Created by Simon P. Garcia, Department of Chemistry, Kenyon College ([garcias@kenyon.edu](mailto:garcias@kenyon.edu?subject=VIPEr%20Learning%20Object)) and posted on VIPEr in August 2010. Copyright Simon P. Garcia, 2010. This work is licensed under the **Creative Commons Attribution Non-commercial Share Alike License**. Please visit <http://creativecommons.org/licenses/by-nc-sa/3.0/> for details about this license.

# Dye-sensitized solar cell

### Description

A dye-sensitized solar cell is constructed from a combination of materials, and its performance is tested.

### Team Size

Prepare materials in a team of 3–4, but each person makes a separate device.

### Review Prior to Lab

*Supplement:* “The Chemistry of Excited States,” section E

*Excerpt:* Greg P. Smestad, 1998, “Education and solar conversion: demonstrating electron transfer,” *Solar Energy Materials and Solar Cells*, vol 55, pp. 161–164.

### Exercises

*Supplement:* “Education and solar conversion: Study Questions”

### Prelab Skills

Prior to this experiment, you should master the following concepts and skills, in addition to those from previous experiments:

* Identify the composition and function of each component used in a dye-sensitized solar cell.
* Relate voltage and current to power.
* Calculate surface-area-volume ratio for material of spherical crystals.

### Postlab Skills

After completing this experiment, you should also be able to:

* Describe the chemical and physical processes that occur in each component.
* Describe the properties of materials that allow each component to function.
* Describe and explain the dependence of cell voltage on output current.

## Introduction

A photovoltaic solar cell is a device that converts the photon energy of sunlight into electrical work. You may have already seen one such device: a silicon solar cell. These devices were originally used for space satellites, which needed their own, self-contained sources of energy, but in the last few decades people have been installing silicon solar cells on their roofs. These cells are efficient, robust (typical warranty is 20 years, but most last twice that long) — and expensive ($12,000–$20,000 to power a small, energy-efficient home). Fabricating them requires specialized equipment and highly purified elemental silicon, which does not occur naturally. Although silicon solar cells are steadily dropping in price, are there less-expensive types of cells?

In this experiment you will make a different type of device: a dye-sensitized solar cell (DSSC). A DSSC is not as efficient or robust as a silicon cell, but it is much less expensive, uses readily available laboratory equipment, and is made of materials that occur naturally or can be made inexpensively. In building the cell, you will become familiar with the way that materials are selected, processed, and combined in order to make a working device. As you read about, and then construct this cell, think about the properties of each material that makes the solar cell work as a useful device.

To the user, only two parts of a dye-sensitized solar cell (DSSC) matter: the electrode, where electrons flow out of the cell, and the counter electrode, where electrons flow back in. To get useful work from a cell, you connect the electrodes to a **load** (such as motor, phone, light, or battery), which forms an electrical circuit. As electrons flow through this circuit, they do work on the load. To understand how a solar cell works, however, we must peek inside the cell, and examine everything between the electrodes.

A DSSC is highly heterogeneous and contains several internal components. These components are arranged in layers with special structures, each containing a different material (or mixture of materials). This heterogeneity helps separate different chemical processes from each other in the same way as a cell membrane or a salt bridge in a galvanic cell.

The components of a DSSC include:

