Introduction to Green Chemistry: Solar Energy Devices Made with Natural Dyes

Introduction

In the course of your lifetime, you have observed significant dependence of the economy on hydrocarbon-based fuels. You have seen the price of standard petroleum fuel increase drastically due to the dwindling supply of feedstocks (or current availability). The terms global warming and alternative energy have become part of your everyday lives.

The pictures above show two cars that have been designed to run on solar energy. The picture on the left is from 1975 and was built to publicize the potential use of solar energy. The picture on the right displays a car that was built in 2007 to use in solar car races. Though the potential for solar cells and their usage in the lives of humans is great, little progress has been made in incorporating solar energy into our everyday lives. Why might this be?

As humans continue to progress, we have become continually aware that it will be necessary at some point in the near future to incorporate alternate energy resources and renewable energy sources, such as hydrogen and bio-fuels as well as solar and nuclear energy, into our progress. The purpose of this lab is to develop an understanding of how solar cells are made and how they function.

Solar cells, or photovoltaic cells, are made out of semiconductors (materials with a gap between the conduction and valance bands). Figure 1, below, shows the general design of a traditional solar cell. The primary component of a solar cell is the junction between $p$-type and $n$-type semiconductors. An $n$-type semiconductor contains extra electrons (“$n$” stands for “negative”), while the $p$-type semiconductor has a deficiency of electrons (“$p$” stands for “positive”). In the most simplistic explanation, when sunlight (i.e., photons) hits the cell, electrons in the $n$-type semiconductor absorb the energy and transfer to “holes,” that is, missing electrons, in the $p$-type semiconductor. This flow of electrons creates a current. When metal or conductive contacts are placed on the top and bottom of the $p$-$n$ type semiconductor junction, the current can be drawn off to use as electricity.
The primary material used in the design of traditional photovoltaics is silicon. Silicon atoms have the electronic configuration of \(1s^22s^22p^63s^23p^2\). Silicon exhibits bonding modes similar to those of carbon, in that it will typically form four bonds to other atoms to satisfy its octet. In crystalline silicon, each silicon atom features bonding to four other silicon atoms via single bonds. Thus all four of the silicon valence electrons are involved in bonding that results in the formation of a very strong crystalline tetrahedral network of silicon atoms.

Because each electron in the silicon’s valence shell would be involved in bonding, it does not exhibit great conducting properties. However, if some of the silicon atoms are replaced with other atoms (this is called doping), the properties of the material can change drastically. An atom with an electronic configuration of \(1s^22s^22p^63s^23p^3\) has five valence electrons, providing an extra electron to the semiconductor. An example of such an \(n\)-type dopant is phosphorous. In fact, silicon doped with phosphorus is an \(n\)-type semiconductor. Likewise, if atoms having only three valence electrons, such as boron, were doped into the silicon, a “hole” (missing electron) would exist in the network, making a \(p\)-type semiconductor.

The anti-reflective coating on the solar cell allows for more photons to be absorbed by the cell, which increases the efficiency of the cell. The efficiency refers to the amount of incident light that is converted into usable electricity. More recent research has focused on increasing the efficiency of photovoltaic devices in addition to decreasing the cost. Single crystal silicon devices are relatively expensive and difficult to prepare so methods that rely on simpler methods of fabricating the devices would allow them to be more broadly implemented. There are several other types of devices that attempt to provide lower cost and are easier to produce. One method involves the incorporation of wide-band-gap semiconductors (typically in nanoparticle form) with chromophores, or molecules that absorb light. These types of solar cells are typically called dye-sensitized solar cells. Several wide-band-gap semiconductors are available, including oxides of titanium, tin and zinc. These dye-sensitized solar cells are easy to fabricate and can be made to cover large areas, such as the roof of a house. However, the efficiency of such cells is much lower than the efficiency of the silicon based devices. In order for these types of cells to be competitive, the efficiency needs to be improved; that is the goal of much of the current research involving these devices.
In these dye sensitized solar cells, the dye molecules absorb the light and an electron gets promoted to an excited electronic state. Once the electron is in the excited state, it can be transferred to the TiO$_2$ nanoparticles, and it will be collected by the conductive electrode. The transfer of the electron from the dye molecule to the TiO$_2$ leaves the dye in a positively charged (oxidized) state. The I/I$_3$ electrolyte solution is there to ensure that the dye molecule is reduced back to the ground state (neutral form) so that it can absorb another photon. Figure 2 shows a schematic diagram of a typical dye sensitized solar cell.

