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Demonstrating Electron Transfer and Nanotechnology: A Natural Dye-Sensitized Nanocrystalline Energy Converter

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A unique solar cell fabrication procedure has been developed, using natural anthocyanin dyes extracted from berries. It can be reproduced with a minimum amount of resources, providing an interdisciplinary approach for lower-division undergraduate students learning the basic principles of biological extraction, physical chemistry, spectroscopy, environmental science, and electron transfer. Electron transfer is the basis of the energetics that drives the processes of life on Earth. It occurs in both the mitochondrial membranes of living cells and the thylakoid membranes in photosynthetic cells of green plants and algae (1). Although we depend on the products of this electron and energy transfer in the form of petroleum and agricultural products, one of the greatest challenges of the 21st century is that we have yet to create devices that can be used to tap directly into the ultimate source of this energy on an economic scale. An experimental lab procedure was therefore created to illustrate the connections between natural and manmade solar conversion within a three-hour lab period.

Technical Background

Nanocrystalline dye-sensitized solar cells (Fig. 1) are promising synthetic nanomachines based on principles similar to the processes in natural photosynthesis. Both use an organic dye to absorb the incoming light and produce excited electrons. A film of interconnected nanometer-sized titanium dioxide particles replaces nicotinamide adenine dinucleotide phosphate (NADP⁺) and carbon dioxide as the electron acceptor, and iodide and triiodide (I⁻, I₃⁻) replace water and oxygen as the electron donor and oxidation product, respectively. A recent review by Meyer in this *Journal* reported on progress in understanding this biomimetic approach to energy conversion (2). Like the coupled processes of photosynthesis and respiration found in the biosphere, the light-driven electrochemical process in the nanocrystalline solar cell is regenerative and forms a closed cycle that converts light energy into useful forms. Although laboratory dye-sensitized nanocrystalline TiO₂ solar cells have achieved greater than 10% conversion efficiencies of sunlight to electrical power and photocurrent outputs greater than 16 mA/cm², the synthetic ruthenium bipyridyl-based dyes used to attain high conversion efficiencies are difficult for the novice to synthesize, purify, and use (3). We have therefore developed a procedure that uses flavonoids and chlorophyllides as sensitizers for the nanocrystalline solar cell. Flavonoids such as anthocyanins are present in the leaves, fruits, and flowering structures of all land plants. They function in the protection against the damaging effects of UV light and as attractors for plant pollinators such as insects and birds (4). Remarkable for their stability, these anthocyanin pigments may be used as natural water-based substitutes for the ruthenium bipyridyl dyes (5–7).

This simplified procedure for solar cell or photodetector fabrication has been successfully used in introductory undergraduate chemistry classes at the California State University Monterey Bay, as a demonstration to more than 1000 high school science students attending the Illmac International Congress for Chemical Techniques in Basel, Switzerland (November 1996), and to 2nd graders in Pacific Grove, California.¹ Depending on how much preparation is made before the lab period, the procedure can be employed as a guided laboratory experiment in introductory or advanced college chemistry classes. This experiment gives a concrete example of how concepts such as oxidation and reduction, optics, and spectroscopy can be used to understand the photosynthetic processes occurring in green plants (8). In an interdisciplinary approach to the teaching of science, the chemistry lab