* **Electrode.** The electrode is made of fluorine-doped tin oxide (FTO), which is sometimes notated as F:SnO2. Like many metal oxides, FTO is conductive, but not as conductive as metals. The electrode cannot be a metal because metals reflect light effectively, which would defeat the purpose of a solar cell. FTO, in contrast, is transparent, so it transmits light into the solar cell, while conducting electrons out of the cell.
* **Substrates.** A *substrate* is any component that supports another component. The SnO2 electrode is so thin that it would shatter in a breeze, so it must be attached to a substrate as a coating. In this case, the substrate is a piece of glass.
* **Dye.** The dye is a molecule that absorbs visible light, enters an excited state, and transfers an electron to an electron acceptor. The dye must be conjugated (to absorb visible light) and it must bind to the acceptor. Upon excitation, the dye becomes an electron donor and transfers an electron to the…
* **Photoanode.** This porous film functions as both an electron acceptor and electron conductor. The film is made of TiO2 nanoparticles, each about 10 nm in diameter, connected together to form a highly branched network of material. It has a large surface area and can thus support a large number of dye molecules. When an excited dye molecule transfers an electron to the film, the electron flows through the conducting TiO2 network until it reaches the electrode.
* **Counter Electrode.** After the electrons have run through the load and done work, they arrive at the counter electrode, which is just another SnO2 layer sitting on a glass substrate. The counter electrode must deliver electrons back into the DSSC because the dye molecules are positively charged and must be neutralized. To ensure a high rate of electron transfer, the counter electrode is coated with a catalyst, such as carbon or platinum. Unfortunately, the dye molecules are tucked away inside the porous film, so we need to transfer electrons through an…
* **Electrolyte solution.** The voids in the porous film are filled with a mixture of iodide (I–) and tri-iodide (I3–). I3– ions are reduced to I– at the counter electrode. The I– diffuses through the void until it reaches an oxidized molecule. The dye is reduced, and I– is oxidized back to I3–, which then diffuses back to the counter electrode and starts the process all over again.

In our particular design, each material is specifically chosen for having the right combination of different properties. For example, nanocrystalline TiO2 is ideal for the following reasons:

It has a high surface area, allowing it to bind many dye molecules.

It is an electron acceptor compared to an excited-state dye molecule.

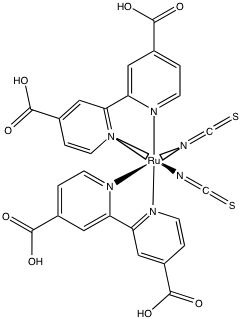
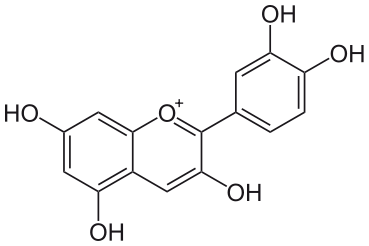
It is conductive, allowing injected electrons to flow to the electrode.

It readily forms bonds with oxygen-containing functional groups, so it binds dye molecules easily.

What properties does the dye need? Obviously, it should absorb visible light, but other properties are important, too. The design of commercial DSSC dyes is currently evolving, but most of them are variations on the ruthenium(II) complex shown below. It is known informally as the “N3” or “ruthenium-535” dye. This dye is special for two reasons. First, it has carboxyl groups attached to the bipyridine ligands. These carboxyl groups readily bind to TiO2, and thus anchor the dye to the porous film.

Second, this dye has large, conjugated ligands bound to a large transition metal. Like tris(bipyridine) ruthenium(II), [Ru(bpy)3]2+, this coordination complex can absorb visible light through a **metal-to-ligand charge transfer** (**MLCT)** transition, and convert into the excited state 1MLCT. The MLCT transition transfers electron density from the metal d orbitals, in the center of the complex, to the ligand π\* orbitals at the edges. (This state rapidly converts into a triplet excited state 3MLCT through an **intersystem crossing**, but the electron density is still concentrated on the ligand.) Because the ligand is attached to the TiO2, the excited electron has a high probability of being accepted by the TiO2, leaving behind an oxidized dye molecule.

This material has one crucial strike against it — it is expensive (~$1000 per gram). The cost is acceptable in large, industrial processes, but prohibitive for our class. For this reason, we will use a class of less-expensive dyes called **anthocyanins**. Anthocyanins are glycosylated versions of **anthocyanidins**. An example of an anthocyanidin is cyanidin (shown below); the corresponding anthocyanin would be cyanidin with a hydroxyl group replaced by a glucose structure. In anthocyanins, the hydroxyl groups are highly acidic (due to resonance with benzene groups) and can bind to TiO2, thus anchoring the dye. Like the N3 dye, anthocyanins are electron donors when they absorb light, although the electron transfer is not as efficient. Anthocyanins are found naturally in many fruits and vegetables, so we will extract a mixture of such dyes from fruits.