![Dye-sensitized solar cell components. Picture drawn by Ryan Murphy, Berrie Research Group (former Chem 189 Student).](image)

Dye-sensitized solar cells have many advantages. One is their relatively low cost, as the materials used for the assembly of these cells are significantly cheaper than those employed in the standard silicon-based photovoltaic devices described above. Efficiencies of dye-sensitized solar cells are typically lower (<10%) than silicon-based devices, which have efficiencies around 40%. The efficiency is a measure of the amount of energy generated per incident photon and tells you how much of the light energy is actually being converted to useful work. Typically, the dyes used in the dye-sensitized solar cells are inorganic, or metal-containing, chromophores. However, solar cells can also be made with natural, organic dyes, as will be done in this laboratory experiment. You will build some of these dye-sensitized solar cells and test their performance under a variety of conditions. In addition, you will be given the opportunity to make modifications to the procedure in order to modify the cells. You will investigate what effect your modifications have on the performance of the cells. You can measure the voltage and current generation of these devices under different lighting conditions to test their performance.
Pre-lab

Safety: Goggles must be worn at all times. Do not dispense or use organic solvents (e.g., acetone or ethanol) until all candle flames have been extinguished. Wait for a go-ahead from your TA before dispensing any acetone or ethanol.

Conductive glass slides become hot to the touch during flame treatment. The glass must be handled with tongs during and after flame treatment, to avoid burns.

Any tools used to cut Parafilm have sharp edges; glass slides may also have sharp edges. Handle cutting tools and glass slides carefully to avoid cuts and scrapes.

Dispose of acetone rinse waste in the non-halogenated solvent container. Dispose of the excess titanium oxide waste in the labeled container.

Pre-lab Assignment: Please write out the following in your lab notebook. This assignment must be completed before the beginning of lab. You will not be allowed to start the experiment until this assignment has been completed and accepted by your TA.

1) Briefly describe the objectives of this experiment.

2) Write out the experimental procedure in your lab notebook according to the “Guidelines for Keeping a Laboratory Notebook” handout. Your procedure must be at least 1-2 pages in length for this experiment.

In addition to these pre-lab requirements, a short quiz will be given at the beginning of lab based on the material in this lab write-up.

Procedure

Part 1 - Building a Dye-Sensitized Solar Cell

In this part of the experiment, you will build a crude solar cell using a natural dye and test its performance. In this case, your dye molecules will be the part of the blackberries that are responsible for their dark purple/black color. Ideally, you would like a dye molecule that would absorb all of the wavelengths of light that the sun is emitting, in order to make the most efficient cell. How could you learn more about the absorbance spectrum of your blackberry dye? Follow the procedure outlined below to build a functioning solar cell. Take digital photos of important steps in the production and assembly of your solar cell. Include at least five such photos in the experimental section of your report. You must be sure to follow the instructions carefully, because if you assemble the cell incorrectly, it will not function properly and you will have to rebuild the cell again. If you have questions, be sure to ask your TA.

1. Obtain a set of alligator connectors (one red and one black per group). Attach the black connector to the middle socket and the red connector to the right socket of a digital multimeter. Obtain two pieces of conductive glass. Using the digital multimeters around the lab, determine which side of each piece of glass is conductive (set the multimeter to the Ohms setting and determine the side of glass that has a measurable resistance).
2. Using a minimal amount of acetone, rinse one piece of glass, keeping track of which side is conductive. Place 4 pieces of tape on the conductive side of the glass so that 3 sides have tape only 1-2mm in from the edge and the 4th side has tape 4-5mm from the edge. (You will need to connect a voltmeter to the conductive side of the glass, so you need to leave room to put the cell together and make the measurement.)

