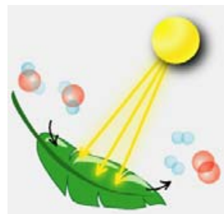
Artificial Photosynthesis:
A Workshop in Solar Cell Design



Joseph P. Harney, Sam Toan, Jonathan Rochford*

Department of Chemistry, University of Massachusetts Boston,
100 Morrissey Boulevard, Boston, MA 02125.
email: jonathan.rochford@umb.edu

Introduction

In reading the title of this workshop you may be asking yourself *"What is artificial photosynthesis?"* or alternatively *"How is photosynthesis related to solar cell research?"* This workshop is aimed at bridging the gap between our knowledge of Natures energy conversion and storage factory, i.e. the photosynthetic reaction center, and current-to-future solar cell technologies. Although it involves a complex sequence of events, the overall photosynthetic reaction can be simply summarized by the chemical equation

$$6\ CO_2 + 6\ H_2O + \textit{sunlight} \rightarrow C_6H_{12}O_6 + 6\ O_2$$

where carbon dioxide and water are ultimately converted to carbohydrates and dioxygen – replenishing the air we breathe. In essence, photosynthesis uses sunlight to power the movement of electrons (aka electrical current) to cause this chemical change. For the chemical sciences, an understanding of photosynthesis is particularly attractive since valuable substances, i.e. fuels, are produced in these reactions from very simple, low-energy starting materials powered by a readily available and abundant form of energy in sunlight. Solar cells mimic the light absorption and electron flow of photosynthesis to produce electricity. The basic components of a solar cell are a *negative electrode* (anode) and a *positive electrode* (cathode) connected by an external circuit. Through irradiation with sunlight, an electron is excited to a high-energy state and transferred from the negative electrode to the positive electrode via the external current. The difference in energy between both electrodes determines the electrical potential (voltage) of the solar cell. Furthermore, the efficiency of photo-to-current conversion will determine the current (amperage) of the cell. There are many classes of solar cells but today we will learn about chemically designed solar cells.

Introduced over 20 years ago by Grätzel and co-workers,[1] dye-sensitized solar cell (DSSC) technology has stimulated vast interest from the academic, federal and private sectors with the maximum reported DSSC efficiency now standing at almost 12%.[2] DSSCs are built around a photoanode (negative electrode) consisting of a mesoporous network of transparent *n*-type wide band-gap inorganic semiconductor nanoparticles in TiO_2 deposited on an optically transparent conducting substrate [fluorine-doped tin oxide (FTO) glass].[3] The mesoporous (sponge like) layer (*ca*. 10 μm) of TiO_2 nanoparticles (*ca.* 10-20 nm diameter) boasts a remarkable surface area (roughness factor ~$1x10^3$). The dye sensitizer is adsorbed on the high surface area TiO_2 by covalent attachment allowing a large absorption cross section (*light harvesting*). The low cost TiO_2 semiconductor mimics the light absorbing proteins found in the thylakoid membrane of the natural photosynthetic system.[4] The function of this protein is to arrange the light-harvesting molecules (chlorophylls and carotenes) in a fixed orientation with respect to one another for optimum vectorial energy transfer to the photosynthetic reaction center. TiO_2 functions similar to this naturally occurring protein as a scaffold for the self-assembly of dye molecules. In fact, TiO_2 plays a dual role in DSSCs as it also acts as an electron acceptor and charge carrier, once again mimicking the natural photosynthetic system.[4-5]

