



Education and solar conversion: Demonstrating electron transfer

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Abstract

A simplified solar cell fabrication procedure is presented that uses natural anthocyanin or chlorophyll dyes extracted from plants. This procedure illustrates how interdisciplinary science can be taught at lower division university and upper division high school levels for an understanding of renewable energy as well as basic science concepts. Electron transfer occurs on the Earth in the mitochondrial membranes found in living cells, and in the thylakoid membranes found in the photosynthetic cells of green plants. Since we depend on the results of this electron and energy transfer, e.g. in our use of petroleum and agricultural products, it is desirable to understand and communicate how the electron transfer works. The simplified solar cell fabrication procedure, based on nanocrystalline dye-sensitized solar cells, has therefore been developed so that it can be inexpensively reproduced and utilized in the teaching of basic principles in biology, chemistry, physics, and environmental science. A water-based solution of commercial nanocrystalline titanium dioxide (TiO_2) powder is used to deposit a highly porous semiconductor electron acceptor. This acceptor couples the light-driven processes occurring at an organic dye to the macroscopic world and an external electrical circuit. Materials science and semiconductor physics are emphasized during the deposition of the sintered TiO_2 nanocrystalline ceramic film. Chelation, complexation and molecular self-assembly are demonstrated during the attachment of the dye molecule to the surface of the TiO_2 semiconductor particles. Environmental chemistry and energy conversion can be linked to these concepts via the regenerative oxidation and reduction cycle found in the cell. The resulting device, made in under 3 h, can be used as a light detector or power generator that produces 0.4–0.5 V at open circuit, and 1–2 mA per square cm under solar illumination. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: Education; Nanocrystalline materials; Electron transfer; Photoelectrochemistry; Titanium dioxide; TiO_2 ; Dye sensitized solar cells

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1. Introduction and background

Conventional solar cells convert light into electricity by exploiting the photovoltaic effect that exists at semiconductor junctions [1]. They are thus closely related to the silicon-based, diodes, transistors and integrated circuits used in computers. The semiconductor in a typical solar cell is a single crystal of silicon which performs two processes simultaneously: absorption of light, and the separation of the electric charges. These charges, electrons and positively charged “holes”, are formed when light absorption excites electrons in the crystal to higher energy levels [1]. To avoid the premature recombination of these excited electrons and holes, the silicon employed must be highly pure and defect-free. This silicon is often expensive. The cost-effective manufacture of this type of solar cell is a challenge which has discouraged the use of such devices in industrial-scale solar electricity production.

In contrast, the novel nanocrystalline solar cells developed at the Swiss Federal Institute of Technology work on a different principle in which the processes of light absorption and charge separation are themselves separated. Light absorption is performed by a single layer of dye that is chemically attached to the rough surface of a layer of interconnected titanium dioxide particles painted on conductive transparent glass [2–5]. The minute particles of titanium dioxide are single crystals that are each between 10 and 50 billionths of a meter in size and, because of this, are called nanocrystalline. After having been excited by light, the colored dye, usually a ruthenium-based organic compound, is able to transfer an electron to the semiconducting titanium dioxide layer via a process called electron injection or sensitization. This transfer is similar to the process used in color photography. The porous titanium dioxide layer facilitates the transport of the electron to the conductive layer on the glass where it is collected. Meanwhile, positive charge is transferred from the dye to a mediator that is an electron donor present in the liquid with which the solar cell is filled (see Fig. 1). The oxidized mediator brings the positive charge from the dye to the opposite side of the cell which is called the counter electrode. After traveling through the electrical load (for example, a motor or light) the electron collected at the titanium dioxide side of the cell reacts at the counterelectrode and the mediator is returned to its original reduced form. The circuit is thus closed and electricity is produced.

Due to their simple construction, the new cells offer the hope of a significant reduction in the cost of solar electricity. This tutorial, or educational text, illustrates how solar principles can be integrated with other mainstream topics such as physics, chemistry, and technology's impact on society [6]. A simplified procedure for demonstrating the new nanocrystalline solar cell is presented and used as a tool for the integration of these topics and for purposes of education. When one examines the operating principle of the nanocrystalline solar cell, the processes found in this new type of solar cell resemble photosynthesis and are almost as old as the Earth itself. A comparison of the principles and evolution of photosynthesis with the nanocrystalline solar cell is made below in order to provide a concrete, and easy to remember, example of the importance, and interrelationship, of chemical and physical principles. The following text has been written with the intent that it can be given to students along with the glossary (appendix) and experimental procedure.

