

Photosynthetic Solar Cells Using Chlorophyll and the Applications Towards Energy Sustainability

By

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Abstract:

As the population increases exponentially so does the need for a greater demand of energy. Even though renewable energy sources are available, humans still receive almost 60% of energy from non-renewable resources such as fossil fuels. Solar energy has been seen as a very promising method of energy collection for electrical use for some time now. The common silica solar cell design has been altered in many ways over the years. The main goal is to improve the absorption and conversion of sunlight into usable energy. The majority of current photosynthetic solar cells make use of non-renewable components. These materials can have an adverse effect on an environment. It is therefore vital to develop a non-toxic and renewable photosynthetic solar cell that can efficiently produce electricity. This project will attempt to demonstrate how to efficiently and sustainably utilize the living chlorophyll found in plant cells for electrical generation in a photosynthetic solar cell application. This can be accomplished by chemically extracting dense amount of chloroplasts from plants. The organic photosynthetic solar cells are synthesized in layers of chlorophyll, a catalyst, agarose, and a final layer of super-conductive material known as graphene. Research of chemistry, physics, biology and environmental science is necessary to complete this project.

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Chapter 1

Introduction

Background of Project

Energy consumption in the United States has increased significantly along with industrial needs and population growth. According to the U.S. Department of Energy, expected energy use for 2011 was 98.35 quadrillion BTU and is expected to increase steadily over the next decade (US Department of Energy, 2009). Projections for these large anthropogenic energy demands indicate that non-renewable resources, such as fossil fuels, will become more costly as a result. Apart from the need for more energy, there exists also the need for a more clean and sustainable process for obtaining it. Today's non-renewable energy sources, such as coal, produce carbon byproducts which promotes the buildup of greenhouse gases, air pollution and ultimately environmental degradation. Therefore, it is vital to find alternative ways to produce electricity in a clean, sustainable, and efficient manner. The future proposed research will focus on producing energy in this way. It is based entirely on the principles of "green chemistry", and if successful, this project will have important implications for energy production in many areas.

As mentioned before, the generation of today's electricity relies mainly on nonrenewable fossil fuels, like coal, natural gas and oil. These sources provide approximately 60% of the current total world energy demand. This serious dependence we have on fossil fuels puts the world in a precarious situation for our future energy needs. First, the increasing depletion of fossil fuels as a result of increasing energy consumption means our resources will become limited. Second, the increased resource consumption could produce financial and political distresses due to the depletion of our planets natural

resources. Third, the combustion of fossil fuels for electricity generation introduces approximately 6 gigatons of CO₂ into the atmosphere every year which in turn increases the risk of climatic changes (Rittmann, 2008). It has become hauntingly apparent that the need for a sustainable, carbon-neutral, and renewable energy source for electricity generation is necessary to supplement the increasing demands of the world. Some of the possible solutions to these problems have been found in renewable energy resources. Renewable energy sources such as, hydropower, wind power, tidal power, and solar cell technologies offer many opportunities to supplement world energy demands. They can also address some of the long term power concerns. Solar cells have enormous potential in creating long term sustainable energy with minimal environmental degradation.

History of Solar Cells

Most solar cells of the 21st century use extremely refined silica in order to convert sunlight to usable electricity. Unfortunately, the use and refinement of silica in solar cells has potential environmental and health hazards on its own. An Oregon study done regarding the process of solar cells found the following:

“Many different potentially hazardous chemicals are used during the production of solar cells. The primary environmental, health and safety concerns are exposure to and inhalation of kerf dust, a byproduct of sawing the silicon ingots into wafers, and exposure to solvents, such as nitric acid, sodium hydroxide and hydrofluoric acid, used in wafer etching and cleaning as well as reactor cleaning. Many of these solvents also pose a risk of chemical burns. Other occupational hazards include the

flammability of silane used in the deposition of anti-reflective coatings.” (ODOT Health and Safety, 2012)

This information poses a serious problem for our past and current photovoltaic systems. It is imperative that the use, collection, and production of silica and its derivatives be altered or even removed from the solar cell manufacturing process. By utilizing current and future advancements of organic materials, this project will attempt to synthesis and characterize a clean photovoltaic cell in a cost effective manner. Current solar cell technology costs anywhere from \$0.20 to \$0.40 per Kilowatt hour and has the potential to be competitive with coal, natural gas or nuclear power. This is due to the theoretical efficiencies of this technology being approximately 85-90% (Table 1). Most solar cells have efficiencies between 6-40% depending on technologies and materials used. Recently, researchers have begun to explore organic solar cell technologies utilizing non-harmful and sustainable methods and practices. These organic cells can cut down on costs and dangers associated with the mining and manufacturing process.

