Increasing the efficiency of a hybrid polymer photovoltaic cell with polymer nanofiber complexes of varied thickness

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Introduction

The purpose of this investigation is to increase the power output of a specific polymer when utilized in a photovoltaic cell. Fossil fuels are an efficient and reliable source of energy, but they are detrimental to the environment, producing pollutants and greenhouse gases.[1] Also, the supply of fossil fuels is quickly diminishing. According to Kaufman,[2] at the rate fossil fuels are currently consumed, the supply will be exhausted within fifty years. Assuming that this statement is true, there is significant need for a new source of energy that will last a long time, be safe, clean, and easy to produce.

Photovoltaic cells convert light energy into electrical energy using the photovoltaic effect.[3] The photovoltaic effect occurs when photons of light strike the active material, the semiconductor. The electrons of semiconductor atoms are excited from the valence band (valence electrons) into the conduction band, where they can move freely between atoms. The excited electron is known as a charge carrier, or an exciton. The electron moving from its original atom into other atoms is known as exciton dissociation. Exciton dissociation results in one free, excited electron, and an electron hole, or the lack of an electron where the excited electron previously occupied. The electrons are captured by a metal electrode (the negative contact),

and the holes are captured by the positive contact, and used as electricity.[4] Silicon is the most common semiconductor used. The photovoltaic effect will be applied in this investigation, but with a polymer in place of silicon.

This polymer, dissolved in a liquid, can be sprayed onto materials, painted onto materials, or even printed in rolls. Its only downside is its efficiency. Unlike conventional silicon solar panels, which have an average efficiency of 15-20%, the polymer solar panels have a typical efficiency of 2-3%.[5] Twenty percent efficiency for conventional solar panels would be perfectly acceptable if the solar panels were more practical. However, they are heavy, fragile and difficult to make. Conventional solar panels require extreme temperatures and pressures to produce, consuming large amounts of energy.[4] Polymer solar cells require no extreme temperatures or pressures, and are thus easier and cheaper to produce. Polymer solar cells have an extreme advantage over silicon solar cells because of their special application properties. Polymer solar cells, if efficient enough, could be painted onto vehicles, buildings, or even clothing as a valuable energy source. Polymer solar cells have the added advantage of being flexible, allowing them to be painted onto curved surfaces such as cars or other vehicles. Finally, polymer solar cells have a significant weight advantage over silicon cells, weighing

significantly less. This is especially advantageous for space applications. Current rocket technology relies on liquid fuel, which is very expensive. With silicon solar panel systems weighing hundreds of pounds,[6] the fuel costs add up very quickly. Lighter, cheaper solar power systems and reduced fuel costs could be as simple as using a different paint on space shuttles or unraveling rolled lightweight polymer cells into space. If the efficiency of the polymer solar panels could be increased, they could provide more than enough energy for sustainable development.