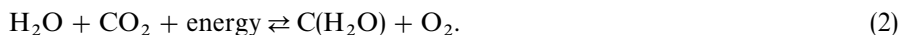
2. Photosynthesis

Three and a half billion years ago, the Earth was much different than it is today. The first photosynthetic organisms were simple, pigmented, one-celled chemical factories [7,8]. They were probably descendants of early chemosynthetic organisms whose importance in our biosphere and in geology is only recently being realized [9]. The early photosynthetic organisms used hydrogen sulfide, H_2S , or organic compounds and sunlight to produce energy-rich materials, sugars, carbohydrates and building materials for themselves and those that fed on them. To convert inanimate chemicals into living material, these organisms employed pigments like green chlorophyll. The electrons removed from an electron donor such as hydrogen sulfide, via the action of light on chlorophyll, reduced the abundant carbon dioxide, CO_2 , in the Earth's early atmosphere. This resulted in the production of carbohydrates, $\text{C}(\text{H}_2\text{O})$, that are used by living organisms as stored energy and food. The reaction for this anaerobic photosynthetic process is given by



As volcanic and other geologic activity subsided, the hydrogen sulfide and other electron-donating compounds became limited. The processes of life needed electron donors, but were faced with a shortage of these materials. The solution to this challenge was remarkable; with the aid of new enzymes coupled to chlorophyll, blue green algae were able to take electrons from abundant water molecules using sunlight. Oceans of water insured that life would never again need to search for electron donors for photosynthesis; they were surrounded by them. As the blue green algae carried out photosynthesis, they released oxygen gas as a waste product. After millennia had passed, photosynthesis by colonies of blue green algae called stromatolites produced high concentrations of oxygen which built up in the atmosphere [7,8]. This O_2 gas oxidized the organic molecules found in all living organisms and was toxic to the chlorophyll-containing organisms. To cope with this radical change in the environment, some of the earlier types of bacteria were forced to avoid the sunlit areas of the oceans, and the new communities of oxygen producers that lived there. Today, these organisms can be found in foul smelling anaerobic mud or in the guts of animals.

The photosynthesizers were forced to evolve complex mechanisms for tolerating their waste products. Some bacteria found that the oxygen could be taken into their cells and used to “burn” the organic compounds after they ate the photosynthetic oxygen producers. These animals, our ancient ancestors, used respiration to reverse the reaction accomplished by plants. Soon, a new cycle arose involving plants, animals and oxygen. Sunlight provided the energy that plants “fixed” into the bonds of complex organic molecules [10]. As organic molecules like carbohydrates were broken down and oxidized by plants and animals, the stored solar energy was released and carbon dioxide originally taken from the atmosphere was returned to it. Today, this reversible and renewable cycle drives the processes of life on the Earth, and is described by the reaction



As a result, food chains and cycles developed and elements such as carbon, oxygen, phosphorous and nitrogen were exchanged along with the biosphere, atmosphere and the geological Earth [9]. Powered by the energy provided by the sun 93 million miles away, the complexity of these cycles, along the biosphere, increased over time. Land plants evolved about 438 million years ago, and were left unmolested for 40 million years until the insects, and then the amphibians, evolved from sea to land. As a consequence of stellar, or solar, physics, our sun releases more power, and grows warmer, as it ages [10]. As the illumination on the Earth increased, and photosynthesis continued, some of the organic compounds produced by plants were not recycled by animals and plants, and were buried within the mud in ancient Permian and Devonian forests and in the coastal areas of the ancient oceans. Over millions of years, this organic material was converted to coal, oil and natural gas by heat and pressure within the Earth. This loss of organic material, e.g. $C(H_2O)$ and CO_2 , was fortunate, because the resulting decrease in carbon dioxide in the atmosphere meant that the increased energy output from the sun, over time, did not overheat our planet. As photosynthesis pulled carbon dioxide from the atmosphere, there was less of the Greenhouse Effect that naturally warms the Earth. Life altered the Earth's climate by controlling the gases that blanket the Earth. The action of photosynthesis also meant that there was an excess of oxygen that is necessary for animal life to flourish. This has kept the temperature and conditions right for the cycles of life, as we know them, to continue to exist.