**Ruthenium-535 dye (N3)** **cyanidin**

## Procedure

**Prepare conductive glass substrates.** Obtain two plates of conductive glass. The glass itself is not conductive, but one side is coated with a thin (10 nm) film of fluorine-doped tin(IV) oxide (SnO2), which *is* conductive. Identify the conductive side: it will feel rough when you scratch with your fingernail. In addition, it’s resistance is about 10 Ω from one edge to the other. Using a diamond or silicon carbide pen, scribe your initials *lightly* in the corner on the *nonconductive* side of each substrate. Wipe each plate clean using 2-propanol and a soft tissue.

**Prepare a suspension of TiO2 nanocrystals.** Add ~6 g of Degussa-P25 to a mortar. This powder is made of 10-nm nanocrystals, but these crystals are clumped together into larger particles. We must separate them by crushing them and suspending them in water. Add 1 mL of 10 mM acetic acid, and then grind the powder with the pestle for 1–2 minutes. Do this in a fume hood, and *avoid inhaling the powder!* Add 1 mL of acetic acid and grind again, using a circular motion for about 1 minute. Some of the suspension will start to climb up the sides of both the mortar and the pestle; use the pestle to scrape it back down into the mortar. Repeat this process, adding 1 mL of acetic acid at a time, until you’ve added a total of 8 mL. Once the suspension becomes smooth, scrape suspension off the pestle with a paintbrush, and use the paintbrush for mixing. Your suspension should have no lumps in it, and it should flow easily. This recipe makes enough for 3–4 people to share, so coordinate with others and spread out the work.

Over time, intermolecular forces will cause the particles to aggregate and form a compact layer. Adding a *surfactant* will help to spread them out, leading to a porous layer. Add a drop of lab soap.Stir it *gently* into the suspension with the paintbrush. The suspension will seem to gel and stiffen up slightly. It should have the texture of thick paint. If its texture is like paste or cake icing, add extra acetic acid 0.5 mL at a time, until it flows easily. If you see any foam, remove them by dabbing the froth with a paintbrush.

To clean the suspension off, wipe thoroughly with a moistened paper towel and discard in the trash (the suspension tends to clog drains, so we want to minimize the amount going down the sink). Wash off any residue with water. Clean the paintbrush by rubbing the bristles gently under flowing water, until no more paint comes out.

**Prepare a uniform coating of TiO2 suspension.** To make a film of porous TiO2, you will coat a piece of glass with the TiO2 suspension and then vaporize the water. The goal is to make a uniform, 40-µm-thick coating on the glass plate. How do you control the thickness of this layer? You could smear the suspension onto the plate, but this approach is not precise enough. The layer would be an unknown thickness, and it wouldn’t be uniform all over the plate. Instead, you will use the “squeegee” technique, in which you define a well with the desired thickness by placing a frame on the edges of the substrate. After filling the well with suspension, you then scrape off the excess that lies above the frame, using an object with a straight edge (the squeegee), such as a razor blade or a glass slide.

Lay the substrate on a sheet of wax paper. Using strips of transparent tape, define a frame on four edges of the substrate. The left and right strips should be as narrow as possible (2–5 mm); the top strip should be 6–8 mm (~ ¼-inch) wide; the bottom strip should be 10–12 mm (~ ½-inch). Make sure the conducting side of the substrate is facing up. Paint the TiO2 suspension uniformly across the substrate. To use a slide as a squeegee, rub the edge against a piece of 400-grit sandpaper to make it smoother; then scrape it across the frame in one, smooth motion to spread the suspension into a film. Repeat this motion several times, adding extra suspension if necessary. Experiment with your technique until the film is uniform. Carefully peel off the tape, without smudging the film, and allow the film to dry for about 10 minutes.

**Sinter the coating to form a porous film.** Place the substrate on a hotplate and heat it to 450 ºC. Sintering removes water and surfactant, and allows individual particles to connect to each together. The layer will be ~10 µm thick after sintering. After 30 minutes, remove the tray from the furnace and allow it to cool for another 30 minutes. **Do not place the hot substrate onto a cool surface as it may shatter spontaneously!** **Do not use cold tongs to touch a hot substrate!**

**Prepare the counter electrode.** Place 10 drops of 1 mM hexachloroplatinic acid (H2PtCl6), dissolved in 2-propanol, on another glass plate (conductive side up). Tilt the substrate slightly and let the liquid evaporate. Heat the substrate on a 450 ºC hotplate for 5 minutes, and allow it to cool for 30 minutes. Upon heating, the hexachloroplatinate will be reduced to Pt. The result is a thin film of Pt nanocrystals that acts as a catalyst for the reduction of I3–.

