



## Blackberry Solar Cells

### Constructing a Dye-Sensitized Solar Cell

**Teacher Background Information:** See teacher background information sheet.

**Educational Goal:**

To expose students to the latest processes being developed for generating a solar cell that harvest sunlight for energy production.

**Student Objectives:** Students will ...

- Learn how traditional solar panels are made
- Consider this process against the 12 principles of green chemistry
- Construct a dye sensitized solar cell
- Evaluate and compare the differences in solar cell technologies

**Materials: (per lab group)**

- 1 transparent indium tin oxide conductive glass slide (ITO slide), 15mm x 35 mm x 1 mm
- 1 TiO<sub>2</sub> coated indium tin oxide conductive glass slide, 15mm x 35 mm x 1 mm
- 4 drops of Iodide electrolyte solution (0.5 M potassium iodide mixed with 0.05 M iodine in propylene glycol)
- 2 small binder clips
- 1 blackberry (thawed, frozen blackberries work well)
- 1 small spatula
- 1 graphite pencil
- 1 piece of parafilm, cut into 20mm x 40 mm size
- 1 small aluminum dish pan (2 inches)
- 1 paper towel
- 1 razor blade
- Multimeter
- Light source (flashlight or sunlight)

**Note:** Handle the glass plates by the edges to avoid touching the faces of the plates.

**Time Required:** 2 x 60-75 minute class periods

**Prerequisites:** An understanding of the 12 principles of green chemistry

**National Science Standards Met:** S1, S2, S3, S6, S7, S8

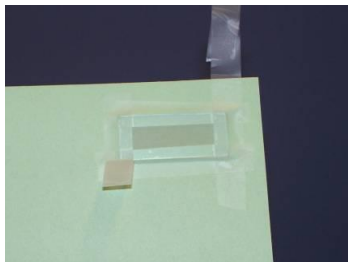
**MA Standards Met:** ES2, ES3

**Green Chemistry Principles Addressed:** 1, 4, 6, 9

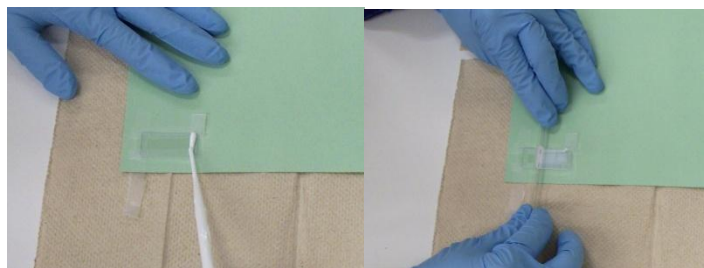
## Procedure:

### PREP (if needed)

- Order/acquire two conductive glassplates coated with ITO per group- see Beyond Benign website for ordering details.
- Purchase frozen blackberries from your local grocery store (you can use fresh but they tend to be a lot more expensive).
- Prepare iodide electrolyte solution (0.5 M potassium iodide mixed with 0.05 M iodine in propylene glycol) Propylene glycol is the more environmentally friendly antifreeze (as opposed to ethylene glycol which is not so friendly).
- Determine which side the indium tin oxide coating is on by using a multimeter with its setting placed on resistance ( $\Omega$ ).
- Cover the glass with tape and secure the glass to the table. To do this, you will “mask”, or cover, the glass with 2mm of tape on 4 sides. Secure the glass by adhering the free side of the tape to the table at a 45° angle. Your glass should look like the diagram below.



- Prepare  $\text{TiO}_2$  paste and coat the inside 80% of the conductive plate leaving a 2 mm border all the way around the slide. (1 per student group) Paste is produced by mixing:
  - 15%  $\text{TiO}_2$ , 0.7 % trimesic acid (1,3,5-tricarboxylbenzoic acid)
  - 84.3 % water by mass
  - Grind  $\text{TiO}_2$  and trimesic acid in a mortar & pestle
  - Add the water slowly and continue to grind as you add more water to make the paste



- Add 3 drops of the  $\text{TiO}_2$  solution uniformly to the conductive glass and spread it across the glass using the body of a stirring rod until the glass is covered completely.
- Allow the  $\text{TiO}_2$  to dry for 10 minutes before removing tape slowly as to not damage the conductive glass.
- Place in 45° C oven overnight. This process is not necessary, but will make a better solar cell, as water interferes with the process. Overnight drying at room temp will also work.