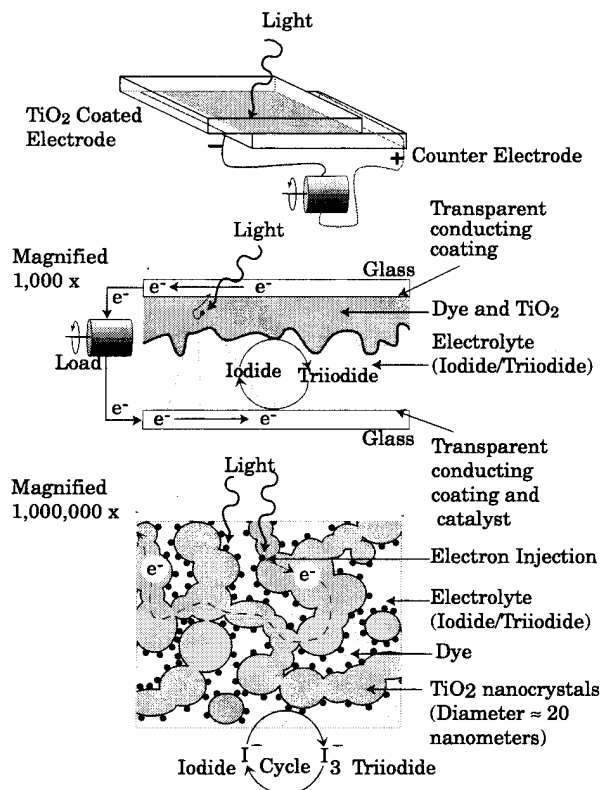


Figure 1. Dye-sensitized TiO₂ solar cell. The photoexcited dye transfers an electron to the semiconducting TiO₂ layer via electron injection. The injected electron is then transported through the porous TiO₂ layer and collected by the conductive SnO₂ layer on the glass surface. Within the electrolyte, the mediator (I⁻/I₃⁻) undergoes oxidation at the dye and regeneration at the catalyst-coated counter electrode as current flows through the electrical load.

class may work collaboratively with a biology class to extract the dye, or with a physics class to determine the current-voltage and power-output characteristics of the resulting dye-sensitized photoelectrochemical solar cell.

Experiments

Equipment and Materials

1. Conductive (tin dioxide coated) transparent glass: Pre-cut commercial (2.5 cm × 2.5 cm) TEC 10 or TEC 15 glass can be purchased from one of several suppliers: Hartford Glass Co. Inc., P.O. Box 613, Hartford City, IN 47348; phone 765/348-1282; Fax 765/348-5435; email hartglass@netusa1.net; or Pilkington, Libbey Owens Ford, 811 Madison Ave., P. O. Box 799, Toledo, OH 43697-0799; phone 419/247-4517.
2. Twelve grams of colloidal titanium dioxide powder: Degussa P25 TiO₂, Degussa USA, 3500 Embassy Parkway, Akron, OH 44333; phone 330/668-2235; or Degussa AG, D-6000, Frankfurt 11, Germany.
3. Iodide electrolyte solution in dropper bottles: 0.5 M potassium iodide mixed with 0.05 M iodine in water-free ethylene glycol.
4. Heat source: hot-air gun or paint-stripper gun: Leister Model Horwind S, Assembly Supplies Co., 11835 Carmel Mtn. Rd., Suite 1304, San Diego, CA 92128; phone 619/451-1859; or Steinel Typ. 3449, Insulation Supply Co.; phone 800/457-7715. An oven or alcohol burner can also be used.
5. Miscellaneous supplies and equipment:
Blackberries, raspberries, pomegranate seeds, or green citrus leaves
2 binder clips, Scotch tape, glass stirring rod, absorbant tissue paper, filter paper, soft graphite pencil or cleaned carbon rod taken from an alkaline battery
Overhead projector or tungsten halogen light source
Volt-ohm meters
500-ohm potentiometer, hookup wire
X-Y recorder (optional)
Motor (optional): Maxon 2522.846.12.112.000, Maxon Interelectric Co. AG, CH-6072 Sachseln/OW, Switzerland; URL <http://www.maxonmotor.com>; or Mabuchi RF-330TK-07800, Mabuchi Motors, 3001 West Big Beaver Rd., Suite 520, Troy, MI 48084; phone 248/816-3100.
Capacitor (optional): 10,000 microfarad, single polarity

Procedures

During the entire procedure, care should be taken not to touch the face of the electrodes. The glass plates should be held with tweezers or by the edges of the glass. If the conductive glass is available and deposition of the TiO₂ layer is carried out by the instructor or in a preliminary lab, the primary part of the experiment (starting with "Stain the Titanium Dioxide") can be carried out within a 3-hour lab period. We also suggest that the iodide electrolyte be prepared before the lab period.