Alternatively, you can use candle soot to catalyze I3– reduction. Light a candle, and use tongs to hold the electrode (conductive side down) above the flame. Sweep the electrode back and forth through the middle of the flame to make a thin, uniform, gray coating. Use a cotton swab to remove soot from the edges. Heat the substrate at 450 ºC for 15 minutes.

**Prepare the dye.** TiO2 accepts and conducts electrons, but it doesn’t generate a voltage in visible light. The reason why is visibly apparent: TiO2 is white, which means it doesn’t absorb visible light (its band gap is about 4 eV). If you attach a dye to the film, however, it will absorb light and transfer an electron to the TiO2.

Crush or blend ~10 raspberries, or ~20 pomegranate pips, to release the juice. Take the resulting slush and place about 20 mL into a large, 50-mL centrifuge tube. Add 10 mL of water, cap the tube, and shake it a few times. Partner with another group and place your tubes into opposite slots in the centrifuge (to keep the centrifuge balanced). Centrifuge at 4000 r.p.m. for ~10 minutes. The supernatant contains a variety of anthocyanin dyes. Store the supernatant in a labeled vial and refrigerate it until Week 2.

**Sensitize the film.** Transfer the supernatant to a watch glass, place the porous film face down in the dye solution, and soak for 10 minutes. If there are any pale spots in the film, let it soak longer. When the film is completely stained, rinse it (gently!) with water to remove any excess dye, and then with ethanol or 2-propanol to remove the water. Dry your film in a 60 ºC oven for 5 minutes.

**Assemble and fill the cell.** Although the dye and the TiO2 is where the photochemistry happens, the electrolyte solution is crucial for the cell to function continuously. Unfortunately, liquids can leak and evaporate over time. To contain the electrolyte, we will sandwich the two electrodes together, and line two edges to prevent leakage. We need something that is thin, inert, and sticks to both electrodes, and it should be flexible enough that we can work with it easily. A double-sided adhesive should do the trick.

On the photoanode substrate, find the “bottom” edge, which has the widest margin between the porous film and the edge. Apply a narrow, ¼″ -strip of double-coated acrylic tape, such as JVCC DC-4109RS, along this edge and right next to the porous film. Make sure that some of the conductive surface is exposed near the edge; later you will attach an electrical circuit to this surface. Apply another strip on the “top” edge. On this edge, you don’t want any conductive surface to be exposed near the edge, so let the tape overlap the edge slightly. It is convenient to cut off a strip that is longer than the substrate, so you can use two hands to align the strip, and cut off the excess afterward. Run a stirring rod or slide across the strips, while applying firm but gentle pressure, to make sure the tape bonds uniformly with the substrate.

Remove the liner to reveal the adhesive on the other side of the tape. Stack the counter electrode on top of the photoanode, with *both conductive sides facing each other*. Make sure they are offset slightly, so that an edge of each conductive face is exposed on each side. Press firmly. Clamp each side with 2 or 3 binder clips and place in an oven at 75 ºC for 10 minutes. The adhesive is thermoplastic, so it softens upon heating. The pressure of the binder clips will cause the adhesive to fill in any microscopic gaps, thus ensuring a good seal. Let the assembly cool for about 10 minutes before removing the binder clips.

Add the electrolyte[[1]](#footnote--1) solution (containing 0.5 M KI and 0.05 M I2 dissolved in ethanediol) through one of the unlined edges. You only need a few drops. Squeeze the cell a few times to help the solution spread throughout the cell, and wipe away any excess solution.

**Test device performance.** Cut 4 inches of adhesive copper foil. Attach the first 2 inches to the exposed, conductive area of one substrate. Fold the remaining 2 inches into a 1-inch stub. You should now have an electrical lead that you can clip a device to. Repeat this process to make a lead on the other electrode. Attach a digital voltmeter to each electrode. Record the voltage *V* in the light and in the dark. Note that the voltage doesn’t change instantaneously. How long does it take for the voltage to change?