Chapter 2

Literature Review

Use of Biological Components in Solar Cells

The first early organic solar cells were based on a single organic layer sandwiched between two metal electrodes (Sze et al, 1981). While successful, these primitive cells could only be operated at very low efficiencies compared to current photovoltaic standards. As of today, the power conversion efficiencies of organic solar cells are in excess of 3% (Hoppe et al, 2004; Battumur et al, 2011). Their inorganic (silicon) counterparts have typical efficiencies of 10-20% (Dittrich et al, 2011) but can reach 40% depending on configuration and materials used (Zhu et al, 2011). The first carbon-based semiconductor to partially replace silicon solar cells has an impressive efficiency of 6.45% (Zhu et al, 2009). This glimmer of hope, frightening realization of resource shortages, and ever increasing environmental degradation has prompted researchers to begin a search for organic PSCs that can match silicon power conversion efficiencies plus have the ecological and economic benefits of this emerging technology.

Energy Source	Costs (\$/kWhr)
Coal	\$0.09 - 0.14
Natural Gas	\$0.06 - 0.12
Nuclear	\$0.11
Wind	\$0.10 - 0.20
Photovoltaic	\$0.20 - 0.40

Geothermal	\$0.10
Biomass	\$0.11
Hydro	\$0.09
Fuel cells	\$0.10 - 0.15

Table 1. Price comparison of modern energy sources

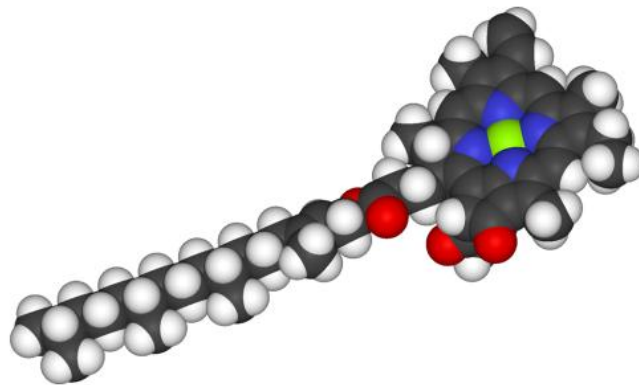


Figure 1. The chlorophyll molecule.

Plants use the process of photosynthesis to convert sunlight into chemical energy using specialized cells.

“Plants use energy from the sun in tiny energy factories called chloroplasts (Figure. 2). Using chlorophyll (Figure. 1) in the process called photosynthesis; they convert the sun's energy into storable form in ordered sugar molecules such as glucose. In this way, carbon dioxide from the air and water from the soil in a more disordered state are combined to form the more ordered sugar molecules.”

(Nave)

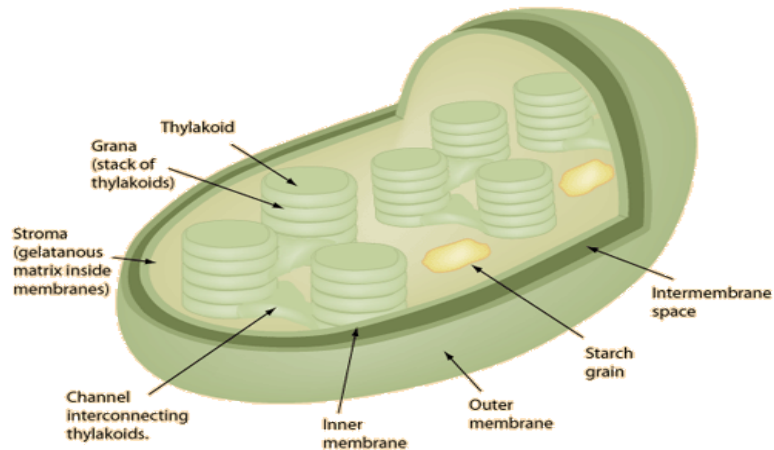
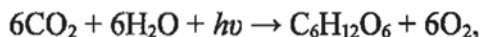


Figure 2. The structure of a chloroplast.

