

Juice from juice

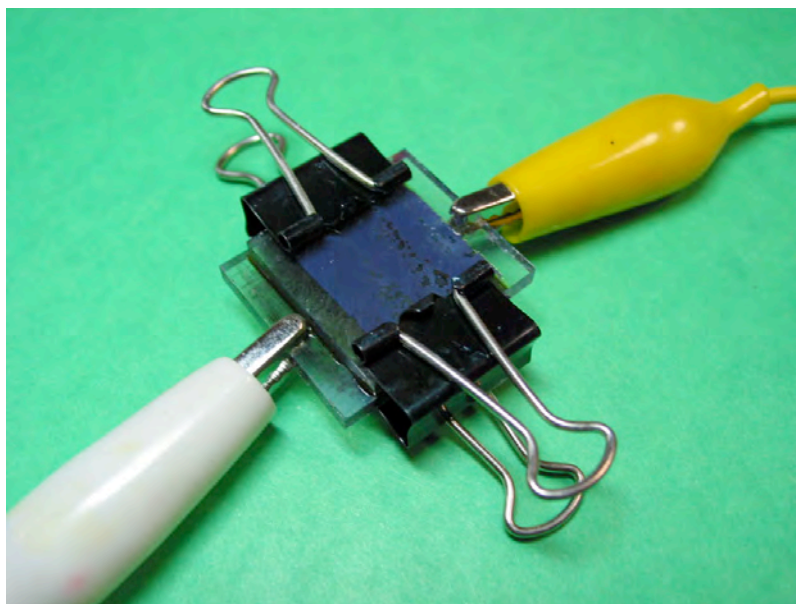
Make your own blackberry juice solar cell

Introduction

With iodine, blackberry juice, and a few simple materials, you can create a working solar cell that mimics the process of photosynthesis. This type of cell is called a *Grätzel cell*. Grätzel cells are in commercial operation and cost half as much as silicon solar cells.

Materials

Distilled white vinegar
Mortar and pestle
Clear dishwashing detergent (Ivory)
Glass stirring rod or similar object
Scotch tape
Blackberries or raspberries
Ethanol or isopropanol
Small shallow dish
Paper towel or Kleenex
Dropper bottle or eyedropper
Washbottle
Distilled water
Soft graphite pencil or graphite stick
Candle
Small binder clips (2 per solar cell)
Multimeter
Two alligator clip leads



Specialty materials

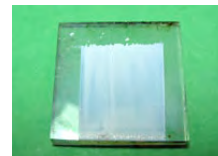
2 conductive glass slides¹
Nanocrystalline Titanium Dioxide (TiO₂) powder²
Iodide electrolyte solution³

To Do and Notice

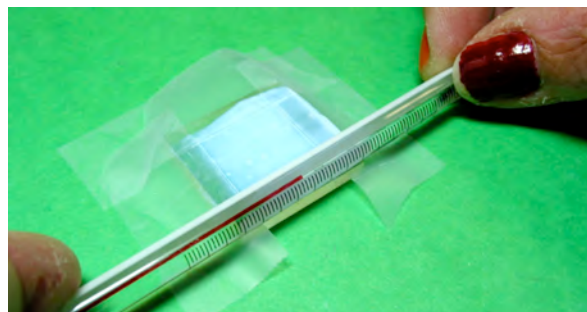
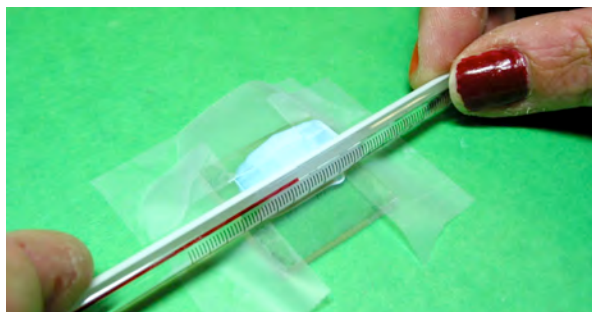
The TiO_2 coated slides and the Iodide electrolyte solution can be prepared ahead of time.