Deposit the Titanium Dioxide Layer

Depositing the nanocrystalline TiO₂ film requires preparing a solution containing commercial colloidal TiO₂ powder, masking a cleaned conductive glass plate, applying and distributing the solution on the conductive glass plate,

and sintering the resulting thin film layer. The resulting TiO₂ film is 7–10 μm thick, with a porous structure that enhances the efficiency of both light absorption and electron collection in a way similar to the thylakoid membrane of green plants (1, 11).

A commercially available glass plate coated with a conductive layer of fluorine-doped SnO₂ may be cut (2.5 cm × 2.5 cm) and used as the starting material for the electrodes. If this is not possible, standard soda lime glass can be coated with a layer of conductive Sb-doped SnO₂ in an additional 3-hour preliminary lab. To do this, spray a tin solution on glass that has been heated on a hot-plate to 450–550 °C. The tin solution is prepared by dissolving 25 g of SnCl₄ · 5H₂O in 6 mL of methanol and heating the solution to 50 °C, then adding 2 mL of an Sb₂O₃ solution. This Sb dopant solution is prepared by dissolving 1 g of Sb₂O₃ in 3 mL of HCl/methanol. For a complete discussion of the SnO₂ coating procedures, please refer to ref 9.

The TiO₂ solution is prepared by incremental addition of 20 mL of nitric or acetic acid solution (pH 3–4, in deionized water) to 12 g of colloidal TiO₂ powder (Degussa P25) in a mortar while grinding with a pestle. Each 1-mL addition of the dilute acidic solution proceeds only after the previous mixing and grinding has produced a uniform lump-free paste. As an alternative to the acid solution, 0.2 mL of acetylacetone in 1 mL of water can be added to the TiO₂ powder; this is followed by the addition of 19 mL of water, again in 1-mL increments while grinding (10, 11). A volt-ohm meter should be used to check which side of the glass is conductive; the reading should be between 10 and 30 Ω. Four pieces of Scotch (3M) adhesive tape are applied to the face of the conductive glass plate to mask a 1–2 mm strip at three of the four edges, and a 4–5 mm strip is masked on the fourth side. Half of the tape extends from the edge of the glass to the table at a 45° angle to secure the glass. This tape will form a mold or channel 40–50 μm deep into which the TiO₂ solution can flow, while masking a strip of the conductive glass so that an electrical contact can later be made. Three drops of the water-based TiO₂ solution are distributed uniformly on the plate (approximately 5 μL/cm²) by sliding a glass rod over the plate (see Fig. 2). The film is then allowed to dry in air. After one minute, the tape is carefully removed and the film is annealed and sintered in an air stream at 450 °C for 30 minutes. A hot-air gun or tube furnace may be employed to heat the film, or an alcohol or natural-gas burner can be used if the film is held on a ring stand at the tip of the flame for 10 minutes. The TiO₂-coated conductive glass is allowed to slowly cool to room temperature. It can be stored in air for later use.

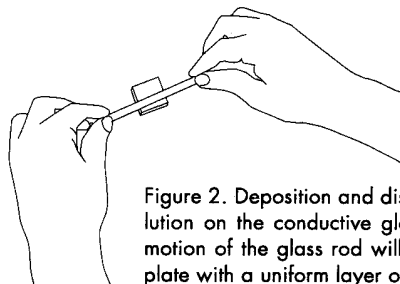


Figure 2. Deposition and distribution of the TiO₂ solution on the conductive glass. A rapid horizontal motion of the glass rod will coat the masked glass plate with a uniform layer of TiO₂ nanoparticles.