Currently, these polymer photovoltaic cells are very inefficient. The main reasons for this are suboptimal band alignment between electron donor and acceptor semiconductors, and low charge carrier mobilities stemming from polymer based semiconductors' disorganized nature.[7] Zinc oxide has been proven to increase efficiency by promoting exciton dissociation. This is due to the physics of the photovoltaic effect. The photovoltaic effect and exciton dissociation occur when there is a difference in potential (Fermi energy) between two areas of the solar cell, where a high potential area is in junction with a low potential area.[4] When the polymer is illuminated, its electrons are excited, making it high potential. Zinc oxide has non-excited electrons, making it low potential. Thus, Zinc oxide provides the potential difference required for the photovoltaic effect at the junction between it and the polymer [Figure 1]. This explains the result of previous studies (year three of this investigation), where zinc oxide was mixed homogenously with the polymer. Zinc oxide had an increased efficiency when mixed with the polymer because it increased the surface area of the high potential/low potential junction, and thus the efficiency on the one molecule thick layer
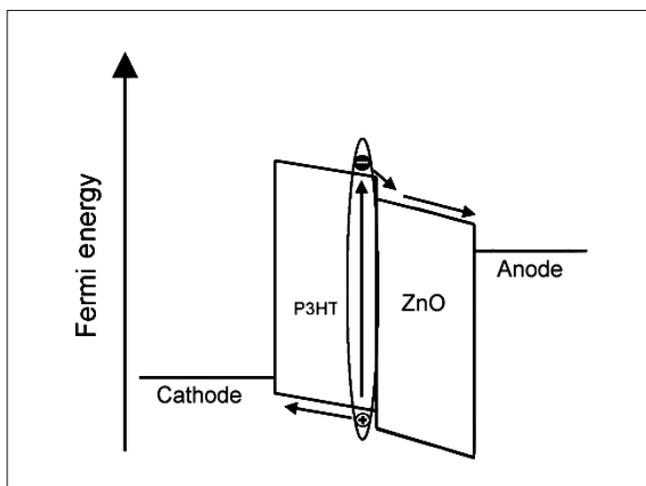
between the polymer and the electrode. Because the zinc oxide only increases efficiency when it is at the interface between the polymer and the electrode, the goal of year 4 of this investigation was to increase the surface area of the zinc oxide/polymer junction by creating zinc oxide nanofibers in replacement of the homogenous mixture, and optimize nanofiber length for maximum efficiency. Year four of this investigation proved that increased nanofiber length resulted in increased surface area and increased efficiency. However, if nanofiber length (thickness of the nanofiber layer) surpassed polymer thickness, the nanofibers penetrated completely through the polymer and caused an electrical short, ruining the devices.

The polymer is applied through a process known as spin-coating. During this process, a substrate is spinning rapidly on a platform, and the liquid polymer is dropped onto the spinning substrate. The polymer spreads out to form a film. The thickness of the polymer is a function of polymer solvent (varying surface tension and density), spin rate (centripetal force), and polymer concentration (viscosity). Previous research has shown that polymer thickness has a significant effect on efficiency.[8] Increased polymer thickness results in higher resistance and thus lower efficiency.

Essentially, there are two conflicting variables when producing hybrid organic/inorganic devices with P3HT and ZnO nanofibers. As nanofiber length increases, efficiency increases. As polymer thickness increases, efficiency decreases. The two variables are linked in that the nanofibers must be as long as possible without surpassing polymer thickness. The goal of this research was to find the optimal thickness of these two layers, the "polymer nanofiber complex" that resulted in maximum efficiency.

Method

Before the production of solar devices it was necessary to develop procedures for reproducibly controlling the thickness of the polymer and nanofiber layers. The spin-coating process was the determining factor for polymer thickness, assuming constant polymer solvent and concentration. During spin coating, polymer solvent and concentration were kept constant at chloroform and 20g/L. Polymer films were produced with spin rates of 8210, 2620, 1110, 557, 313, and 190rpm. These rates were determined by previous research from Chang *et al*,[8] to predict polymer thicknesses of 130, 180, 230, 280, and 330nm based on a regression equation matching known data. Profilometry was used to determine

Figure 1: The ZnO provides the Fermi energy potential difference required for the photovoltaic effect (adapted from Sun *et al.,* 2005)