If you’re trying to optimize the design of a solar cell, you need some way to compare different solar cells in a quantitative, systematic way. We will use an overhead projector to illuminate the solar cell. This is cheating slightly, since the point of a solar cell is to generate electrical power from a *renewable resource*, but at least you can test its performance under a reproducible condition. While illuminating the cell, you will attach a load resistor to it and measure its voltage as a function of resistance.

The **open-circuit voltage *VOC*** is one measure of the solar cell’s performance. It is caused by charge separation between the two electrodes, which is sustained by the chemical reactions within the cell. In practical terms, it tells you the energy of each electron at the anode.

Place your solar cell in the center of the overhead projector and illuminate it. (Think: which side should be facing up?) The testing station has a resistor box and a voltmeter connected in parallel. Attach the clips to the leads on your solar cell. To determine the open-circuit voltage, you need to measure the voltage when the resistance is so high that almost no current flows. Set the resistance to the highest setting and record the voltage.

The open-circuit voltage doesn’t tell the whole story. The rate of electrons flow — the current *I* — is also important, because the power produced by a device is determined by both current and voltage: *P* = *IV*. For this reason, we also want to know the **surface power density** *Pd* of the solar cell, which is the power produced by a solar cell per unit area: *Pd* = *IV/A*.

The surface power density depends on the resistance, so you need to measure the power for different resistance values and determine the *maximum* power. Measure the voltage as a function of resistance, starting with the highest resistance. The voltage will decrease as you decrease the resistance. Take a new measurement for every drop of ~25 mV. The maximum power usually occurs when the voltage drops to 60–80% of the open-circuit voltage, so be sure to have several measurements within this range. You can calculate the current at each point using Ohm’s law (*I* = *V*/*R*). Remember to measure the area as well.

### Optional activities

**Seal the cell with epoxy.** If you have time, you can seal the cell completely to prevent loss of the electrolyte. The unlined edges of the cell have a thin gap, which you can seal using “5-minute” epoxy. This viscous liquid quickly turns solid when mixed with a hardener. You really only have 5 minutes to work with it, so set everything up ahead of time. Start by placing a sheet of wax paper on the bench top. Place a piece of tape on each unlined edge of the cell — not on the side, but on the substrate surface. You will eventually fold the tape over the side. Squeeze 5 drops of epoxy and 6 drop of hardener onto opposite sides of a weighing boat. Make sure you have 3 or 4 clean cotton swaps in front of you. Ready? Use a swab to mix the hardener into the epoxy, and stir the mixture thoroughly for 10 seconds. *Place the used swab on the wax paper, not on the bench top*. Dip a new swab into the epoxy and apply it to the gap on each side of the solar cell. If you look through the cell, you should see some of the epoxy seep into the gap, forming a seal all the way across edge. If there are gaps in the seal, rub the swab over the gap to force the epoxy in. Fold the tape over the side. You can take your solar cell home at this point, but wait 24 hours before peeling off the excess tape.

**Seal the cell with glue.** You can also seal the gaps with hot-melt glue, but this method requires some finesse. Attach a piece of tape to one edge of the substrate. Using a glue gun, add a line of hot glue over the gap. Fold the tape over the gap, and press on it (wear gloves!) to distribute the glue over the edge. Wait for the glue to cool before peeling off the tape.

**Play outside.** If it’s a sunny day, take your solar cell outside, with a portable multimeter, to see how it fairs. You can also try to power a simple device, such as an LCD display clock, using your solar cell. Some devices require a certain voltage, so you may need to connect several solar cells in series.

## Analysis

Why does the output voltage depend on load resistance? The voltage of a galvanic cell is the result of net charge separation, which is sustained by electrochemical reactions within the cell. These reactions cause electrons and holes to accumulate at the anode and cathode, respectively. The cell voltage thus depends on the concentration of charges in the electrodes.

For a solar cell to be useful, it must be connected to an external circuit, so that current can flow into the circuit and transfer energy to it. Current flow, however, tends to deplete charges from the electrodes. For this reason, the concentration of charges — and thus the cell voltage — is determined by a balance between charge accumulation (caused by electrochemical reactions) and charge depletion (caused by current flow).