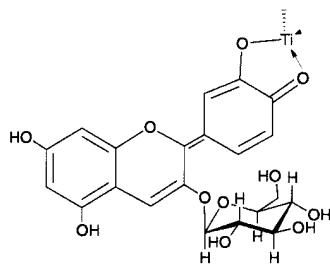


Figure 3. Cyanin-Ti^{IV} complex formed via the adsorption of the dye from solution onto the titanium dioxide surface. The sugar (glucose) is linked to the chromophore by an ester linkage at the 3 position.

Stain the Titanium Dioxide with the Dye

Fresh or frozen blackberries, raspberries, or pomegranate seeds are crushed with 3–4 drops (1/2 mL) of water, filtered, and used as a crude dye solution. Alternatively, the film can simply be placed on top of crushed berries to which a small amount of water has been added. The extract obtained by soaking red *Hibiscus* tea leaves in water at room temperature may also be used. Several fruits and leaves contain anthocyanins that, although colored, may not chelate to the TiO₂ surface (e.g., strawberries). These pigments are not suitable for the dye-sensitized cell. A requirement for the dye structure is that it possess several =O or –OH groups capable of chelating to the Ti^{IV} sites on the titanium dioxide surface (see Fig. 3). A mixture of cyanin 3-glycoside and cyanin 3-rutinoside are the main (sugar-bound) anthocyanin pigments from California blackberries (*Rubus ursinus*) and are excellent natural dyes for sensitization (13). For an advanced class, the cyanin may be further purified by crushing the berries in methanol/acetic acid/water (25:4:21) and passing the filtered extract through a Sephadex LH 20 (Pharmacia) column in the same solvent (13).

Soak separate TiO₂-coated glass plates for 10 minutes in each of the various types of cyanin extracts. If white TiO₂ can be seen upon viewing the stained film from either side of the supporting glass plate, then the film should be placed back in the dye for 5 more minutes. Adsorption of cyanin to the surface of TiO₂ and complexation to Ti^{IV} sites is rapid, forming a complex capable of electron injection (Fig. 3). The dark-purple-stained film is washed first in water and then in ethanol or isopropanol, and gently blotted dry with a tissue. If the cyanin-stained electrode is not used immediately, it should be stored in acidified deionized water (pH = 3–4, acetic acid) in a closed dark-colored bottle.

As an option for an advanced class, a second type of dye can be obtained from chlorophyll. This is accomplished by using the naturally occurring enzymes that cleave the phytol tail and convert chlorophyll into a chlorophyllide possessing carboxyl groups capable of chelating to the surface of the TiO₂ particles (12). Natural dyes derived from chlorophyll and Cu have achieved significant energy conversion efficiencies (2.6% and 9.4 mA/cm²), but these results require pigment purification and the coadsorption of other compounds on the TiO₂ surface (14). As a simplified procedure, fresh young green leaves are ground in a mortar with 2–3 mL of acetone. Lemon or citrus tree leaves have been successfully used, but several other species can be tested as well. The dark-green acetone solution obtained from this procedure is filtered into a dark-colored (or aluminum-foil covered) bottle, and five or six 4 × 4-mm pieces of unground leaves are placed in the

container. An unstained (white) TiO₂ film is also placed in the bottle and additional acetone is added until the film is completely covered by the solution. The solution is left to react for 24 hours in a dark place, to allow time for the enzymes to react with the chlorophyll as well as for the attachment of the dye to the TiO₂. After 24 hours, the electrode should be stained to a light green–yellow color. Before assembly, this stained electrode is washed in acetone and blotted dry. If the stained electrode is not used immediately, it should be stored in the acetone and chlorophyllide solution until the electrode is ready to be assembled into the light-detector device. Chromatography can be used to compare the purity of the crude extract with the enzyme-processed materials (12).