actual polymer thickness. These data were plotted, and a new regression function was calculated to relate spin rate and polymer thickness for given polymer solvents and concentrations [Figure 2]. To confirm the reproducibility of this regression, new slides were produced using the regression function. These thicknesses were measured, and a new regression function created. The difference between the first and second regression functions was less than the margin of error of the surface profiler equipment.
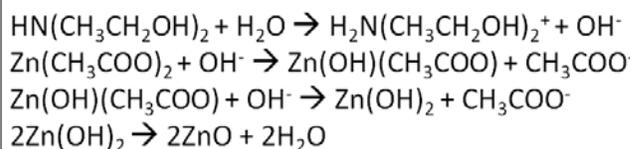
The zinc oxide nanofiber production procedures were also analyzed for nanofiber length. The nanofibers are produced using the sol gel process from zinc nitrate and zinc acetate precursors. Due to the surface properties of glass, zinc oxide nanofibers can not be grown directly onto glass. There must first be a flat layer of zinc oxide from which to grow the nanofibers. This is known as the nucleation layer. The nucleation layer is produced by spin coating at 2000rpm the following solution: 0.823g Zinc Acetate, 0.223mL Ethanolamine, 5mL 2-methoxyethanol. The slides were annealed at 300 degrees for 10 minutes, initiating the reaction seen in Figure 3, and resulting in a flat layer of zinc oxide. The unwanted ions were washed away by subsequently washing the slides in acetone and isopropanol. The nanofibers were produced in a solution of 1mM zinc nitrate at 70 degrees, according to the reaction seen in Figure 4. The pH was raised to 13 using sodium hydroxide. Previous research has shown that nanofiber length is a function of the reaction time in the zinc nitrate solution. Nanofiber slides were produced with reaction times of 5, 10, 15, 20, 25, and 30 minutes. Nanofiber length was measured using scanning electron microscopy [Figure 5]. Average
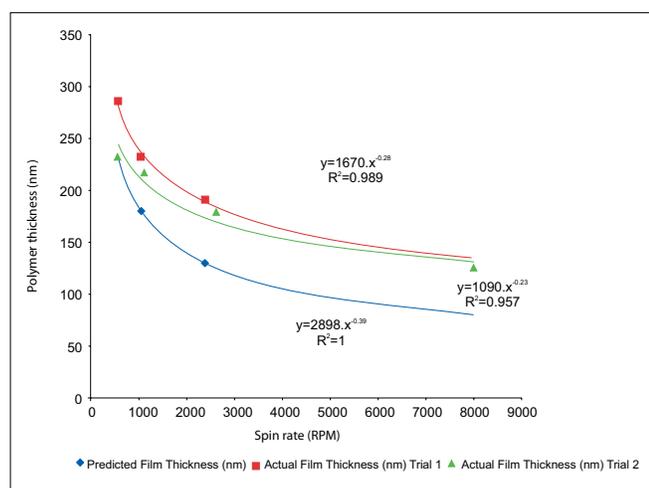
fiber length was taken from three locations on each slide. The SEM images were taken from a 45 degree angle. Using the Pythagorean Theorem, the measured nanofiber length was multiplied by the square root of 2 to find actual nanofiber length. Reaction time was plotted against nanofiber length [Figure 6] and a regression function was produced to relate the two variables. This process was repeated to confirm the accuracy of the regression function.

The solar devices were produced using slides of patterned Indium Tin Oxide (ITO). Ten 1"x1" glass slides pre-coated with (ITO) underwent intense cleaning procedure using a micro weave cloth to remove dust and impurities [Figure 7]. It is important to note that the entire solar cell, when completed, is only ~1000nm thick, meaning that any dust or particle on the slide during production could be thicker than the entire solar cell, causing an electrical short and a ruined device, so the cleaning procedure is critical to the production process. The slides were placed into an ultrasonic vibrator with 100ml isopropyl alcohol for ten minutes. This was repeated with deionized water and acetone. The slides were placed into an ozone and ultraviolet light generator for thirty minutes. This was to ensure the absence of any impurity which could interfere with electrical conduction of the slide, and to enhance hydrophilic properties of the slides' surface to facilitate spin-coating. The nanofiber layer was produced according to the procedure described above, in thicknesses (nanofiber lengths) of 100, 150, 200 and 250nm [Figure 8]. The ITO contact area was wiped with a Q-Tip soaked in ethanol prior to annealing to prevent fiber growth in this area.[9] Two slides were produced with each nanofiber length, leaving two