Over time, the evolution of plants and animals continued, sometimes gradually and sometimes punctuated by rapid changes in the environment. About two million years ago, our earliest human ancestor began the long evolutionary progression towards our modern civilization. Along the way, humans learned to control fire to utilize stored photosynthesis to heat homes, power industry and move people and goods across the planet. This "burning" is what all animals do in order to live. What sets humans apart from other animals is that we combine oxygen with the organic materials produced by photosynthesis to obtain energy inside our bodies as well as outside our bodies. In the last century, wood and plant materials became depleted and we learned to mine the stored solar energy that was buried millions of years ago in ancient oceans, forests and swamps. At our present rate of burning, the ancient "fossil" fuel reserves are non-renewable. It is estimated that only a few hundred years supply of fossil fuels are available at our current rate of consumption, and the rate is increasing as developing nations compete for their share of the global economy [11]. As the carbon dioxide concentration in the atmosphere increases due to fossil fuel consumption and the burning of forests, we are returning the Earth to a carbon dioxide concentration present when the sun was weaker. It has been predicted that over the next 50 to 100 years, the warming of the Earth, via an artificially enhanced Greenhouse Effect, could allow the sea levels to rise, agriculture and crops to fail, global climate to change, and economic development to be damaged in ways that are very difficult to predict [6,10]. Local problems like air pollution and acid rain are also directly linked to the burning of fossil fuels. One method to avoid these undesirable consequences involves conserving fossil sources of solar energy, and directly utilizing the sunlight-energized electrons to produce fuels and electricity. Sunlight on the Earth

drives the wind, fills hydroelectric reservoirs with rainwater and produces heat, light and biomass. Today, photosynthesis on the land and in the oceans produces eight times the current combined energy requirements of humanity. Converting solar energy at 10% efficiency using 1% of the Earth's land area would supply us with twice our current energy needs [11]. The nanocrystalline solar cell is a thin film device that is one of the more recently developed technologies that may help us to tap this renewable energy source.

3. The nanocrystalline dye-sensitized solar cell

The history of the nanocrystalline cell starts in the late 19th century with the principles of photography. It was discovered that certain colored organic dye molecules could allow the silver chloride (halide) based photographic film to respond to a wider range of visible wavelengths. The mechanism for this sensitization in modern photography involves the electron, or energy transfer, from the organic molecule to the semiconducting silver halide particles in the photographic film [2,4,5]. The first photovoltaic cells were measured by Becquerel in 1839 and used copper oxide or silver halide coated metal electrodes immersed in an electrolyte solution. To demonstrate this so called "photoelectrochemical" effect, one can place two copper sheets vertically in a glass and half immerse them in water containing copper sulfate or magnesium sulfate (an electrolyte). After a few days, an oxide will form, and the illumination of one plate in this solution will produce a small voltage that can be measured by using a voltmeter connected to each plate via alligator clips.

Modern solar cells, on other hand, are not wet photoelectrochemical cells. They were first developed over 40 years ago by Bell Labs and are used today to power satellites or to provide reliable electricity in remote locations. These solar cells use a solid state junction which separates regions of electron and hole conduction within the thin silicon wafer. Electrons and holes created by the absorption of light in the silicon diffuse at different rates within the regions of the wafer and are eventually collected at the junction. This "P–N" junction is created by a multi-step process that resembles that used by the semiconductor industry to manufacture integrated circuits and computer chips. A silicon solar cell is a large area diode. New technologies, which use thin films of semiconductor materials such as amorphous silicon and polycrystalline silicon, are under development and are finding applications in world markets such as remote residential and third world village power sources, and in consumer applications such as watches and calculators [1]. Although over 100 million watts of conventional solar cells are currently produced each year for these applications, no solar cell technology has produced an efficient, reliable and cost effective solar module that can be widely used to replace fossil fuel energy sources.