3. In a mortar, combine 1.5 g of titanium oxide (TiO$_2$ nanoparticles) and 8.5 g of deionized water. Thoroughly grind these together to a uniform consistency with the pestle. While grinding, add 0.015 g of tri mesic acid. The mixture will become very viscous. Continue to grind for 15-20 minutes.

4. Using a glass rod, place 3-4 drops of the titanium oxide suspension onto the un-taped portion of the conductive glass. Gently roll the glass rod across the top of the conductive glass to make an even, thin coating of the suspension on the surface. (If the coating gets too thick, wipe it off with a Kimwipe and try again.) Allow the suspension to set for 10 minutes. Remove the tape, and then place the slide in the oven for 1 hour.

5. Obtain 3-4 blackberries in a Petri dish. Add 10 mL of deionized water to the dish and crush the blackberries with a spatula or your hand. Set this aside for later use.

6. Rinse the second piece of conductive glass with ethanol. Hold the conductive side of the glass over the flame of the candle using tongs. This will provide a coating of carbon on the surface. Conductive glass slides become hot to the touch during flame treatment. The glass must be handled with tongs during and after flame treatment, to avoid burns.

7. When the titanium oxide-coated plate is ready to be removed from the oven, let it cool to room temperature. Place this glass in the blackberry mixture with the coated side down and soak for 10 minutes. Remove the glass from the mixture and rinse with deionized water. Then, rinse the glass with ethanol and gently blot dry with a Kimwipe.

8. Obtain a piece of Parafilm large enough to cover the entire glass piece. Lightly place the piece of Parafilm over the glass with the titanium oxide coating. Remove the paper backing off the Parafilm and lightly trace an outline of the coated section onto the Parafilm with a pen. Gently lift the Parafilm off the glass and cut out the rectangle from the middle of the film. (Any tools used to cut Parafilm have sharp edges; glass slides may also have sharp edges. Handle cutting tools and glass slides carefully to avoid cuts and scrapes.) Place the Parafilm back onto the piece of glass so the rectangle lies over the coated portion of the surface. Put the Parafilm pa-
per on top of the Parafilm and gently rub to cause the film to adhere to the glass. Remove the paper carefully from the corner making sure not to pull up the Parafilm. This leaves a well over the titanium oxide surface:

9. Place 3-4 drops of the iodide electrolyte solution in the well of the glass plate. Place the carbon coated glass plate over the titanium plate so that the two plates are offset, as shown in the image below:

![Diagram of Parafilm and TiO2]

10. Make sure that electrolyte solution covers the entire coated section of the titanium oxide glass. Use small binder clips on each side to hold the plates tightly together. Make sure there are no bubbles between the glass surfaces, especially in the iodine solution. Also make sure that no electrolyte solution has spread out onto the exposed surfaces of glass. Use a Kimwipe to remove any excess electrolyte solution.

![Diagram of Carbon coated glass and TiO2]

**Part 2 - Testing Your Solar Cell**

In this part of the experiment, you will measure the current and voltage produced by your solar cell when it is exposed to light of different types.

1. Test the device by attaching the voltage probe to it using alligator clips, connecting the red clip to the conductive side of the carbon plate (known as the counter electrode or positive electrode) and the black clip to the conductive side of the titanium oxide plate (the negative electrode).
2. Place the device in direct sunlight to obtain results for “outdoor light.” Use the multimeter to measure the current (in $\mu$A, microamps) before and after exposure of the cell to sunlight. Also measure the voltage (in V) before and after exposure of the cell to sunlight.