Inside the chloroplasts are stacks of discs called thylakoids. They are located within the walls of the chloroplast, and they act to trap the energy from sunlight. These coin-like stacks of thylakoids are called grana. These structures are connected with an extensive system of interconnecting tubules which transports necessary materials to the proper location. The thylakoid membranes are the structures that actually contain chlorophyll and other pigments that give plants their green color. The thylakoids are arranged in antenna arrays to capture light energy. There are two photosystems called Photosystem I and Photosystem II, and in most plants, both photosystems are used in an electron transport process. This yields energy in the form of Adenosine triphosphate and reduced coenzymes to the stroma of the chloroplast to be used in the synthesis of carbohydrates (Nave). The green pigmented chlorophyll (Figure 1) has the desirable photovoltaic properties that are utilized in today's organic photosynthetic solar cells. (Antohe et al, 1996; Diarra et al, 1986). Chlorophyll is a light harvesting pigment that absorbs light in the visible spectrum of solar radiation (Figure 3.), which promotes electron transfer (<http://en.wikipedia.org/wiki/Chlorophyll>). Carotenoids are also an important part of the photosynthetic process. They aid in energy transfer to the chlorophyll molecule, and serve to

supplement the light gathering properties of chlorophyll. Explicitly, the overall chemical equation for plant photosynthesis is given by the following equation:



In this double replacement reaction new, more complex compounds are synthesized from smaller ones. In this particular equation, $h\nu$ represents the amount of energy from a one photon of light.

Two types of chlorophyll that are found throughout organisms with chloroplasts are known as chlorophyll alpha (α) and chlorophyll beta (β). These pigment systems are necessary in order to properly absorb the different parts of the visible solar spectrum as shown in Figure 3. Once absorption of light energy occurs and photosynthesis takes place, a process known as electron transfer begins. Without the transfer of electrons, no energy will flow through the photovoltaic system.

One way to increase electron transfer of chlorophyll is to replace the magnesium (Mg) atom with another metal such as copper (Cu) or iron (Fe). This must be done carefully. The introduction of too much heavy metal will cause damage to sensitive plant cells and tissues. This will ultimately interrupt the process of photosynthesis and cause the system to fail.

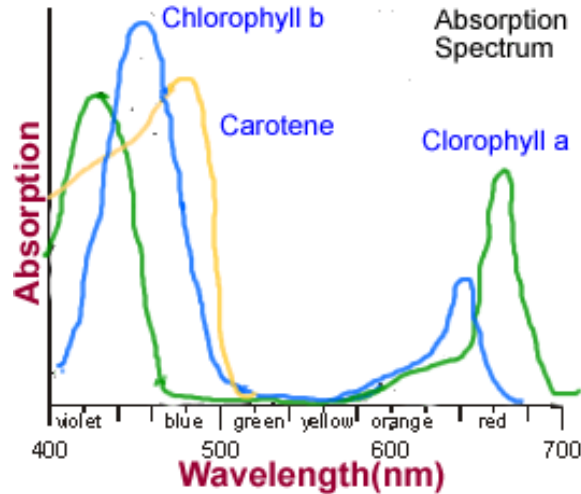


Figure 3. The absorbance of the chlorophyll molecules.

Similar to the natural process of photosynthesis, organic PSCs convert light into electricity in four steps. First is the maximum absorption of light; which in turn forms an excited state of electrons as the second step. Next, exciton diffusion into regions, where charge separation occurs, and finally this then leads to charge transfer (Hoppe et al, 2004). The typical characteristics of a photovoltaic device are described by the following equation:

$$I = I_0 \left\{ \exp \left[\frac{e}{nkT} (U - IR_S) - 1 \right] \right\} + \frac{U - IR_S}{R_{SH}} - I_{PH}$$

This equation can be explained in the following terms: I_0 is the dark current, e is the charge of the electron, n is the diode ideality factor, U is the applied voltage, R_{SH} is the series resistance, R_{SH} is the shunt resistance, and I_{PH} is the photocurrent (Honsberg & Bowden). A similar circuit diagram representative of this equation is found in Diagram 1.