Figure 2: Polymer film thickness vs. spin rate for a given polymer solvent and concentration, using power regressions. The R-squared values for the first and second trials were 0.989 and 0.957, respectively

$$HN(CH_3CH_2OH)_2 + H_2O \rightarrow H_2N(CH_3CH_2OH)_2^+ + OH^-$$
$$Zn(CH_3COO)_2 + OH^- \rightarrow Zn(OH)(CH_3COO) + CH_3COO^-$$
$$Zn(OH)(CH_3COO) + OH^- \rightarrow Zn(OH)_2 + CH_3COO^-$$
$$2Zn(OH)_2 \rightarrow 2ZnO + 2H_2O$$

Figure 3: The reaction mechanism for the production of a zinc oxide nucleation layer from a Zinc Acetate precursor (adapted from Bahadur et al., 2007)

$$2Zn(NO_3)_2 \rightarrow 2ZnO + 4NO_2 + O_2$$
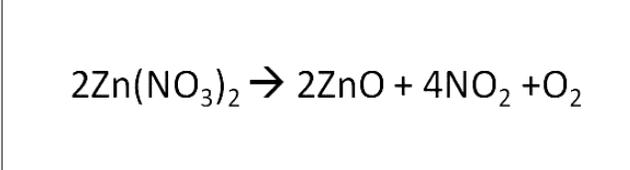
Figure 4: The reaction mechanism for the production of the zinc oxide nanofibers in solution from a zinc nitrate precursor (adapted from Bahadur et al., 2007)
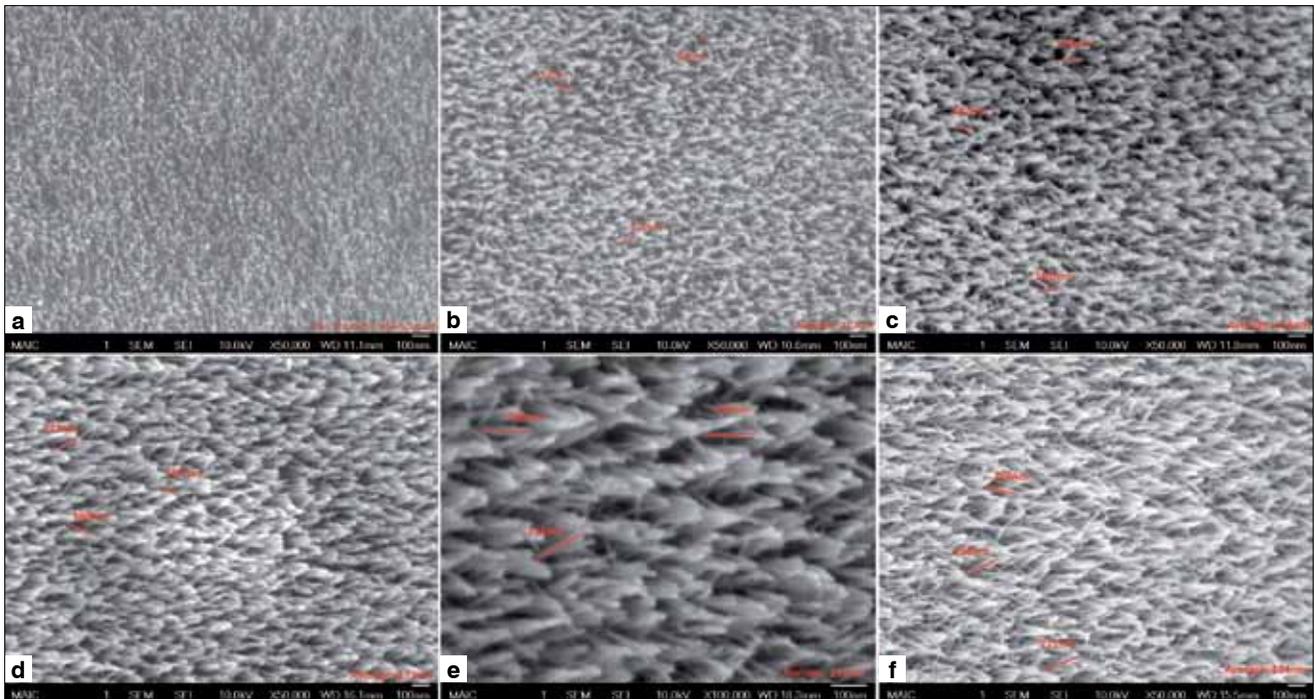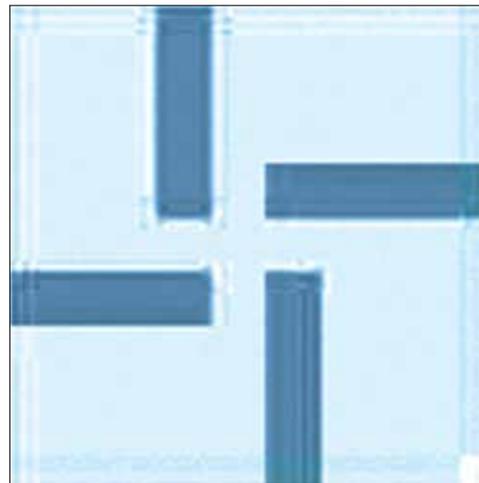
Figure 5: Scanning electron microscope images of the ZnO nanofibers. After 5 minutes reaction time (a), there was no fiber growth. After 10 minutes (b) the average fiber length was 103nm. After 15 minutes (c), the average fiber length was 151nm. After 20 minutes (d), the average fiber length was 173nm. After 25 minutes (e), the average fiber length was 212nm. After 30 minutes (f), the average fiber length was 264nm