Coat slides with nano Titanium Dioxide

To make the nano Titanium Dioxide suspension, add 10 mL vinegar (or dilute acetic acid) gradually to 6 g Titanium Dioxide, stirring and grinding with a mortar and pestle until smooth and lump-free (about 5 minutes). You should have a smooth solution that looks like White-Out and is just barely thin enough to be taken up into an eyedropper. Add one drop of clear dishwashing detergent, mix lightly, and let sit for 15 minutes. This surfactant, and the grinding, helps break up the nanoparticles. If your detergent makes the solution clumpy, leave it out or try another detergent.



Test one of the glass slides with a multimeter to determine which side is conductive. The side with a resistance reading of 10-30 ohms is the conductive side. Mask about 3 mm on three sides. Extra tape on the sides can help fasten the slide to the table. Drop 3-5 drops of the TiO_2 solution in a row on one side of the slide. Deposit a uniform, thin layer across the unmasked portion of the slide by drawing a stir-rod (a glass thermometer also works well) along the slide.

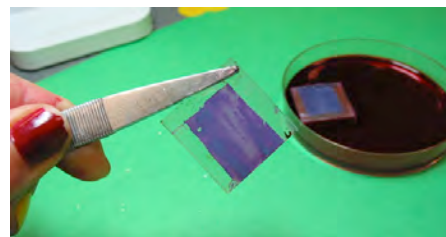


Allow the slide to dry for a few minutes before removing the tape. Place the slide directly on the flame of a gas burner for about 10 minutes, or in an oven broiler for about 60 minutes, to sinter the film. Make sure the slides turn yellow and then white again. Let them cool slowly to room temperature.

The resulting TiO_2 layer is *nanoporous*, meaning that it has pores, like a sponge, which are only a few nanometers (10^{-9} m) wide. The TiO_2 particles themselves are about 20 nm wide. The film is about 7-10 micrometers thick (the thickness of the Scotch tape). The slides can be stored in air for later use.

Stain Titanium Dioxide with the Blackberries

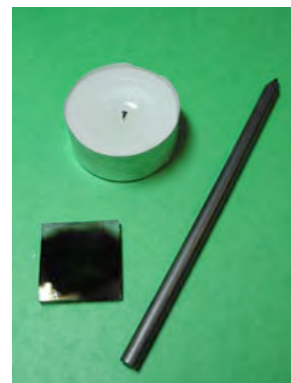
Blend or crush fresh or frozen blackberries or raspberries in a blender or by hand, adding a tablespoon of water for every 10 blackberries, or simply take the juice from the bottom of frozen berries after they have thawed. A different type of dye can be obtained from chlorophyll using green citrus leaves – see the first article under Resources.



Pour a few mm of juice into a shallow clean dish, and place the TiO₂ coated slide face down in the juice for 5-10 minutes. It should be soaked until a deep purple and no white TiO₂ can be seen. Rinse the slides in water, then in isopropanol or ethanol, using a washbottle, and blot dry with a tissue. These films should be used immediately (once dry), or stored in deionized water with acetic acid added (pH 3-4) in a closed, dark colored bottle.

Carbon-coated Counter Electrode

While the films are being stained, prepare the carbon-coated electrode. Use a soft pencil or graphite stick to coat the entire surface of conductive side of the second slide. An alternative is to hold the substrate above a candle flame until it is coated black. Or do both, to be sure!



Assembling the Solar Cell

Place the graphite coated slide face down on top of the dry blackberry juice soaked TiO₂ coated side of the second slide. The slides should be placed slightly offset to allow enough room on the end to place an alligator clip. Use two binder clips to hold the two slides together.



Now with an eyedropper add 1-2 drops of liquid Iodide/Iodine electrolyte solution to the crease between the two slides. The solution will be drawn into the cell by capillary action and will stain the entire inside of the slides.