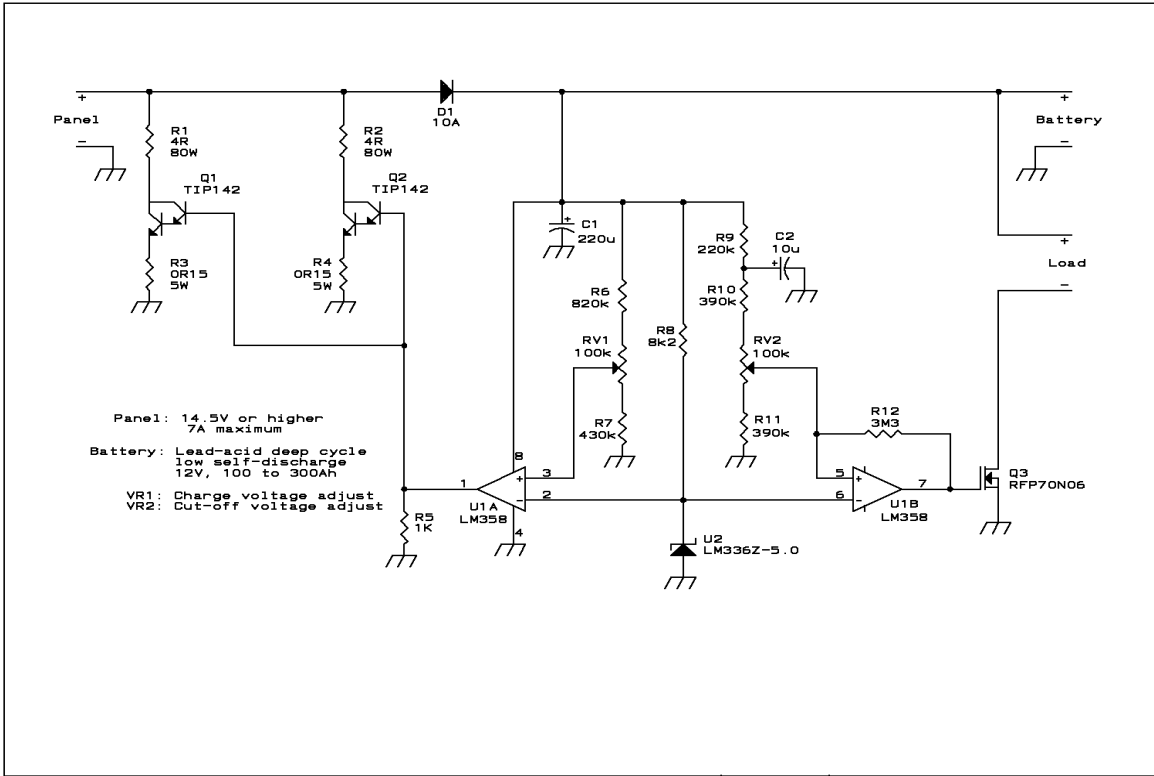


Diagram 1. Circuit diagram of solar controller with shunt regulator

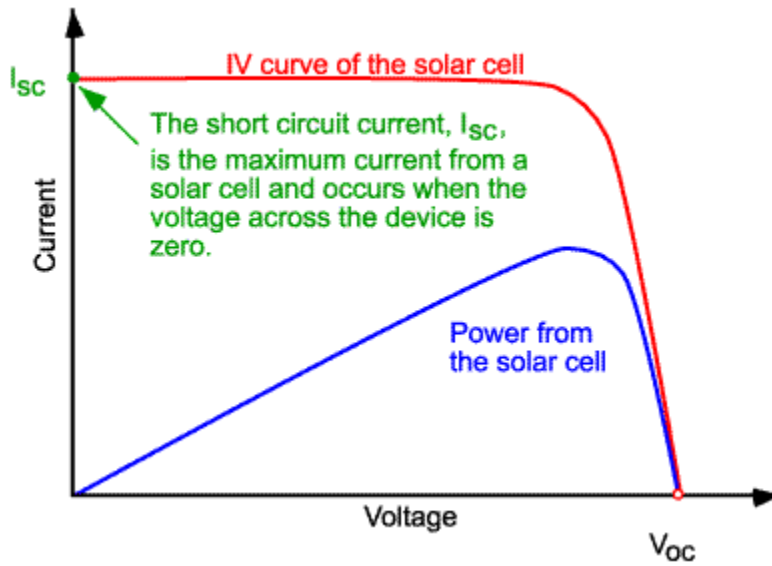


Figure 4. current-voltage curve of solar cells

Specific current- voltage curves and power density curves are used to determine maximum power of a photovoltaic device such as shown in Figure 4. The power conversion efficiency $\eta_{power} = FF \cdot I_{sc} \cdot V_{oc} / P_{IN}$, depends linearly on the open circuit voltage V_{oc} , the short-circuit current I_{sc} , and the filling factor FF of the photovoltaic device, where P_{IN} is the input power (Honsberg & Bowden). The filling factor is defined as the ratio of the actual maximum power, to the product of the open circuit voltage and short circuit current (Honsberg & Bowden). Modern commercial solar cells generally a fill factor larger than 0.70. Cells with a high fill factor have a low equivalent series resistance and a high equivalent shunt resistance, so less of the current produced by light is dissipated in internal losses (Honsberg & Bowden).

Work in the field of photosynthetic solar cells has focused on the insertion of nano-scale electrodes into a single chloroplast of a particular species of algae. Using this process, one is able to harness the energy produced by photovoltaic cells. Although this is may be innovative proof that it is possible for electricity to be produced from dense concentrations of chlorophyll alpha and beta, it does not necessarily prove that chlorophyll alone can be a viable source of electricity.

Proposed Methods and Expected Results

This project focused on tapping into the main source of energy production in plants, chloroplasts on a dense scale. First, extraction of chlorophyll from plant species with high concentration of Chlorophyll α and β should occur in the most non-toxic and sustainable way possible. Then, the organic photosynthetic solar cells (PSC) can be synthesized into layers. These layers may be constructed in the following order: chlorophyll, a catalyst, agarose, and graphene. We believe the layering of these