## IN CLASS

- Ask the class what they know about solar cells and if they know anyone who has them on their house.
- Hand out the article “Solar panels pose an environmental hazard, claims report”. Have students read the article or read it as a class. (You may also want to assign this article as homework reading prior to class)
- Discuss the article and ask the students what they now think about solar panels.
- Explain that as good scientists we should scientifically evaluate the process of making solar energy panels.
- Hand out the “How solar panels are currently made” worksheet.
- Give students time to read the information and answer any questions.
- Now hand out the student sheet for evaluating the solar panel process against the 12 principles of green chemistry.
- Discuss the results.
- Explain to students that green chemists obviously have cause for concern when it comes to solar panels and that there is an opportunity for a chemist to develop a better way of making solar panels.
- Explain that they are going to now make a dye sensitized solar cell that is one of the ways that green chemists are working to improve solar energy production.
- Hand out student lab sheets and review.
- Discuss what kinds of applications the volts generated by the class can power. Could the solar cell power a calculator for instance?
- Discuss the different locations that a small flexible solar cell can be placed.



## Dye Sensitized Solar Cell Student Lab Procedure

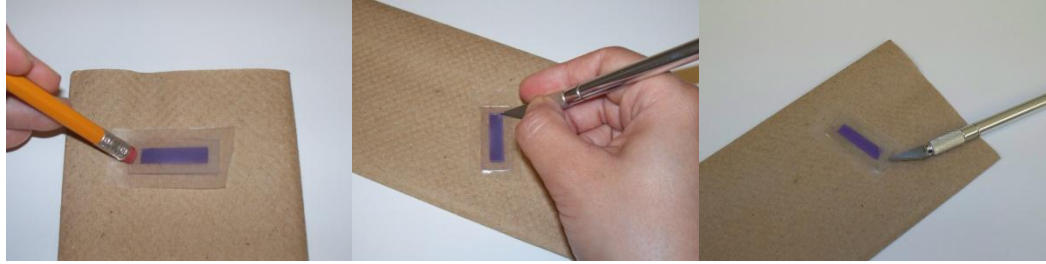
### Procedure:

Collect the following materials from the supply area:

- 1 transparent indium tin oxide (ITO) coated glass slide (referred to as ITO slide)
- 1  $\text{TiO}_2$  coated indium tin oxide glass slide (referred to as  $\text{TiO}_2$  slide)
- Iodide electrolyte solution (0.5 M potassium iodide mixed with 0.05 M iodine in propylene glycol)
- 2 small binder clips
- 1 blackberry (the fruit, not the phone)
- 1 spatula
- 1 pencil
- 1 piece of parafilm, cut into 20mm x 40 mm size
- 1 small aluminum pan
- 1 paper towel
- 1 razor blade/scalpel/exacto knife
- Multimeter

*Note: Handle the glass plates by the edges to avoid touching the faces of the plates*

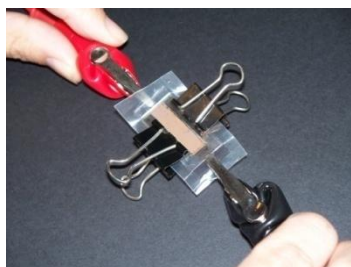
1. Place the blackberry in the aluminum pan.
2. Using a spatula, crush the blackberry to extract the juices. Scoop out the solid pulp.
3. Remove the glass slide containing the white  $\text{TiO}_2$  coating from its bag. **Handle the glass slide by the edges only.** Determine which side the  $\text{TiO}_2$  coating is on.
4. Place the glass slide with the  $\text{TiO}_2$  face down into the aluminum pan. Allow to sit for 3-5 minutes.
5. Remove the ITO coated glass slide from its bag. Determine which side the coating is on by using a multimeter with its setting placed on resistance ( $\Omega$ ). The indium tin oxide coating is on the side of the slide that gives a non-zero reading on the multimeter.
6. Using the tip of a graphite pencil, lay down the carbon catalyst by shading the indium tin oxide coated side of the slide. The graphite may not leave a visible mark.
7. Remove the  $\text{TiO}_2$  slide from the blackberry juice. Use the paper towel to gently blot the excess juices off the slide. Dry the slide as much as possible, but do not remove any of the  $\text{TiO}_2$  coating. Do not wipe the slide as this may remove some of the  $\text{TiO}_2$  coating.
8. Remove and discard the wax paper backing from the parafilm and place the parafilm on top of the dye coated  $\text{TiO}_2$  slide. Use the eraser end of the pencil to press the parafilm to the glass slide in the area that borders the  $\text{TiO}_2$ .
9. **READ ENTIRE STEP CAREFULLY BEFORE BEGINNING:** Using a razor blade, carefully cut out the area of the parafilm that sits on top of the  $\text{TiO}_2$ . Press lightly with the blade, so that the conductive coating does not scratch off. Reinforce the parafilm seal around the edges of the  $\text{TiO}_2$  area with the eraser end of the pencil.