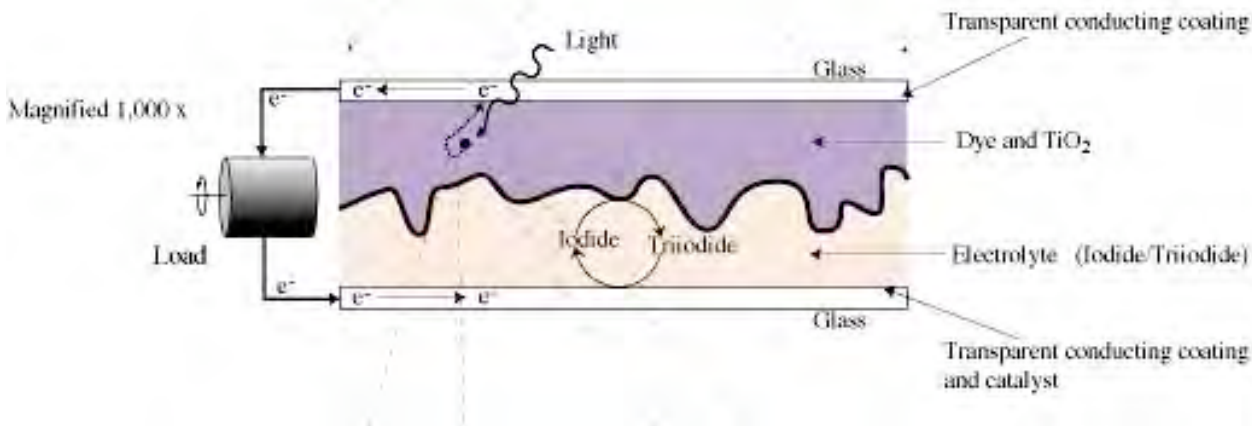
Attach the alligator clips to the two overhanging edges of the slide and attach the clip leads to your multi-meter with the negative terminal attached to the TiO₂ coated slide and the positive terminal attached to the graphite coated slide. Measure both the current and voltage of the cell in direct sunlight and indoors. The maximum voltage in direct sunlight should be about 0.1 – 0.5 volts. You may also attach several cells in series and parallel, to see which configuration will power a small motor or fan.

What's Going On?

In all solar-powered devices, an incoming photon from sunlight boosts an electron from a semiconductor into a state where it is mobile, and can conduct to produce energy. In a semiconductor (as opposed to a metal), there is an energy gap between the valence electrons (which are tightly bound to the atom and unavailable for conduction) and the conduction electrons (which are mobile). TiO_2 is a wide band gap semiconductor. The gap is so wide that energy from sunlight can't excite electrons enough to make them conduct, but sunlight can excite the electrons in the blackberry dye:

$\text{photon} + \text{dye} \rightarrow \text{electron} + \text{dye}^+$. Those excited electrons are transferred from the blackberry dye to the TiO_2 , which transfers it to the electrode, producing electricity. But this leaves the blackberry dye slightly positive (oxidized), and it needs an electron to make it neutral again. That electron is available at the counter electrode (the one coated with graphite). The dye isn't in physical contact with that electrode, so the Iodide/Iodine electrolyte acts like a ferry, bringing electrons from the counter electrode to reduce the dye. It does that by cycling between Iodide (I^-) and Tri-iodide (I_3^-):

$\text{dye}^+ + I^- \rightarrow \text{dye} + I_3^-$. The Tri-iodide is restored to Iodide by taking the electron from the carbon-coated counter electrode: $I_3^- + \text{electron} \rightarrow I^-$. This reaction is catalyzed by the carbon coating (analogous to a docking port for the ferry).



So, the TiO_2 is an electron acceptor, the Iodide is an electron donor, and the dye is a photochemical pump which excites electrons to a mobile (conductive) state. Any porous semiconductor with the right band gap will work, and generally oxides like ZnO , NiO_2 or TiO_2 are used. The dye in blackberries and raspberries is an anthocyanin (called cyanin 3-glycoside and cyanin 3-rutinoside), which makes poppies red. Strawberries and other colored fruits do not work because these dyes do not chelate (bind) to the TiO_2 – only compounds with an $=\text{O}$ or $-\text{OH}$ group will do. The resulting voltage across the cell is the difference in energy between the redox potential of the electrolyte and the conduction band of the TiO_2 .

Etc.

This is the same basic process as photosynthesis, in which chlorophyll replaces the blackberry dye and TiO_2 as a light absorber, and the oxidization of water (to produce oxygen, hydrogen, and electrons) replaces the I/I_3^- cycle, replenishing the electrons released from chlorophyll. In photosynthesis, the resulting voltage is used to generate ATP and NADPH, instead of an electrical current. Ultimately, carbon dioxide acts as an electron acceptor, resulting in the fixing of carbon dioxide.

Additional Resources

Dr. Greg Smestad originally developed this activity, and he has a wealth of information about it on his website at <http://www.solideas.com/solrcell/cellkit.html>

A useful article is Demonstrating electron transfer and nanotechnology: A natural dye-sensitized nanocrystalline energy converter. G. Smestad and M. Gratzel, J. Chem. Ed. (75), 1998, pp. 752-756. <http://www.solideas.com/papers/JCE98.pdf>

Lots more detail in this article: Education and solar conversion: Demonstrating electron transfer. G. Smestad, Solar Energy Materials and Solar Cells (55), 1998, pp. 157-178.