components will produce better efficiency due to the chemicals composition and unique properties of each substance. The chlorophyll will provide the main component for light absorption and conversion. The graphene should aid greatly in electron transfer between layers of chlorophyll by acting as a superconductor. The catalyst should also provide aid for movement of electricity within the cell. Expected results may be as follows: (1) Insight for managing electricity generation using photosynthetic solar cells, water resources, land use and operation costs of a solar system; (2) Determination of the characteristics of a photosynthetic solar cell using chlorophyll; (3) Collection of scientific data essential for future implementation of a photosynthetic solar cell system; (4) Analysis of socioeconomic and cultural factors that underlie contemporary patterns of energy demand and a quantitative evaluation of the environmental benefits for this solar energy; (5) Comparison of photosynthetic solar cells to current silicon solar cells presently in use.

Chapter 3

A Proposed Method

Flora Identification and Collection

Appropriate plant species for use in photosynthetic solar cell applications are those with high concentrations of chlorophyll alpha and chlorophyll beta. Even some plants that are currently produced on a large scale for crop production can be used for this application. Green tea leaves (*Camellia sinensis*), broccoli leaves (*Brassica italic*), pimento fruits (*Capsicum annum*), carrots (*Daucus carota*), soybean seeds (*Glycine max*), alfalfa (*Medicago sativa*), purslane (*Portulaca oleracea*), and spinach (*Spinacia oleracea*) all have been found to contain high concentrations of chlorophyll alpha and beta (Griffin, Quach & Steeper, 2004). *Spinacia oleracea* is one of most well studied plants for its high chlorophyll concentrations. The leaves of *Spinacia oleracea* have been found to contain anywhere from 300 milligrams to 600 milligrams of chlorophyll per ounce of plant material (Evans, Levin, Mayer & Gailing). If chemical measurement of chlorophyll is not possible at the time of identification it is a safe assumption to make that the more green a particular species of plant appears the more chlorophyll it contains. This is due to the large amount of red and blue light that the chlorophyll absorbs. This along with various other photosystems and pigments means the majority of the light reflected from a plant is green, therefore giving plants a variety of greenish hues. Many freshwater and marine species of algae also have high concentrations of chlorophyll (Hosikian, Lim, Halim & Danquah, 2010). Some species have been considered and successfully experimented with in order to extract chlorophyll for a wide variety of uses.