10. Place 1-2 drops of the iodide electrolyte solution on top of the  $\text{TiO}_2$ . The parafilm should act as a wall that prevents the electrolyte solution from leaking out.
11. Place the ITO coated glass slide on top of the  $\text{TiO}_2$  slide so that the conductive sides face each other. Stagger the slides so that as much of the glass slide is exposed and the entire  $\text{TiO}_2$  is covered.



12. Use the 2 small binder clips to hold the slides together. Attach the clips on the longer sides.
13. Carefully push back a small amount of the parafilm wall to expose a tiny part of the conductive side of the slide.
14. Place the multimeter probes on opposite ends of the solar cell's conductive glass slides.



15. Place the solar cell under light, using either sunlight or a flashlight.

16. With the multimeter set to measure electric potential, measure the voltage of the solar cell.
17. Collect class results on the teacher's chart at the front of the class.
18. Sum up how many volts the class made as a whole if the cells were connected in series
19. Clean up workspace and work on the Discussion Questions



## Background Reading

### [Solar panels pose an environmental hazard, claims report](#)

Cleantech Magazine [Chris Morrison](#) | January 14th, 2009



Sometime in the late 1970s, toxic chemicals from semiconductor plants in San Jose, Calif. began [leeching chemicals into the local water supply](#). As birth defects soared and families sickened, investigators began a search for the culprits, eventually fingering IBM and Fairchild Semiconductor in 1981.

At the time an extremely high-profile case, the episode helped introduce public safeguards to high-tech manufacturing. It also provided for the birth of the [Silicon Valley Toxics Coalition](#), a group that is today releasing a report on the solar

industry, which is blossoming much as semiconductors did in the 1970s and 1980s.

Making solar panels, which are in many ways directly descended from semiconductors, also produces toxic byproducts that could sicken living beings, warns the SVTC. Among these are caustic liquids like silicon tetrachloride, dusts and nanoparticles like kerf (a remnant from cutting silicon ingots), and potent greenhouse gases like sulfur hexafluoride.

Of course, nearly any manufacturing industry outside of cottage crafts produces a long list of potentially harmful byproducts. The SVTC's executive director, Sheila Davis, admits that the solar industry is not an immediate problem except for in countries with lax standards, like China. After all, we've had our mistakes like the IBM / Fairchild spills to learn from.

The reason to look at solar now has everything to do with its racetrack position. The solar industry has been ramping up and, albeit with the recession hanging overhead, is ready to take flight. But where other new manufacturing techniques might automatically meet with suspicion, solar has an inherent advantage: an excellent environmental reputation. That comes from its lack of CO<sub>2</sub> emissions, but careless onlookers might mistake solar's CO<sub>2</sub> reputation with a more general environmental harmlessness.

“What needs to happen, and what we're slowly moving towards, is a systems thinking approach to products and their entire life cycle,” says Davis, who wants the solar industry to take a hard look not just at how panels are manufactured but also at how they're disposed of at the end of their life — which can last 25 years or more. Davis is concerned that discarded panels could release chemicals or harmful nanoparticles into the environment.

Each chemical contained within a panel, which could become a pollutant if panel is thrown away, must be weighed against the ingredients required to make the panel in the first place. Standards for this sort of analysis don't exist today, and the SVTC report is no help; a year in the making, Davis refers to it as an "introductory" study that requires years more work.



Whether solar companies would be willing to take part in that process is anyone's guess. Many companies do, in fact, offer panel recycling plans, although it's often the installer rather than the manufacturer doing the collection. But for all aspects of manufacturing a panel — whether it's traditional silicon, thin-film or a variant — rely on a single metric: cost. Changes that interfere with the end cost of a panel may encounter fierce resistance.