The materials are available from the Institute for Chemical Education (ICE) in a pre-assembled kit good for making 5 solar cells for \$45
<http://ice.chem.wisc.edu/catalogitems/ScienceKits.htm#SolarCell>

Specialty Materials

¹ Precut commercial (2.5 cm x 2.5 cm) TEC 10 or TEC 15 (that's 10 or 15 ohms per square meter) Tin dioxide (SnO_2) coated glass can be purchased from Hartford Glass Co. Inc., PO Box 613, Hartford City, IN 47348; phone 765-348-1282, Fax 765-348-5435, email hartglass@netusa1.net. Price: 50 cents each. They prefer orders over \$50 but will do smaller ones for educational use if you ask. Contact: Mike Reidy.

² Degussa P-25 Titanium dioxide can be obtained from Dorsett and Jackson, at 323-268-1815. If you are outside of California, call Degussa USA to find your local distributor, at 973-541-8536. Dorsett and Jackson only sells large quantities, but I was able to obtain a sample size for free by calling either D&J or Degussa.

³ You can make your own Iodide electrolyte solution by dissolving 0.127 g of 0.05 M Iodine (I_2) in 10 mL of water-free ethylene glycol, then adding 0.83 g of 0.5 M potassium iodide (KI). Stir and store in a dark container.

Nanocrystalline Solar Cell

Introduction

In this activity we will explore photogeneration of electricity using dye-sensitized nanocrystalline titanium dioxide.

Material

Nanocrystalline Titanium Dioxide Powder
Two glass microscope slides
Distilled white vinegar
Dish washing detergent
Small paint brush
Broiler
Blackberries
Distilled water
Small shallow dish
Tweezers
Sand Paper
Pencil
Two binder clips
Iodide electrolyte solution
Eye dropper
Two alligator clip leads
Digital multimeter



To Do and Notice

The TiO_2 coated slides and the Iodide electrolyte solution can be prepared ahead of time.

Nano Titanium Dioxide

To make the nano titanium dioxide suspension, add 9 mL vinegar to 6 g titanium dioxide and mix until smooth. Add one drop of dishwashing detergent and let sit for 15 minutes.

Using a small paintbrush distribute a thin layer of the TiO_2 solution across the surface of one microscope slide. Allow the slide to dry for a few minutes. Place the TiO_2 coated slide film side up in the broiler for 30 minutes to an hour. You will notice the slides turn yellow and then white again. Turn off the broiler once the slides have turned white again and let them cool to room temperature slowly.

Iodide Electrolyte Solution

To mix your own Iodide electrolyte solution, dissolve 0.127 g Iodine (I_2) in 10 mL of ethylene glycol. Next add 0.83 g Potassium Iodide (KI), stir and store in a dark container.

Preparing the Electrodes

Blend or crush fresh or frozen blackberries in a blender or by hand periodically adding distilled water until the mixture is mostly liquid. You should add about a tablespoon of water for every 10 blackberries. Coat the bottom of a shallow clean dish with about 2 mm of blackberry juice. Place the TiO_2 coated slide face down in the blackberry juice for 5 to 10 minutes. While the TiO_2 coated slide is soaking a carbon catalyst layer must be added to the second slide. Scuff up one side of the clean slide using sand paper. Use a soft pencil to coat the scuffed up side of a microscope slide. Make sure the entire surface is coated.

After about 10 minutes the TiO_2 coated slide soaking in the blackberry juice should be stained dark purple. At this point remove the slide and rinse with distilled water. Use a tissue or paper towel to gently dry the slide.

Assembling the Solar Cell

Place the graphite coated slide face down on top of the dry blackberry juice soaked TiO_2 coated side of the second slide. The slides should be placed slightly off set to allow enough room on the end to place an alligator clip. Use two binder clips to hold the two slides together.

Now with an eyedropper add one to two drops of liquid iodide/iodine electrolyte solution to the crease between the two slides. The solution will be drawn into the cell by capillary action and will stain the entire inside of the slides.