Material Uses and Graphene Applications

The materials and chemicals for the extraction of chlorophyll can be relatively few in number. The materials used for this particular project are as follows: Erlenmeyer flask, Buchner flask, shallow beaker, centrifuge, centrifuge tubes, solder, soldering iron, sheathed copper wire, and double-sided copper plating. The chemicals used in this process are Ethanol and Hexane. The main source of chlorophyll is finely fragmented leaf blades of a chlorophyll-rich plant species. More materials can be used in order to refine the process and possibly get a higher amount of chlorophyll. But in this case it was important to try and minimize materials that are being used in order to reduce the environmental impact of excessive items and toxic chemicals. Ethanol and Hexane are both naturally occurring chemicals with little to no damage to the environment. Ethanol is a byproduct of the anaerobic fermentation of sugars by fungi known as yeast; this is the major process behind making alcoholic beverages. Millions of humans ingest some form of ethanol every day in various quantities and concentrations. Hexane is a constituent of crude oil as well as natural gas and can be even be synthesized from plant wastes such as sugar cane scraps (Agency for Toxic Substances and Disease Registry, 1999). Mixing the sugar cane matter with special catalysts enables the material to break down and produce hexane as a product. Nearly all 50 states in the US have at least 1 facility that produces hexane; Texas currently has about 120 facilities, the largest number of hexane producing facilities in America (Agency for Toxic Substances and Disease Registry, 1999). These two compounds may be toxic or dangerous if excessive quantities are handled or used inappropriately. However, they are much safer and cleaner than the large majority of the current chemicals used in the production of solar cells. Graphene was originally intended to be used in this experiment but the project proceeded without it. The addition of transparent layers of conductive graphene may have

improved the efficiency of the solar cells by a large factor and will need to be tested in greater detail in the future.

Chlorophyll Extraction Process and Solar Cell Configuration

First, whole leaves of a chlorophyll rich plant species are collected by hand. The leaves are then trimmed using scissors to remove the petiole, mid rib, and any leaf veins. The leaf blades are then trimmed further to achieve the smallest size of leaf without causing too much damage to the fragile chlorophyll cells. Next, the blade particles are placed into an Erlenmeyer flask with sufficient volume to contain all the blade pieces and ethanol. Ethanol is then poured into the flask containing the blades. The amount of ethanol should be enough to completely cover the leaf blades. The flask is then swirled lightly for approximately 30 seconds to ensure the ethanol has saturated the plant matter. The flask is then left undisturbed for approximately 24 hours in a completely dark location. The mixture of ethanol and leaf blades is run through a Buchner flask to separate the particulate matter from the chlorophyll-containing ethanol and stored in centrifuge tubes. Depending on the amount of ethanol in the centrifuge tube a complimentary amount of hexane is added. The hexane will ensure the separation of the chlorophyll from other less dense material. Approximately 2mL of hexane is added to each centrifuge tube and the tubes are weighed to correctly balance the tubes in the centrifuge. The tubes were then centrifuged for approximately 5 minutes around 5000rpm. Two distinct layers are formed and the chlorophyll is pipetted away. At this time a small double sided-copper plate approximately 3 inches long and 2 inches wide is cut from a larger sheet. The copper then gets scoured by a fine course sand paper in order to allow the chlorophyll to have a good contact surface. The now semi-rough copper plate is placed in a shallow beaker that is as close to the shape of the plate as possible. The chlorophyll solution is then poured into the shallow beaker

covering the entire surface of the copper plate. The beaker is then left to sit undisturbed in a dark room until everything except a layer of chlorophyll is dried on the copper plate. Finally, negative and positive sheathed copper leads are then soldered onto opposite sides of the copper plate and the solar cell is complete. At this point, sensors can be connected to the leads to take various readings. A small battery can be connected to collect and store the power from the photosynthetic solar cell using chlorophyll for later use.