Although other factors weigh on buyers, including the cost of maintenance and perceived reliability of panels, they also are most interested in cost; simply put, the cheapest panel wins. However, Davis's view of the future is radically different. "The ones that succeed that should be the ones that achieve sustainable practices. That should be the Litmus test," she says.

The two ideas aren't likely to meet in the middle without encouragement. But if they don't, says Davis, problems are likely in the future. "The way we operate now means it takes a serious accident to get people's attention," she says.

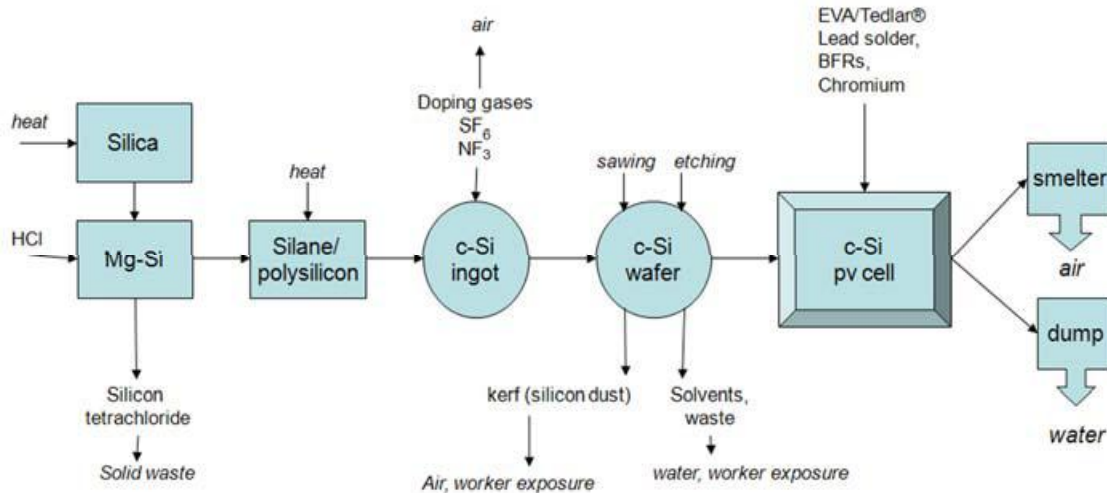
Instead of just letting businesses operate as they please, Davis advocates a regulatory framework that rewards manufacturers who continually improve the production of their product.

Starting on such rules now will be immensely helpful in a future in which solar branches out in many directions other than traditional solar panels. "I think solar will be ubiquitous. We'll have solar in electronics, in paint, in windows," Davis says. "Each manufacturer needs tools to do lifecycle assessment. I think that's a tremendous opportunity, and it's shifting policy. There's a whole new sector out there to create software and monitoring and other detection devices for these different industries."



## How are solar panels currently made?

### Solar Manufacturing Process Diagram



**Step 1.** Silica is mined and refined into metallurgical grade silicon. This is reacted with hydrochloric acid (HCl) using very high temperatures where silane/polysilicon feedstock and silicon tetrachloride waste is produced.

**Step 2.** The resulting silane/polysilicon is heated to produce a crystalline silicon (c-Si) ingot that is doped to make c-Si into a semiconductor. The potent greenhouse gases sulfur hexafluoride (SF<sub>6</sub>) and nitrogen fluoride (NF<sub>3</sub>) are used in this step to clean the reactors and also in doping (doping is to add impurities to a semi-conductor to produce or modify its properties).

**Step 3.** The c-Si ingot is cut into wafers, which are etched with reactive solvents such as Hydrofluoric Acid to remove surface imperfections.

**Step 4.** Finally, the wafers are encapsulated with ethyl vinyl acetate (EVA) or Tedlar® to protect the surface, mounted onto a frame and wired into the PV cell.

**Step 5.** Without extended producer responsibility, these cells will end up in smelters and dumps where any hazardous materials will cause air and water pollution.

### **About the chemicals named above:**

**Silicon (Si)** is a element, and it is the main component of sand. It is the 2<sup>nd</sup> most abundant element found in the earth's crust. Silicon is considered non-toxic in its elemental form and most of its other forms (silicates). Only after it has been refined and under certain conditions will the form become hazardous.