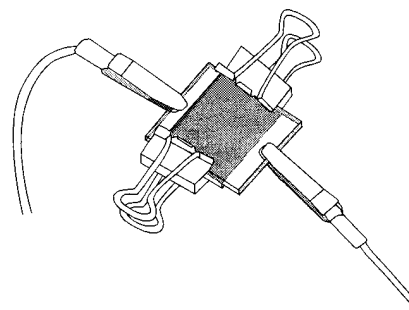
Prepare the Carbon-Coated Counter Electrode

While the TiO₂ electrode is being stained in the berry juice or chlorophyll solution, the counter electrode can be made from another (2.5 × 2.5-cm) piece of conductive SnO₂-coated glass. A graphite rod or soft pencil “lead” is used to apply a light carbon film to the entire conductive side of the plate. This thin carbon layer serves as a catalyst for the triiodide-to-iodide regeneration reaction. No masking or tape is required for this electrode, and thus the whole surface is catalyst coated. A longer-lasting coating can be obtained by annealing the carbon-coated counter electrode at 450 °C for a few minutes. The counter electrode should be washed with ethanol and gently blotted dry before the device is assembled. As an alternative to the carbon coating, the counter electrode can be prepared by chemically depositing a transparent fine-grained platinum layer (3, 11).

Assemble Device and Determine Output Characteristics

The cyanin-stained TiO₂ electrode is carefully removed from the storage bottle or the staining solution and rinsed with water. It is important to dry the stained electrode and to remove the water from within the porous TiO₂ film before the iodide electrolyte is applied to the film. One way to insure this is to rinse the electrode with ethanol or isopropanol before gently blotting it dry with tissue paper. The dried electrode is then placed on the table so that the film side is face up, and the catalyst-coated counter electrode is placed on top so that the conductive side of the counter electrode faces the TiO₂ film. The two opposing glass plates are offset so that all of the TiO₂ is covered by the counter electrode, and the 4-mm strip of glass not coated by TiO₂ is exposed (see Fig. 4). The two exposed sides of the device will be the contact

Figure 4. Assembled solar cell or detector showing offset glass plates, clips, and electrical contact points. The stained TiO₂ layer is in contact with the carbon-coated conductive layer. Light enters the sandwich through the TiO₂-coated glass plate, which is the anode of the electrochemical device.



points for the negative and positive electrodes so that electricity can be extracted to test the cell. Two binder clips are used to hold the plates together loosely at the other edges. One or two drops of the iodide/iodine electrolyte solution can then be placed at the edges of the plates and the two binder clips are alternately opened and closed while in place. The liquid is drawn into the space between the electrodes by capillary action, and can be seen to "wet" the stained TiO_2 film.

The completed solar cell/light detector can be taken outside and measured under illumination by sunlight. To protect the cell from damage by excessive UV light, a plastic filter

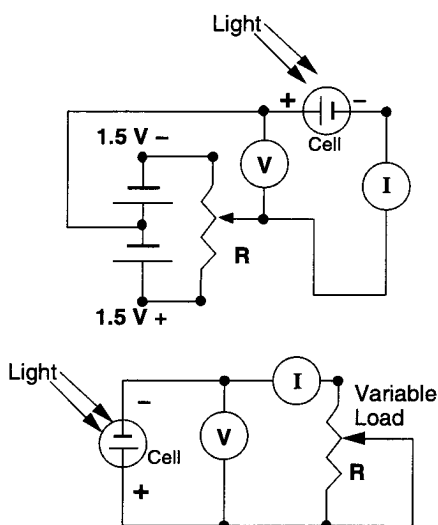


Figure 5. Two possible experimental setups for measuring the current-voltage characteristics of the finished device. Voltage (V) is measured by a voltmeter and current (I) by another meter set to 0–5 mA scale. The top circuit can be used to bias the cell beyond the power producing portion of the I – V curve measured using the simplified circuit shown at the bottom.