A research group in Lausanne, Switzerland has used our knowledge of photosynthesis and photography to produce a new kind of solar cell that may meet the challenge [2–5,12] (see Fig. 1). The nanocrystalline dye sensitized solar cell is a photoelectrochemical cell that resembles natural photosynthesis in two respects: (1) it uses an organic dye like chlorophyll to absorb light and produce a flow of electrons,

and (2) it uses multiple layers to enhance both the light absorption and electron collection efficiency. Like photosynthesis, it is a molecular machine that is one of the first devices to go beyond microelectronics technology into the realm of what is known as nanotechnology. To create the nanocrystalline solar cell, a solution of nanometer size particles of titanium dioxide, TiO_2 , is distributed uniformly on a glass plate which has previously been coated with a thin conductive and transparent layer of tin dioxide (SnO_2). These are not exotic materials. Large amounts of TiO_2 powder are used in the manufacture of white paint, and large areas of tin dioxide-coated glass are used in buildings as heat reflective (and energy saving) windows. The titanium dioxide film is dried and then heated to form a porous, high surface area TiO_2 structure that, when magnified, looks like a thin sponge or membrane. This TiO_2 film on the glass plate is dipped into a solution of a dye such as a red ruthenium containing organic dye or green chlorophyll derivative. Many dyes can be utilized, but they must both possess a chemical group which can attach and adsorb to the titanium dioxide surface, and they must have energy levels at the proper positions necessary for electron injection and sensitization. A single layer of dye molecules coats and attaches to each particle of the TiO_2 and acts as the absorber of sunlight. To complete the device, a drop of liquid electrolyte containing iodide is placed on the film to percolate into the pores of the membrane. A counter electrode of conductive glass, which has been coated with a thin catalytic layer of platinum or carbon, is placed on top, and the sandwich is illuminated through the TiO_2 side as shown in the diagram.

Thicker layers of organic dyes have been used in the past for solar cells. The mobility for charge transfer within the dye layer is low, and so it was found that only a very thin layer is active for charge or electron injection. This meant that if a single thick layer of dye were used to absorb all the light, it would not be as effective a series of thin layers which are interconnected. In the nanocrystalline solar cell, each layer of dye does not absorb much light, but the interconnected particles of the porous membrane can absorb 90% of visible light when added together. This is much like the way that light is forced to pass through the multitude of leaves in a forest or through the stacked thylakoid membranes found in the chloroplast contained within each cell of a plant's leaves. This novel aspect of the nanocrystalline cell involves the use of a rough semiconducting layer to increase the light absorption while allowing for efficient charge collection. Since the dye layer is so thin, almost all of the excited electrons produced from light absorption can be injected into the TiO_2 and this sensitizes it to the wide range of wavelengths, or colors, of light absorbed by the dye. The TiO_2 serves the same role as the silver halide grain in photography except that the injected electrons produce electricity instead of forming an image. The electrons lost by the dye via light absorption are quickly replaced by the mediator which is the iodide ion in the electrolyte solution. The oxidized mediator forms iodine or triiodide, which in turn obtains an electron at the counter electrode after it has flowed through the electrical load. From Fig. 1, the energy producing reactions found in the nanocrystalline dye-sensitized solar cell are