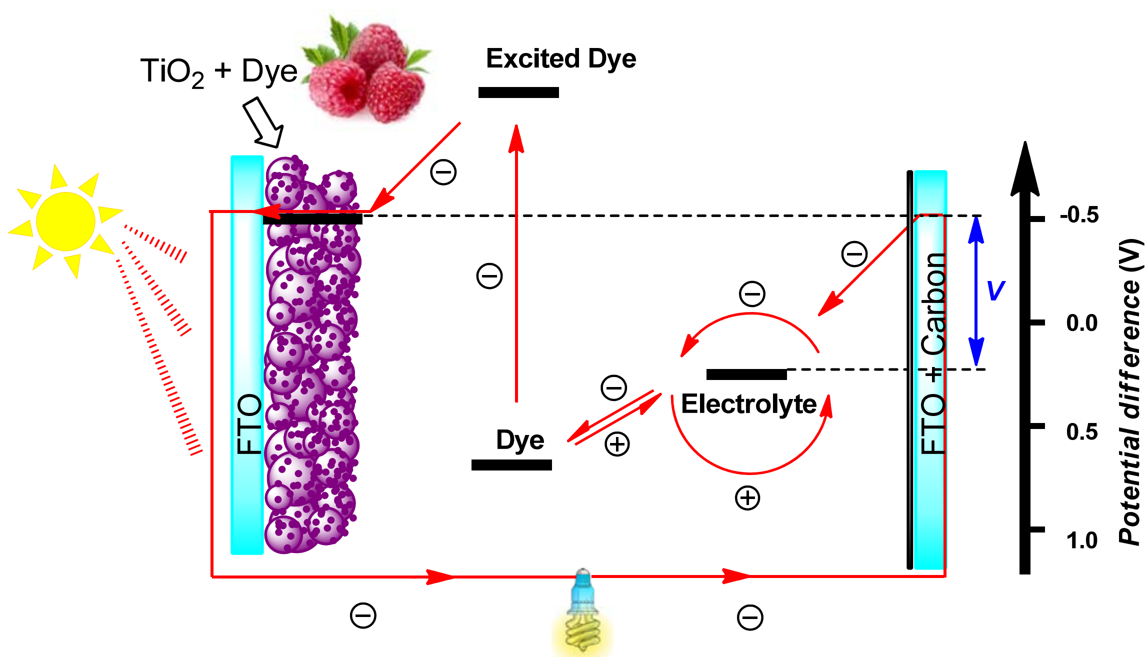


Fig 1: Schematic diagram of a dye-sensitized solar cell operation.

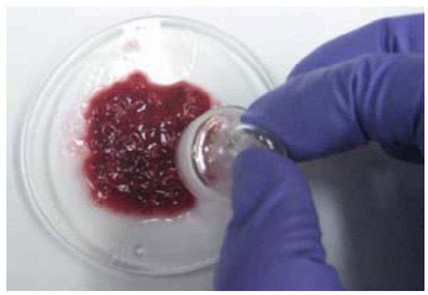
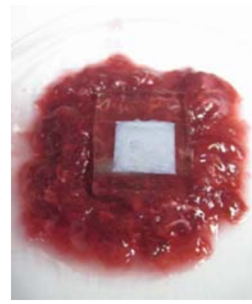
Materials

- 2 x transparent fluorine-doped tin oxide (FTO) conductive glass slides (20 mm x 15mm x 2.2 mm)
- Scotch tape
- Mortar and pestle (or alternatively a glass dish and stopper)
- 18 % wt. TiO_2 / α-terpineol paste
- Electrolyte solution (0.5 M lithium iodide : 0.05 M iodine in acetonitrile)
- 2 small binder clips
- Fruit ! (raspberry, concord grape, blackberry or acai berry)
- Deionised water
- 1 candle
- 1 piece of parafilm spacer (U-shaped; 15 mm x 15 mm OD; 10 mm x 10 mm ID)
- 1 glass pipette
- Multimeter
- Light source

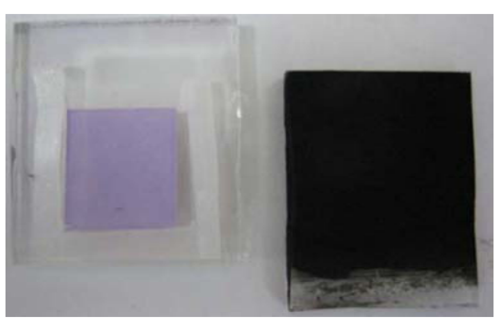
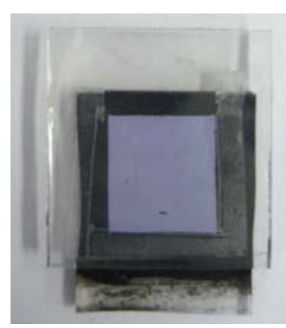
Solar Cell Fabrication

1. Determine which side of the conductive glass has the FTO coating by using a multimeter with its setting placed on resistance (Ω - *the instructor may have labeled this already!).*
2. Facing the glass FTO face-up, carefully tape the glass to the benchtop on four sides using Scotch tape. It is critical here to expose just 1 cm^2 of the FTO surface (leaving roughly 2 mm from one end of the glass and about 8mm of bare FTO on the opposite end; ref. picture below).
3. Add 2-3 drops of the TiO_2 paste uniformly to a single side of the Scotch tape. Using gentle pressure with adequate momentum spread the paste across the exposed FTO surface using the smooth edge of a glass pipette.

4. Allow the TiO_2 to settle for 2 min. Very carefully remove the tape and, keeping the FTO/TiO_2 side-up, dry the paste over a heat source for about 30-60 seconds (a hot plate set at ~ 250 °C will work fine; alternatively use a Bunsen burner on low flame below an aluminum sheet – do not use an open flame on the electrode).
5. Place the berry of choice in the glass dish and mash it gently with the glass stopper. Gently place the FTO/TiO_2 electrode face-down into the fruit for about 10 min. (this is where natural dye molecules from the fruit will attach themselves to the white TiO_2 nanoparticles producing a bright colorful electrode surface).