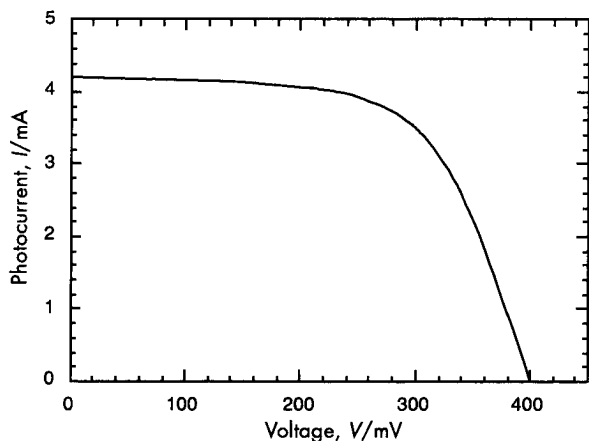


Figure 6. Typical current-voltage (I – V) curve for a 4-cm² sunlight-illuminated solar cell or light detector stained with blackberry juice (cyanin). The open circuit voltage and short circuit current are obtained from the x and y intercepts, respectively.

should be placed over the cell. Light should enter the glass "sandwich" through the TiO_2 -coated glass plate. Maximum current and voltage output can easily be determined by attaching a volt-ohm meter directly to the two sides of the cell using wires with alligator clips attached to their ends. The negative electrode is the TiO_2 -coated glass, and should be attached to the black (–) wire of the meter; the positive electrode (+) is connected to the counter electrode. Use a ruler to measure the dimensions of the active (stained) area of the solar cell and divide the output current by this area. Record the electrical output values and compare the various types of dye extraction procedures used.

For indoor measurements, the cell can be illuminated by a 50-W (GE 12V or equivalent) tungsten halogen lamp equipped with integral parabolic reflector and UV and IR blocking filter, or placed in the beam of an overhead or slide projector. One can calibrate the indoor light sources by adjusting the light intensity or distance from the cell to the light source so that the maximum current values are identical to the outdoor measurements. The full current-voltage (I – V) curves are then measured using a 500- Ω potentiometer as a variable load (see Fig. 5). Point-by-point current and voltage data can be gathered at each incremental resistance value and plotted on graph paper. A chart recorder can also be used to sweep out the full curve as the potentiometer is turned. If a cell dries out, another drop of electrolyte can be added to the edges of the plates to revive it.

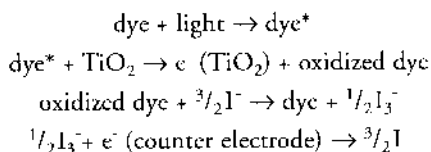
As an optional demonstration of the electrical power output of the TiO_2 blackberry-juice-sensitized solar cell, cells can be connected in series to increase the voltage and in parallel to increase the current. This will produce enough electrical output to power a small motor. A 10,000 microfarad capacitor can be charged using the solar cell(s) and then rapidly discharged through the motor to illustrate the unequal rates of storage and depletion of the solar energy represented in fossil fuels. The cell may also be heat-sealed using a gasket made from a low-melting-point polymer film used in food packaging, such as Dupont Surlyn 1702. Unsealed devices can be stored while assembled for several months in sealed containers and revived by washing the electrodes with ethanol (or acetone, for the chlorophyll based cell), blot drying with a tissue in air, reassembling the cell, and reapplying fresh electrolyte.

Results and Analysis of Data

Using the volt-ohm meter, the open-circuit or maximum voltage produced under direct sunlight should be between 0.3 and 0.5 V. Switching the meter to current (milliamperes) mode, one should obtain a short-circuit current of 1–2 mA/cm² of dyed area in bright sunlight. This means that a 2 × 2-cm² cell should produce at least 3 to 4 mA. The full I – V plot for a typical sunlight-illuminated cyanin-sensitized TiO_2 film, of active area 4 cm², is shown in Figure 6. For this cell, the TiO_2 film was simply placed in berry juice as described above and the counter electrode was carbon coated. Similar outputs are also obtained from chlorophyllide-based cells, which often produce more than 0.6 V. The maximum product of current and voltage (obtained near the "knee" of the curve) in Figure 2, is divided by the incoming solar power (approximately 800–1000 W/m²) to obtain the conversion efficiency of sunlight to electrical energy (15, 16), which is between 1 and 0.5% for anthocyanin or chlorophyllide-based cells.