$$y = 70.73e^{0.044x}$$
$$R^2 = 0.973$$
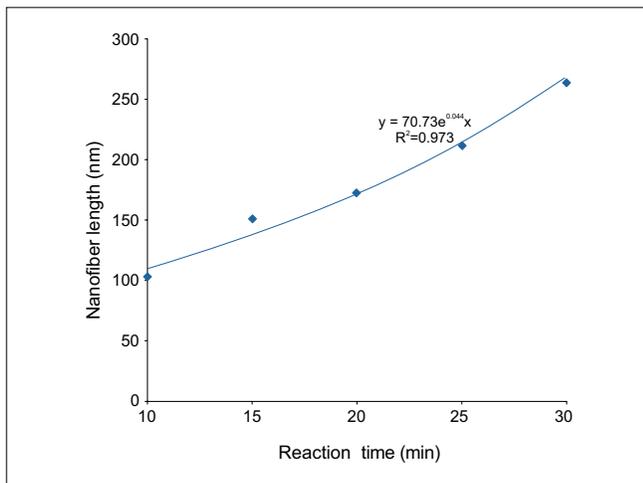
Figure 6: Reaction time vs. nanofiber length. After an exponential regression, the R-squared value was 0.973


Figure 7: The solar cell begins as a pre-patterned ITO (indium tin oxide) substrate. The ITO (grey) is transparent enough to allow light to pass through to the solar cell, yet conductive, allowing it to act as the top electrode

slides with no fibers as the control. The polymer layer was applied on top of the nanofiber layer using the process described above [Figure 9]. The polymer was applied such that it was always 30nm thicker than the nanofiber layer, to account for small variances in fiber length and minor residuals in the regression function. For example, to the 100nm nanofiber device, a polymer layer was added of 130nm. This process was completed in nitrogen to prevent the oxidation of the polymer. The slides were annealed at 200