If the external circuit has a high resistance, it restricts electron flow and only allows a tiny current. In this condition, the cell reactions can maintain the charge separation, with little change to the voltage. As you decrease the resistance, the current increases and the rate of charge depletion also increases. Eventually, depletion will be so fast that the cell reactions cannot keep up. The steady-state charge concentration will drop, along with the voltage, and further increases in current will not be possible. The current is thus limited by the rate of redox reactions in the cell.

The behavior of voltage and current in a solar cell implies that the cell’s power depends on resistance as well. The power *P* dissipated by a circuit is given by *P* = *IV*, where *I* is the current flowing through the circuit and *V* is the voltage drop across the circuit, so you can calculate the power corresponding to each data point. How will you find the maximum power density from your calculated values? Think about what variables you will plot and how you will interpret the plot.

## Lab Report

### Introduction

What materials will you use? Draw a diagram of the solar cell in cross section, labeling each component according to its function in the cell.

### Procedure

What materials did you use and how much of each? How did you make functional components out of these materials? Draw diagrams to illustrate how you: (a) coated the substrate with TiO2, and (b) sealed the cell. Record all measurements necessary to calculate the surface power density of your device.

### Analysis

How well does your device perform? Describe how you evaluated its performance. Report the maximum power density of your device, and under what conditions you get this output.

### Attachments

Include any graph(s) necessary to support your analysis.

## Materials and Preparation

### Group Size: 4

Although students make their own devices, amounts below are on a group basis because they work in groups in some steps (to use materials more efficiently).

### TiO2 , Degussa P-25 powder (Aerosil), (6 g per group)

### Acetic acid (0.010 M) or nitric acid (0.001 M), 12 mL per group)

### Laboratory soap solution (1 mL per group)

AP Contrex, 20 g in 1 gallon of water.

### Soft bristle paintbrushes, 1 inch width (1 per group)

### Mortar and Pestle (1 pair per group)

### F:SnO2 coated glass plates, 10 ohm-cm, 2 in. by 2 in., (8 per group)

### Transparent 3M Scotch Tape

### Glass microscope slides and a piece of 400-grit sandpaper (4 per group)

### Fruits or fruit juice

Raspberries, blackberries, pomegranate pips, Bing cherries, cranberries, red cabbage. If frozen, thaw completely.

### Oven set to 75 deg C

### Binder clips, small (12 per group)

### 100 % ethanol or 2-propanol in wash bottles (2 for entire class)

### Hexachloroplatinic acid, H2[PtCl6], in 2-propanol (1 mM, 1 mL per group)

26.4 mg of H2[PtCl6] in 50.0 mL 2-propanol

### Double-coated acrylic tape, polyester-backed, ¼” width, 0.0035” thick (24” per group)

JVCC DC-4109RS has these characteristics.

### Iodine electrolyte solution (20 mL for entire class)

The solution is 0.50 M KI and 0.050 M I2 in anhydrous ethylene glycol. Use solution from ICE kit, or dissolve 830 mg KI and 127 mg I2 per 10 mL of ethylene glycol. Store in flexible dropper bottles for easy application to the device. Store bottles with vermiculite when not in use.

### Strip of adhesive copper foil, ¼” width (16” per group)

JVCC CFL-5CA has these characteristics

### Diamond or carbide scribing pen (2 for entire class)

### Glue gun with hot-melt glue (1 or 2 for entire class)

### 5-minute epoxy (1 for entire class)

### Cotton swabs

### Old hotplates capable of reaching 420 deg C (1 per group)

Because the hotplates will be at the highest setting, they are more likely to burn out. For this reason, use old hotplates that don’t have a stirrer, so that when it does burn out, we don’t lose the stirrer as well.

### Aluminum foil

### Wax paper

### Centrifuge tubes, 50-mL

## Testing Materials

### Resistor substitution box covering at least 10 Ω – 10 kΩ (1 per group)

If multimeters are plentiful, use a 1-kΩ or 500-Ω variable resistor instead.

### Multimeter with alligator-clip leads (1 per group)

If using a variable resistor, use 2 multimeters per group, with one reading voltage and the other current.

### Banana plug cables (2 per resistor box)

### Overhead projector

### Color filters

1. I2 combines with I– to form I3– in solution [↑](#footnote-ref--1)