07</td>
<td>5.82E-07</td>
<td>4.29E-07</td>
</tr>
<tr>
<td>Efficiency (vs. 100mW/cm², 1 sun)</td>
<td>0.00045%</td>
<td>0.00058%</td>
<td>0.00043%</td>
</tr>
<tr>
<td>FF</td>
<td>35.42%</td>
<td>16.48%</td>
<td>16.12%</td>
</tr>
<tr>
<td>VO</td>
<td>0.06</td>
<td>0.24</td>
<td>0.28</td>
</tr>
<tr>
<td>Jm</td>
<td>-7.49E-06</td>
<td>-2.42E-06</td>
<td>-1.53E-06</td>
</tr>
</tbody>
</table>

Figure 3.4.5: Log scale bar graph of maximum power density, Jm (current density at maximum power), and Jsc (short circuit current density). Because of the log scale, note that shorter bars mean higher values.
Figure 3.4.6: Power output (linear scale of sets with the same magnitude) of cells with CdS only and a combination of CdS and PCBM showing reversal of power trend with addition of PCBM. Label indicates percentage of CdS (PCBM percentage is constant).

Figure 3.4.7: $V_m$ (voltage at maximum power) and $V_{oc}$ (open circuit voltage) of cells with CdS only and a combination of CdS and PCBM. With the exception of 50% CdS w/ PCBM, the addition of PCBM reverses the voltage trend seen in the “CdS Only” data set. Label indicates percentage of CdS (PCBM percentage is constant).
Chapter 4
Conclusion

While polymer solar cells offer the possibility of low cost, environmentally
friendly energy conversion from sunlight, current technology has not yet made it a
reality. Efforts are, however, underway to remedy this. Many polymers are under
investigation, as well as different cell geometries, enhancement materials and transport
phenomena. Currently, PCBM is becoming a consistent addition to polymer solar cells
because its ability to increase current density is virtually indisputable.

However, at ~$150 for 100mg (Sigma-Aldrich – 99.5% purity), PCBM is ~21
times more expensive than Platinum (~$70.50/g as of 2/14/08). Because of this, this
project was not focused on PCBM, but rather considered as an addition to work on the
primary CdS enhancement. As mentioned before, part of the motivation for research in
organic photovoltaics is the potential for cheap solar cells. In fairness, it should be noted
that P3HT is ~6 times the cost of Platinum already, so the addition of PCBM effectively
quadruples the cost of each device.

As research grows, however, production will increase and prices will eventually
drop. The organic materials themselves are not rare and will not require destroying our
environment to mine like other materials; they are simply tedious to produce and difficult
to store.

It should also be noted that conjugated polymers like P3HT and PEDOT:PSS are
used for many things other than power conversion. They are inherently semiconducting
meaning they can be used in just about any scheme inorganic semiconductors are used,
such as a variety of electronic circuit components, Light emitting diodes (LEDs), and
even light sensors [21]. They still offer the same benefits such as low-cost, light-weight, mechanically flexible and environmentally friendly. They may even be considered disposable one day if cost reductions permit it. These other applications might be more practical applications of conjugated polymers because they can be more easily protected from ambient air and light (which both degrade the polymers) meaning the issue of short lifetimes would be less important.

Even the process I was using could be vastly improved through slightly different methods. First and foremost, fabrication and testing under an inert atmosphere in a glove box would severely decrease degradation. Also, if different electrodes were used like Fluorinated Tin Oxide (instead of ITO) on the substrate and Calcium or Lithium Fluoride layers (instead of or in conjunction with Aluminum) deposited on top of the device would immediately improve dissociation due to a higher work function differential [18, 20, 24, 25, 29].

While this project did not break any power conversion efficiency records or bring to light any new materials, it did break down some of the roles nanomaterials can and do play in polymer semiconducting. Uniform dispersion will always be a problem with nanotechnology, but PCBM is a shining example that this problem can be overcome. Entire labs focus solely on treatments and functionalizations of nanomaterials to improve dispersion in various solvents. It will definitely take a multi-faceted, combined effort from researches around the world to eventually put all the pieces together, if it is at all possible.
REFERENCES