Attach the alligator clips to the two overhanging edges of the slides and attach the clip leads to your multimeter with the negative terminal attached to the TiO_2 coated slide, and the positive terminal attached to the graphite coated slide. Measure both the current and the voltage of the cell in direct sunlight and indoors. The maximum voltage in direct sunlight should be about 0.3 to 0.5 Volts.

What's Going On?

TiO_2 is a wide band gap semiconductor. In semiconductors there is an energy gap between the electrons that are tightly bound to the atom, unavailable for conduction, and the electrons that are farther from the atom and free to move and conduct. The blackberry dye is adsorbed on the TiO_2 ; energy from the sun excites electrons in the blackberry dye, which are then transferred to the conduction band in the TiO_2 and through the outer circuit. The blackberry dye is oxidized, so the electrons are replaced by the iodine electrolyte, which in turn obtains electrons from the graphite-coated

electrode thereby completing the circuit. The TiO_2 acts as an electron acceptor, the Iodide/iodine electrolyte solution is an electron donor, and the blackberry dye acts as a photochemical pump to promote the movement of electrons.

Where to Purchase Materials

Nanocrystalline TiO_2 can be purchased from Degussa USA. The product is called Aeroxide TiO_2 P25. www.aerosil.com Phone: 1-330-668-2235

This activity is based on a journal article from Smestad, G.P.: Gratzel, M. *J. Chem. Educ.* **1998**, 75, 752-756.

Converting Photons to Electrons: Build your own Solar Cell

Introduction

Solar cells, also known as photovoltaic cells, convert the sun's energy directly into electricity. Build your own solar cell using common household items to produce up to 50 microamps of current.

Material

Copper sheet, or copper flashing

Metal shears

Electric Burner

Plastic water bottle

Table salt or Epsom salt

Water

Two alligator clip leads

Multimeter



To Do and Notice

Use the metal shears to cut two pieces of copper approximately 3" x 4". Place one piece of copper directly on the electric burner at high heat. As the copper starts to heat up, you will see an oxidation pattern start to form. After a few minutes, the colors from the oxidation pattern will be replaced by a thick black cupric oxide (CuO) coating. Leave the copper plate on high heat for one half hour to develop a thick black oxide layer. After one half hour turn off the burner and let the copper sheet slowly cool on the burner allowing the cupric oxide layer to flake off exposing a reddish-orange cuprous oxide (Cu_2O) layer underneath. Once cooled, remove the copper plate from the burner and gently flake off the remaining black cupric oxide using a paper towel or by running water over it.

Cut the top off of the plastic water bottle. Bend both the heat-treated copper plate and the clean copper plate to fit on the inside of the plastic water bottle. The two

sheets should not touch. Next attach an alligator clip to each sheet and attach the positive terminal of the meter to the clean copper plate and the negative terminal to the cuprous oxide coated plate.

Dissolve two tablespoons of salt in about two cups tap water, and fill the water bottle with salt water leaving about an inch at the top to avoid getting the alligator clips wet.

Once the cell is complete take a meter reading both indoors and outside. In direct sunlight, the multimeter should read a current of up to 50 microamps and a voltage of approximately 0.25 volts.

What's Going On?

Solar cells are made up of a class of materials called semiconductors. In semiconductors there is an energy gap between the electrons that are tightly bound to the atom, unavailable for conduction, and the electrons that are farther from the atom and free to move and conduct. Energy from the sun gives the tightly bound electrons enough energy to bridge the energy gap and move into the conduction band where they are free to conduct electricity. Cuprous oxide is a semiconductor.

Ammeters read positive values when positive charges flow into the positive terminal or when negative charges, electrons, flow into the negative terminal. Free electrons excited in the cuprous oxide plate flow into the negative terminal of the meter through the outer circuit and towards the clean copper plate. They then return to the cuprous oxide plate through the salt water, or the electrolyte. In the shade the meter should read a few microamps of current while in the sun, the meter can reach up to 50 microamps at approximately 0.25 volts.

Going Further

How might one increase the current in the cell? The voltage?

What is the power produced by your solar cell? Power is voltage times current.

What is the area of your solar cell's cupric oxide plate?

What is the efficiency of your solar cell? Divide the power produced by your solar cell by the incident power of the sun. To find the power incident from the sun multiply the solar constant of about 1000 watts per meter squared by the area of your solar cell in square meters.

How much cuprous oxide would you need to power a 100 Watt light bulb?