Chapter 4

Anticipated Results and Complications

Efficiency of Chlorophyll Based Solar Cells

It was estimated that the efficiency of a single solar cell produced from this method performed at less than 1%. Although sensor data was unavailable, a current could be detected using an ohm meter. Even though this number is small it does in fact confirm the hypothesis that living chlorophyll can be extracted and used to transfer light energy into electrical energy. However, a number of things can be done to improve the efficiency of the solar cell as long as the necessary resources are available. Varying the configuration of the cell, improved layering techniques, utilizing conductive material such as graphene to enhance electrical transfer, extracting chlorophyll from multiple sources, and varying methods of extraction can all be utilized to enhance the performance of a photosynthetic solar cell using chlorophyll.

Longevity of Chlorophyll and Solar Cell

Chlorophyll is a fragile component and functions most efficiently in its natural setting such as inside of a plant or algae cell. Degradation occurs rather quickly once outside the plant cell. Chemicals and large amounts of turbulence can also damage the chlorophyll. Sunlight will also cause the chlorophyll to decompose. One aspect of the future of this field is to develop a way in which the chlorophyll can be harmlessly extracted, applied, and then kept stable for an extended period of time. The solar cell created that utilized a single layer of ethanol and hexane chlorophyll that is open to the air was estimated to last anywhere between 30 minutes to 2 hours in sunlight. With improvements mentioned previously it may be possible to adequately maintain chlorophyll for much greater amounts of time. However, this does not mean that the cell is

totally useless now. If extracted in large enough quantities a chlorophyll paste can be made. This is used to apply another layer of chlorophyll onto the solar cell plate, thus replenishing the cell.

Sustainability and Affordability

The production of flora with high concentrations of chlorophyll on a large scale is currently happening all over the world. Soybeans and spinach, two common edibles that have high amounts of chlorophyll, make up a sizeable portion of the crops currently grown in America. The methods by which the majority of these plants grown on a global scale can sometimes be questionable and arguably not the most sustainable compared to “organic” farming methods. This is an issue that has been up for much debate for the last 3 or 4 decades. To this day the future of farming is rather still ambiguous. Regardless, history has shown that many plants can be grown sustainably and responsibly on a commercial scale. Crops that are used in applications such as these also take less hassle to grow. If used in an electrical application, the plants do not necessarily have to pass standard food and health regulations as they are not being ingested. This takes a lot of pressure off of those who are growing the crop. The extraction process of chlorophyll on a commercial scale is also currently happening around the world. The methods and chemicals vary depending on how the chlorophyll will be used and in what state it is most beneficial for a specified task.

Many of the floras sought after for high chlorophyll concentrations are relatively cheap to produce. Things such as cleanliness and yield of crops are not as important compared to the same crop grown for food production. This makes the cost of growing less expensive to produce useable plants. Ethanol and hexane are also relatively cheap chemicals and offer a mostly non-toxic solution for large scale extractions. Corn has also been considered as a low cost plant that can provide chlorophyll as well as ethanol in large amounts that could even be subsidized by the

government to be grown. Current silica solar energy is comparable if not more expensive in price when compared to other fuel sources like coal, wind, or natural gas. This is due to the large amount of materials used and extensive manufacturing process of silica. By utilizing renewable plants that are currently in production the need for extra processes like mining becomes unnecessary and money as well as the environment is spared. If done properly and efficiently this process of producing photosynthetic solar cells using chlorophyll can be completed in a very affordable and sustainable manner.