**Silicon tetrachloride (SiCl<sub>4</sub>)** is a corrosive and is used in silicon-based PV cell production. It reacts with water to form hydrochloric acid and can cause tissue damage. It causes severe respiratory problems when inhaled. Skin contact causes severe pain, and eye contact can cause permanent damage. It is one of a group of chemicals known as chlorosilanes.

**Silicon dioxide (SiO<sub>2</sub>)**. Refined crystalline silica(fine powder) is a potent respiratory hazard, irritating skin and eyes on contact. Inhalation causes lung and mucus membrane irritation. Eye irritation results in watering and redness. Lung cancer is associated with occupational exposures to crystalline silica among miners, diatomaceous earth workers, granite workers, pottery workers, brick workers, and others.

**Hydrofluoric acid (HCl)** Hydrofluoric acid is a solution of hydrogen fluoride in water. While it is extremely corrosive and difficult to handle, it is technically a weak acid. The danger in handling hydrofluoric acid is extreme, as skin saturation with the acid in areas of only 25 square inches (160 cm<sup>2</sup>) may be relatively painless, yet ultimately fatal. High concentrations of hydrofluoric acid and hydrogen fluoride gas will also quickly destroy the corneas of the eyes

**Nitrogen trifluoride (NF<sub>3</sub>)** is used to clean reactors and dope polysilicon semiconductors. It emits toxic fumes when burned or reacted and can cause asphyxiation. The IPCC considers NF<sub>3</sub> a significant greenhouse gas, making fugitive emission control very important.

**Polysilicon** is the most widely used solar PV semiconductor. It is obtained by heating silane or trichlorosilane gas to 1500°C.

**Sulfur hexafluoride (SF<sub>6</sub>)** is used to etch and dope semiconductors and clean reactors in PV manufacturing. It is relatively inert and is considered an asphyxiant. The IPCC considers SF<sub>6</sub> the most potent greenhouse gas known.

**Ethyl vinyl acetate (EVA)** is used to encapsulate solar PV cells. It is a non-toxic alternative to soft plastics like polyvinyl chloride (PVC), but may release volatile organic compounds during manufacture.

Information for this handout was taken from The Silicon Valley Toxics Coalition Report: "Toward a Just and Sustainable Solar Energy Industry".



## Evaluate Solar Panel technology against the 12 principles of Green Chemistry Student Sheet

Using the 'How are Solar Panels currently made?' handout, evaluate each step against the 12 principles of green chemistry. Record which principles you could identify as ones which chemists need to find an alternative and why.

Step 1:

Step 2:

Step 3:

Step 4:

Step 5:



## Evaluate Solar Panel technology against the 12 principles of Green Chemistry Student Sheet -Teacher Key

Using the 'How are Solar Panels currently made?' handout, evaluate each step against the 12 principles of green chemistry. Record which principles you could identify as ones which chemists need to find an alternative.

Step 1: *Example*

*#1 – The waste should not be generated or should be incorporated in to the final product.*

*#6 – Excessive use of heat. A process should be developed that is at ambient temperature.*

Step 2:

Step 3:

Step 4:

Step 5:

### Dye sensitized solar cell materials:

**Indium tin oxide (ITO)** is a solid solution that is characterized by its combination of electrical conductivity and optical transparency. It is generally used to make transparent coatings for flat panel and plasma displays as well as solar cells.

**Titanium Dioxide (TiO<sub>2</sub>)** is a common substance that can be produced at ambient room temperature. It is known for its wide range of applications. It is widely used as a white pigment because of its brightness and refractive index. It is found in items such as toothpaste, paint, sunscreen, food coloring and powdered doughnuts. Other applications include waste water remediation and semiconductor use. It is non-flammable and generally considered benign.

**Potassium iodide (KI)** is an inorganic compound. This white salt is commonly used medicinally in tablets, as a nutritional supplement in animal feeds and added to hair chemicals. It is a mild skin irritant and chronic overexposure has been known to cause adverse effects on the thyroid.

**Iodine (I)** is a nonmetallic element used especially in medicine, photography and dyes. It is found naturally occurring in the environment as a dissolved iodide in seawater as well as found in kelp.