Discussion

From Figure 1, the reactions found in the solar cell are:



Students are asked to sketch a diagram of these electron transfer events based on the polarity of the cell. They are also asked to explain the fabrication and operation of the device and to draw parallels between the components of the cell and the redox compounds found in photosynthesis. They are encouraged to draw upon concepts learned in organic, biological, and physical chemistry as well as basic physics, electronics, and optics. The role of catalysts and enzymes may be discussed in relation to the carbon-coated counter electrode and during the enzymatic processing of the chlorophyll. Since the TiO_2 and dye serve the same roles as the silver halide grain and dyes used in photography, a parallel can also be made between these two photochemical dye-sensitized systems (10). It should be apparent, however, that the photo-excited electrons injected into the TiO_2 produce electricity in the nanocrystalline solar cell instead of forming an image.

The absorption spectrum of the dye solutions can be taken using a standard spectrophotometer. The students can then use this to determine the portion of the solar spectrum (air mass 1.5, 1000 W/m^2 standard spectrum) where light absorption can occur (13, 15–18). It should be made evident that not all the energy from sunlight can be converted into electrical energy, only the chemical potential or free energy (1, 18). A consequence of the second law of thermodynamics is that not more than 33% of solar energy can be converted into electricity, or work, for a solar converter with a single pigment illuminated by daylight (19–21). The literature references can be read to improve the understanding of both the operation principles and the fabrication of nanocrystalline solar cells (2, 22–24).

One can often revive a dead cell by disassembling it, washing both electrodes in water, and restaining the TiO_2 in the berry juice. The TiO_2 is then washed, dried, and assembled as previously described. When the nanocrystalline cell is no longer functional, it can be disassembled and the two conductive glass electrodes can be recycled for future use. The stained TiO_2 -coated glass can be recycled by wiping off the stained TiO_2 with a tissue dampened with isopropyl or ethyl alcohol. The conductive transparent tin dioxide layer will withstand this, but effort should be made not to scratch it. The carbon-coated glass should be used for a counter electrode only, and the titanium dioxide-coated glass should be recycled for the stained side of the cell.

Conclusion

Concepts of energy and electron transfer are introduced via the building of the nanocrystalline solar cell or light detector. The advantage of this experiment is that the use of natural products facilitates discussions of biotechnology as well as physical and chemical principles. Materials science and semiconductor physics are emphasized during the deposition of the sintered TiO_2 nanocrystalline ceramic film. Chelation and complexation is evident from the attachment of the dye to the

surface of the TiO_2 semiconductor particles. Environmental chemistry can be linked to these concepts via the regenerative cycle found in the cell. It should be emphasized to students that the regeneration of the dye and mediator is much like the coupled cycles of energy and materials that have existed on Earth for billions of years (8). Since our dominance of these biogeochemical cycles, and in particular our use of fossil fuels, may lead to changes in the physical state of the planet (e.g., greenhouse effect and ozone layer depletion), the creation of artificial photosynthetic systems is not merely to present ourselves with alternatives for powering our society, but it is a search for our place in the biosphere.

Note

1. This procedure is being developed as an education kit. It will be available from the Institute for Chemical Education (email: ice@chem.wisc.edu; URL <http://ice.chem.wisc.edu/ice>) beginning in September, 1998. Correspondence and requests for materials before September should be addressed to Greg Smestad (email: gsmestad@mbay.net, or Michael.Graetzel@icp.dce.epfl.ch; URL <http://ldcwww.epfl.ch/icp/ICP-2/icp-2.htm>). This procedure was presented, in part, at the International Symposium of New Materials for Hydrogen-Fuel Cell-Photovoltaic System-1, Cancun, Mexico, Aug. 31–Sept. 5, 1997.

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