3. Place the device in the light of an overhead projector to measure performance under “indoor light.” Use the multimeter to measure the current (in $\mu$A, microamps) before and after exposure of the cell to the light. Also measure the voltage (in V) before and after exposure of the cell the light.

4. Test the device in two other locations of your choice or as directed by your TA.

5. Examine the effect that the incident angle of light has on your solar cell. Place your solar cell directly below the light of an overhead projector with the titanium oxide plate facing up towards the light. Define this position as 0 degrees. Rotate your solar cell clockwise in 45 degree increments until you have made a complete circle. At each position, record the current produced.

You may find the following data tables helpful when you organize your results:

<table>
<thead>
<tr>
<th>Location</th>
<th>Maximum Current ($\mu$A)</th>
<th>Maximum Potential (V)</th>
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Table 1 – Meaningful and Descriptive Title that Includes the Type of Device that was Tested

<table>
<thead>
<tr>
<th>Location Tested</th>
<th>Current at Specified Angle ($\mu$A)</th>
<th>0°</th>
<th>45°</th>
<th>90°</th>
<th>135°</th>
<th>180°</th>
<th>225°</th>
<th>270°</th>
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Table 2 – Meaningful and Descriptive Title that Includes the Location Tested

After you have completed your experiment, disassemble and clean the solar cell. Rinse the carbon electrode with water and blot dry with a Kimwipe. Place this plate in the counter electrode container. Remove the Parafilm from the titanium oxide electrode and gently wipe the surface with a Kimwipe moistened with ethanol. Blot the glass dry and place in the titanium oxide electrode container. Dispose of acetone rinse waste in the non-halogenated solvent container. Dispose of the excess titanium oxide waste in the labeled container, using ethanol and a paper towel to remove the residue.

**Part 3 - Devise and Test a Hypothesis**

1. Week 1: now that you have successfully built and tested a solar cell using blackberries as a molecular dye, discuss with your group ways to either modify or improve upon this design. **You must submit to your TA by e-mail a list of 3 potential modifications, in order of preference, and a brief (at least 1 sentence) explanation concerning why you chose that modification.** Your TA will then verify with you, by e-mail, whether the materials and equipment for your modification can be provided. If the appropriate materials and equipment cannot be provided, then you may have to work with your second or even third choice.
2. Week 2: Build your solar cell based upon the procedure in Part 1 and your proposed modification.

3. Week 2: Test your solar cell by following the procedures in Part 2.

**Report**

Your lab report should be a formal, individual report prepared according to the “Guidelines for Laboratory Reports” you have been given. In addition to the categories discussed in these guidelines you should provide answers to all the questions posed in this laboratory experiment write-up as well as addressing the following:

1. Explain how the solar cell works. Your explanation should consider the following: What reactions are occurring in the solar cell that allows a current to be observed? Identify the red-ox equations related to these reactions. What purpose does the electrolyte solution serve in the solar cell?

2. Examine the procedure for creating your solar cell.

3. Evaluate the power generation of your solar cell as demonstrated by Table 1. Did your cell produce a significant amount of current? Can this current be directly converted into energy that would power a light fixture?

4. Consider the angle dependence of your solar cell as demonstrated by Table 2. What practical implications might this have on using a solar cell to generate electricity?

5. Explore the functionality and ruggedness of your solar cell. If you used your solar cell to power an actual device, such as a flashlight, calculator, or watch, what problems might you encounter? Hint: consider your answers to points 1-4.

6. Evaluate your solar cell modification. What reasoning did you use when you made your modification? Was your reasoning valid? Did your solar cell improve?

7. Discuss at least one additional topic of your choice concerning this experiment. If you cannot think of an original topic, feel free to explore a previous topic in more detail.

8. Include at least five photos throughout the report.

9. Don’t forget to include an error analysis and answer any other questions posed in the body of this write-up!

Each of these points should be addressed with at least one well-developed and structured paragraph. Reminder: your paragraphs should include a topic sentence and at least 4-6 full sentences supported by specific data and sound chemical reasoning.

**Reference**