**Propylene glycol (C<sub>3</sub>H<sub>8</sub>O<sub>2</sub>)** is an organic compound that is industrially produced by propylene oxide hydration at 200°C. It has a variety of applications and is found as a moisturizer in medicines, solvent for food colorings, the main ingredient in deodorant sticks and is also known as the less-toxic antifreeze. Oral toxicity is very low and is generally recognized as safe.

**Graphite** is the most stable form of carbon in standard conditions. It is found in pencils, zinc carbon batteries, brake linings and assorted other specialized applications. Generally considered abundant and inexpensive, graphite is semimetal and can conduct electricity.

**Blackberry** is a fruit that grows from the bramble bush. Blackberries are known for their high nutritional value. The dye is naturally dark purple.

Information for this handout was obtained from Wikipedia.



## Solar Cell Technology Comparison

Using the 12 principles of green chemistry chart the differences between traditional solar cell production and dye sensitized solar cell production. Refer to handouts and lab to complete the grid. Remember Green Chemistry is a growing, evolving and dynamic field; use the last column to highlight areas where the solar cell production process can still be improved.

Principle	Traditional Solar Cell Production	Dye Sensitized Solar Cell Production	Areas of improvement
#1 Pollution prevention			
#2 Atom economy			
#3 Less hazardous synthesis			
#4 Design safer chemicals			
#5 Safer solvents and auxiliaries			

#6 Energy efficiency			
#7 Renewable feedstocks			
#8 Reduce derivatives			
#9 Catalysis			
#10 Design for degradation			
#11 Real-time analysis			
#12 Accident prevention			



## Teacher Background Information

There is a growing need to investigate alternative energy resources due to the depletion of petroleum, a widely used energy source. Solar energy, energy from the sun, is a free, readily available, plentiful resource, and it can be collected by solar cells to generate electricity.

Although solar cells have been around for a long time, their use for energy generation is not widespread. This is because traditional solar cells are expensive and inefficient. In keeping with a green chemistry technology, the technology must demonstrate 3 standards: performance, safety and cost benefits. In this experiment your students will make a dye-sensitized solar cell (DSSC) that is efficient, uses safe materials and is inexpensive.

Unlike traditional solar cells that generate electricity through p/n junctions, the chemistry of the nanocrystalline  $\text{TiO}_2$  is based on red-ox (reduction-oxidation) chemistry. This means that the excitement of electrons to generate electron movement through the system is what drives electricity, which can be measured in terms of voltage (V). The mechanism of a photovoltaic cell has three steps (Figure 1):

1. A dye, adsorbed on a layer of semiconductor ( $\text{TiO}_2$ ) interacts with the visible light provided by the sun (just like the green pigment does in a leaf), promoting an electron from a lower level orbital to an excited one.
2. The excited electron is injected by the dye into the semiconductor and, through the bulk of it, reaches the electric contact with the outside circuit.
3. The electrons return to the cell to complete the circuit and bring the dye back to its “normal” state by using an electrolyte solution that helps carry electrons through the cell.

The cells are a “sandwich” in which two conducting glasses are overlapped. The photoanode is coated with the layer of  $\text{TiO}_2$  sensitized with the dye, and the other is coated with graphite in order to enhance the interaction with the electrolytic solution which is contained between the glasses themselves.

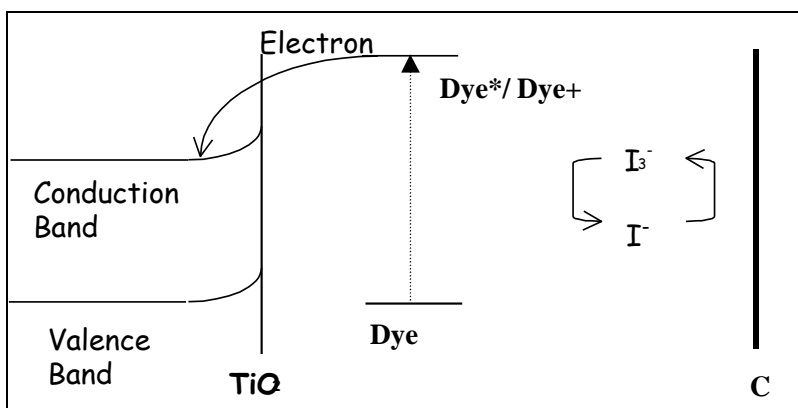


Figure 1. Mechanism of a dye-sensitized solar cell.