degrees for 1 minute, to melt the polymer between the nanofibers, further increasing the surface area of the junction. A thermal evaporator was used to achieve zero humidity and a complete vacuum environment. Four slides at a time were placed into the thermal evaporator and each underwent application of both an 8nm BCP (bathocuproine) layer, and an aluminum electrode directly to the polymer surface of the slide [Figures 10, 11]. The BCP effectively increased the
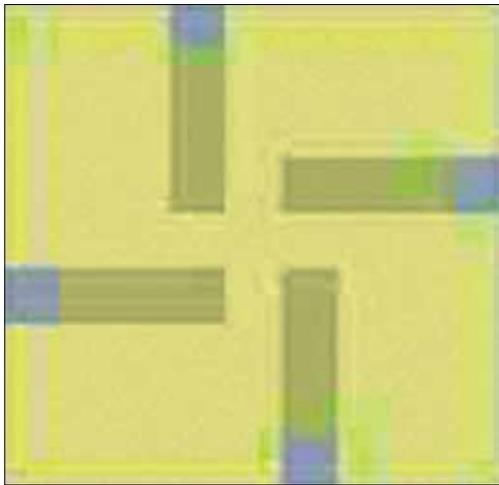
Figure 8: Zinc Oxide nanofibers are applied, starting with the Zinc Oxide nucleation layer. Ethanol wipes on the ITO contact areas are used to dissolve the nucleation layer, preventing fiber growth in these areas. The fibers (yellow) are then grown from solution
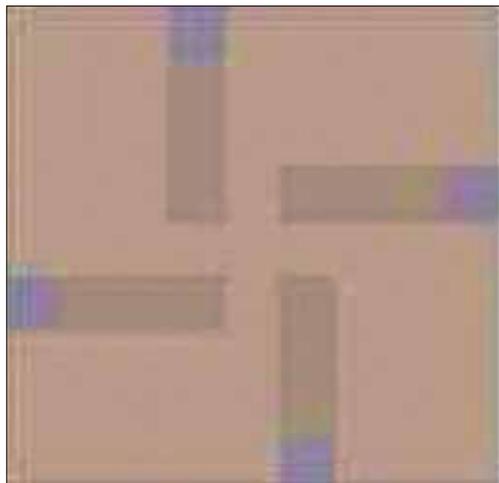

Figure 9: The active layer, P3HT (red) is applied via spin-casting. This is to ensure even thickness on all slides
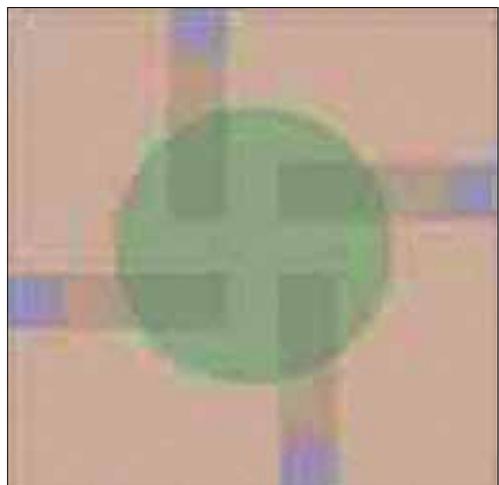
Figure 10: The BCP layer (green) is applied via vacuum thermal evaporation. This effectively increases the thickness of the solar cell, reducing the chance of an electrical short due to dust or impurities
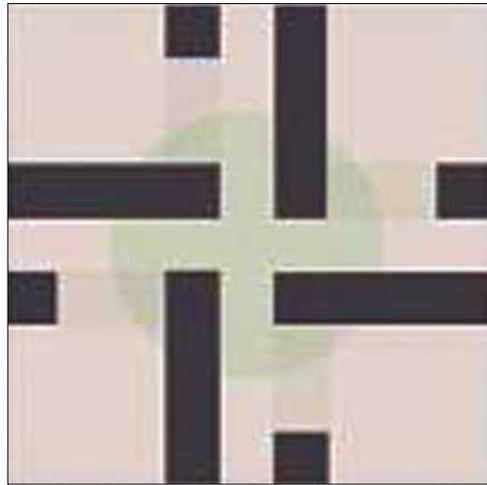
Figure 11: The aluminum electrodes are applied via vacuum thermal evaporation at an even thickness. Aluminum contact points are applied above the ITO for optimal contact. The circuit is completed through the polymer. Because that area is not illuminated, it does not add to the overall device area
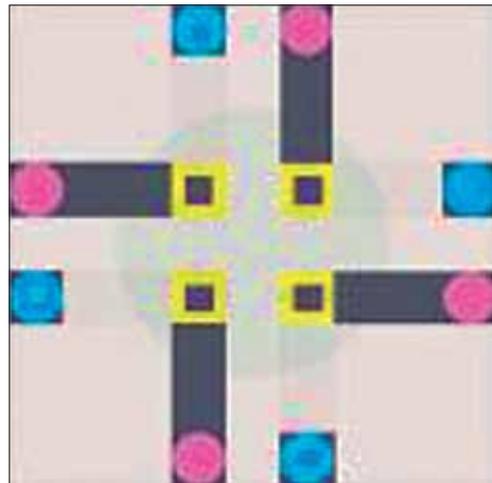
Figure 12: The completed solar device. The device area (yellow) is the intersection of the ITO and aluminum electrodes, with 4 devices per slide. The two contact points are ITO (blue) and aluminum (pink)