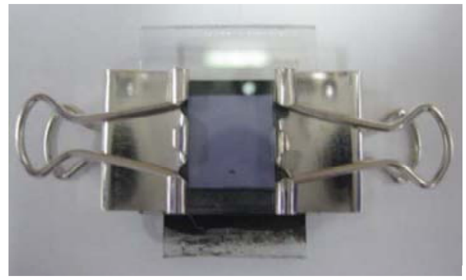




6. In the meantime (while the FTO/TiO_2 is absorbing the natural dye) take the second piece of FTO conductive glass. Confirm using the multimeter which side is conductive *(the instructor may have labeled this already!) .*
7. Take this second piece of FTO using a tweezers and glide (FTO face-down) over a burning flame from a wax candle to deposit carbon directly onto the FTO surface. This will leave a black film of carbon on the FTO surface which will be used as our *positive electrode*.
8. Remove the TiO_2 slide from the fruit juice and gently rinse with deionized water. Allow to air dry (gently blot with a tissue if needed but do not damage the surface!).
9. Next carefully place the U-shaped parafilm spacer around 3 sides of the TiO_2 layer.
10. Now place the FTO/Carbon *positive electrode* face down on top of the FTO/TiO_2/dye *negative electrode* making sure to offset both ends by a few mm (see picture below ↓).

THE POSITIVE AND NEGATIVE ELECTRODES SHOULD BE FACE-TO-FACE BUT NOT IN DIRECT CONTACT!

11. Taking extreme care, fix both electrodes in place using the binding clips.
12. Now, place the multimeter alligator clips on opposite ends of the solar cell's conductive glass slides and put 1-2 drops of the provided electrolyte solution between the two electrodes (capillary action should carry the solution throughout the solar cell – spacer and electrolyte allow the chemistry to occur without short-circuiting the cell!)



13. Finally we are ready to expose the solar cell to our light source and with a multimeter measure electrical potential (V) and current (A) of the solar cell under ambient (alternatively cover the cell for dark) and illuminated conditions.

Now compare with your colleagues and determine which fruit generates the greatest electrical power density in a dye sensitized solar cell.

[note: each cell must be measured equidistant from the light source so they are exposed equal intensity irradiation]

$$\text{power density } (\mathrm{W.m^{-2}}) = \frac{\text{current (A)} \times \text{voltage (V)}}{\text{area } (\mathrm{m^2})}$$

Fruit	**Potential (V)**	**Current (A)**	**Power density (Wm^2)**
Concord grape			
Raspberry			
Acai berry			
Blackberry			

Supplies

We would like to emphasize that this procedure has been optimized so that it can be reproduced in a K-12 teaching environment with both non-science and science students at relatively cheap cost. To reproduce this experiment please see the following list of suppliers but do check for alternatives if more convenient…and no harm to inquire about educational samples!

- Fluorine-doped tin oxide (FTO) conductive glass slides (2 per solar cell). Pre-cut commercially available at 2.5 cm × 2.5 cm TEC 8 or TEC 10 (TEC = "transparent electrically conductive"; 8 or 10 = resistivity per square cm^{-2}…either will work well)
  Vendor: Hartford Glass Co. Inc., P.O. Box 613, Hartford City, IN 47348
  (Tel) 765/348-1282; (Fax) 765/348-5435; e-mail: hartglas@netusa1.net;
- TiO_2 nanoparticles (commercial name: Aeroxide© P25) were donated by….
  Vendor: Innovadex, 7930 Santa Fe, Overland Park, Kansas 66204.
  sales@innovadex.com; (Tel) 913-307-9010
- α-terpineol (technical grade); Parafilm; Lithium Iodide (reagent grade); Iodine (reagent grade); acetonitrile (reagent grade – alternatively anti-freeze can be used as a solvent but the solar cell with not be as efficient!)
  Vendor: Wilkem Scientific, PO Box 301, Pawtucket, Rhode Island 02862.
  jim@wilkem.com; (Tel) 800-766-5676; (Fax) 401-724-8760
- Scotch tape; candles; multimeter; light source (your local hardware store)
- For fresh fruit support your local market!

References

1. Vlachopoulos, N.; Liska, P.; Augustynski, J.; Gratzel, M., *J. Am. Chem. Soc.* **1988,** *110*, 1216-1220.
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3. Gratzel, M., *Nature* **2001,** *414*, 338-344.
4. Blankenship, R. E., *Molecular Mechanisms of Photosynthesis*. Blackwell Science: 2002.
5. Barber, J., *Chemical Society Reviews* **2009,** *38*, 185-196.