Chapter 5

Implications of Research

Sustainable Solar Cells

The need for sustainable, clean, cheap, and effective methods of energy is greater now than ever before in history. Postulations of global warming, polar ice cap melting, and general global concern about energy dominate news headlines every once in a while. Many are concerned about the future of energy for America and the rest of the world. Having the ability to manufacture an effective and low cost solar cell made from something as renewable as a corn or spinach plant would be extremely helpful in the scheme of energy demand and usage. It is evident that further intensive focus and research needs to be given to a project like this in order to create something in the best manner possible on multiple levels. As with any idea or science, the experiment must be worked on and scrutinized by a number of people in order to make something truly unique and hopefully world changing. If this concept is perfected and chlorophyll containing organisms can be utilized effectively and efficiently it may very well revolutionize the world of renewable energy. A sustainable and non-toxic solar cell would greatly reduce the need for large scale excavation and manufacturing of silica. Such an innovation would allow us to cut down on energy costs and reduce future impacts on fragile and non-renewable ecosystems.

Ease of Manufacturing and Replacement

As mentioned before, the process of extraction has been around for centuries and could even be considered to be perfected in these modern times. With the aid of technologically advanced machinery and computer systems, manufacturing on large scales has never been easier.

Copper is used in thousands of manufacturing processes and is readily available. Many techniques of coating something like a copper plate also exist. Even without the aid of machinery this process of extraction and manufacturing can even be done at home if one were so inclined. It does however seem necessary to replace the chlorophyll at some point as the cells eventually dry out and perish. Theoretically, this should be as simple as reapplying a chlorophyll coat on the solar cell surface. In a future design of ours, it has been proposed that the chlorophyll come in something similar to a rectangular case in which old cases containing the decomposed chlorophyll are slid out and a new case be slid in. Once the process of keeping chlorophyll alive in a suitable environment is perfected, this step will be easier than changing a light bulb.

Job Market

Production of something like a multiple component device such as a photosynthetic solar cell utilizing chlorophyll on a large scale would create a sizeable job market in many different fields. The production of the organism deemed best suited for chlorophyll harvesting would have to be cultivated and harvested, therefore increasing the need for those who are skilled in agriculture, aquaculture, botany, phycology, and other fields. Chemists, as well as technicians, would be needed to carry out the extractions on a large scale. Technicians and engineers would be necessary in building and manufacturing the cells. Positions would also be available for the installation process of the solar cells. On the back end or production, another job market for replacing the chlorophyll and maintenance on the cells would be created. Those who have knowledge of modern silica solar cells would also be appropriate to repair, maintain, and regulate the solar cells.

Implementation of Solar Cells into Less Wealthy Countries

The possibility of small scale extractions utilizing local crops and potentially available extraction chemicals makes this project feasible for use in less wealthy countries that have difficulty obtaining electricity. This could be a slippery slope as the potential of unsustainable production of chlorophyll is possible. If a particular flora is seen as a potential energy source it may lead to over harvesting and can cause deforestation. It should be noted that this method is only applicable if a renewably sustainable chlorophyll containing organism can be steadily produced. It would be unreasonable for this type of solar cell to replace all renewable energy resources, as it would with any green technology on its own.

Clean and green energy is most effective when working in conjunction with other green technologies. This method of cooperative energy production alleviates the strain on any single resource and evenly disperses the demand amongst a handful of separate sources. It is crucial to understand this concept of *collective sustainability*. While a perfect photosynthetic solar cell that utilizes chlorophyll may sound like a cure-all, it most certainly is not. We propose that the best and only way to have complete renewable sources of clean energy is to collaborate and synergize all possible green technologies globally. We only hope this humble organic solar design will someday grow and be utilized in a clean and sustainable way to alleviate some of the energy pressures in a continuously power hungry world.

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Time Table for Project

September 15th, 2012

Task 1. We ordered measurement equipment for solar cells.

October 1st, 2012

Task 2. Performed more extensive literature review on the topic of organic solar cells and the history of silicon solar cells.

January 1st, 2013

Task 3. We constructed photosynthetic solar cells utilizing literature review and acquired materials.

February 3rd, 2013

Task 4. We characterized each photosynthetic solar cell by monitoring the battery voltage and current, and the light level.

March 1st, 2013

Task 5. We monitored the battery voltage and current of each photosynthetic solar cells that utilizes chlorophyll.

April 25th, 2013

Task 6. Completed Thesis paper on entire project using recorded data and experience from experimentation.