thickness of the slide, reducing the chances of an electrical short due to dust or other impurities. It is also a hole-blocking layer. The use of the thermal evaporator assured intimate contact of the entire electrode with the entire surface of the polymer. The procedure of BCP layer and electrode application was repeated for all test slides. Each side of each test slide had the BCP and aluminum electrode layers applied, allowing each slide to serve as four different test trials. Each slide was inserted into a solar simulator, and attached to a semiconductor parameter analyzer, which was connected to a computer to graph and record power output [Figure 12]. Power output from the device was recorded in amperes using a sweep mode from minus

to plus one volt. This was repeated for each of four test sites on each slide, and repeated for all ten test slides. The entire process was repeated, resulting in two slides, or 8 solar cells for each test group, and two slides for the control. The process of testing each solar cell for efficiency was repeated after 72 hours of air exposure to test the effects of air exposure on the devices. All slides, polymers, and used chemicals were disposed of as per safety protocol. All results were analyzed using Microsoft Excel.

Results and Discussion

Efficiency was calculated based on number taken from the J-V curve from the semiconductor parameter analyzer [Figure 13]. According to the data, nanofiber length, polymer thickness, and air exposure had an effect on solar cell efficiency. The addition of nanofibers initially decreased the efficiency compared to the control [Figure 14]. However, after 72 hours exposure to air, the nanofiber devices showed an increased efficiency, while the control decreased in efficiency [Figure 15]. This increase in efficiency may be due to the reduction of oxygen vacancies in the ZnO nanofiber crystals, and thus an increase in carrier concentrations. Some nanofiber devices had efficiencies greater than the control after 72 hours. The device with nanofiber length/polymer thickness of 100/130nm had an efficiency 29% greater than the control. The trend of air exposure over time indicates that further exposure would continue to increase efficiency in nanofiber devices, and would likely show asymptotic behavior after the polymer and nanofibers are completely oxidized. Maximum efficiency within nanofiber devices was seen in 100/130 and 250/280 devices. This indicates that both polymer thickness and nanofiber length have an effect on efficiency, with low polymer thickness increasing efficiency in the 100/130 devices, and long nanofiber length increasing efficiency in the 250/280 devices. After 72 hours, efficiency was measured using arbitrary units. This was due to the fact that the BCP layer degrades over time, decreasing efficiency, while maintaining the trend of efficiencies over all devices, so the efficiencies themselves are irrelevant. The solar devices initially have a low efficiency due to device conditions. Due to limited polymer availability, reduced polymer concentrations were used from the optimal 32g/L. As a result, the trend of efficiencies is more important than the efficiencies themselves. This trend indicates that after 72 hours, the solar device with nanofiber length/polymer thickness of 100/130nm increases

$$PCE = \frac{V_{OC} \cdot J_{SC} \cdot FF}{P_o} \cdot 100$$

Figure 13: The calculation of power conversion efficiency from open circuit voltage (Voc), short circuit current density (Jsc), fill factor (FF), and power input (Po). All units cancel to result in power output/power input, which is mechanical efficiency
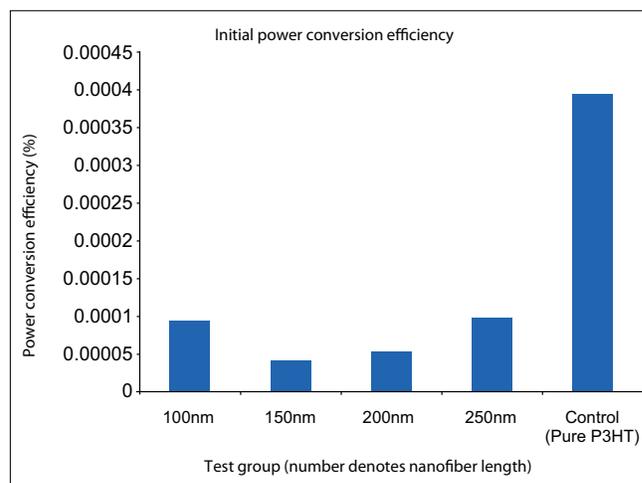
Figure 14: Immediately after device production, there is a strong parabolic trend with increasing complex thickness. However, all nanofiber devices have an efficiency lower than the control
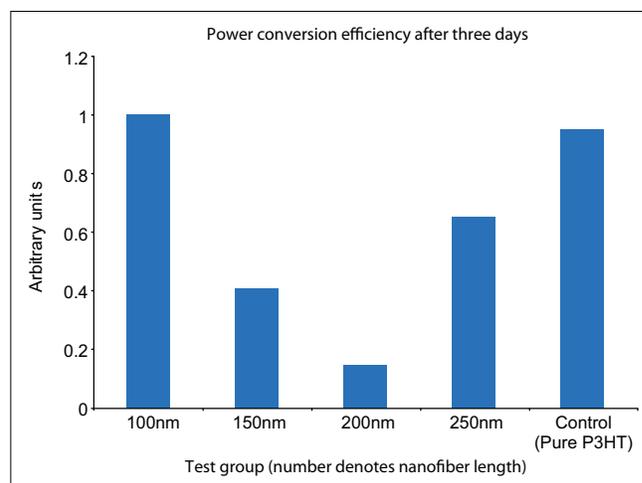
Figure 15: After three days, the parabolic trend is preserved with increased complex thickness, yet the nanofiber devices have an efficiency frame shifted above the control. This may be due to the oxidation of the polymer and the reduction of oxygen vacancies in the ZnO nanofiber crystals

efficiency 29% over the control, and continues to increase efficiency over time. Applying this trend to solar cells with optimal polymer concentrations would result in a final theoretical efficiency of 5.2%. After a 2 sample T-test, the p-value when comparing the 100/130 device and the control was calculated

to be less than 0.0001, indicating that the results were statistically significant.

There were some minor errors in the procedures. First, the slides were intended to be removed from the annealing oven simultaneously. However, this was not possible because it took time to remove each device from the annealing oven, so there was a 10-15 second variation. Next, there was a slight technical problem with fiber growth. The fibers were grown in a 70 degree solution. However, the solution was heated from the bottom, resulting in a temperature gradient across the slides. This would have resulted in varying fiber diameters across the slide. However, this would have had a minimal effect as the gradient was the same on all slides. Finally, the polymer is laterally conductive. This means that energy is collected on the slide in an area slightly larger than the intended device area. However, since light was only being shined on the intended device area, and the effect was the same for all devices, the efficiency ratios are preserved and the effects are minimal. These problems had miniscule effects on the final efficiencies, and any effect would have been the same across all test groups, having minimal, if any effect on the data trend. Despite these small effects, this research generated new knowledge on polymer solar cells, in hopes of one day replacing fossil fuels with solar energy, reducing humanity's effects on the environment and achieving true sustainable development.

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About the Author

Nathan Monroe is 19 years old and is an undergraduate at the Massachusetts Institute of Technology, studying Electrical Engineering and Physics. In his free time, he enjoys playing guitar and mandolin, singing, and running. He hopes one day to become a researcher for an electronics company, or start his own green energy company.