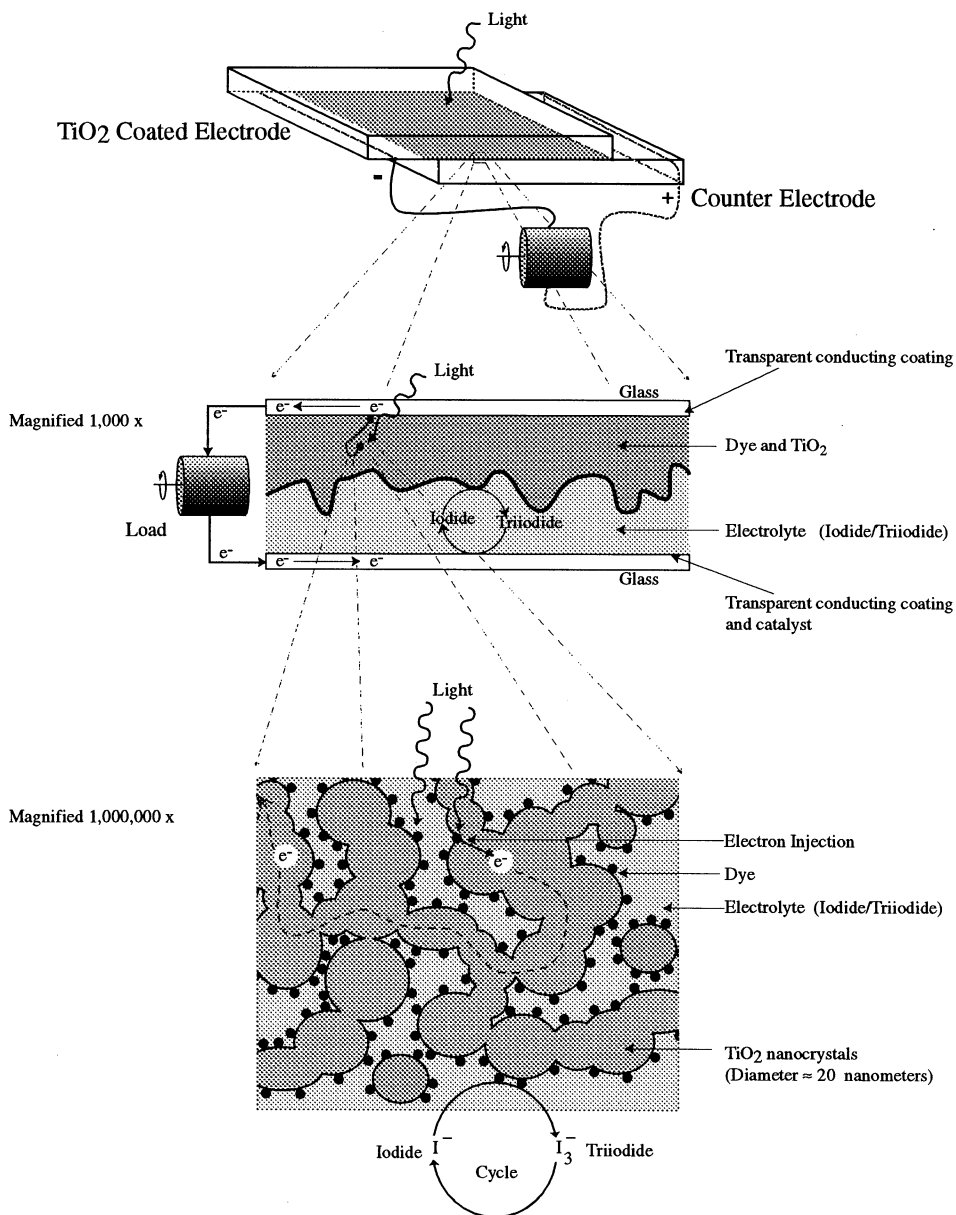
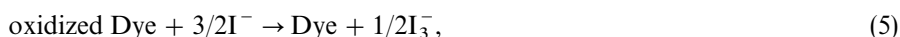


Fig. 1. Nanocrystalline dye-sensitized solar cell operating principle. The iodide/triiodide mediator forms a regenerative cycle that accepts the negatively charged electrons that are transferred from the excited dye to the titanium dioxide and the load.



The interconnected titanium dioxide particles serve as the electron acceptor, the iodide serves as the electron donor, and the dye functions as a photochemical “pump” which excites the electrons to higher energy levels by using the energy of the light that is absorbed. This configuration is like that found in natural photosynthesis in which the electron acceptor is inevitably the carbon dioxide, water is the electron donor, and the organic molecule chlorophyll is the photochemical pump. The voltage produced by the nanocrystalline solar cell is the difference in energy levels between the titanium dioxide and the mediator, and depends on the mediator and solvent used, as well as the condition of the titanium dioxide and the intensity of illumination [2–5]. The current produced by the cell is directly related to the amount of light absorbed by the dye, which itself depends on the intensity of the illumination and type of dye attached to the titanium dioxide. The power output, or energy per second measured in watts, of any solar cell is the voltage across between the two electrodes multiplied by the current (amperes) flowing through the load. Of course, all the energy from sunlight can not be converted into electrical energy. It is a consequence of the second law of thermodynamics that not more than 33% can be converted for a solar cell with a single pigment illuminated by daylight [3]. The overall sunlight to electrical energy conversion efficiency of a nanocrystalline solar cell using the best dyes currently available is 7–10% under direct sunlight. This is to be compared with 0.5–5% for natural photosynthesis and 15–20% for commercial silicon solar cell modules. One process that limits the efficiency of the dye-sensitized solar cell is the re-capture of the injected electron by the oxidized mediator before the electron has been collected and passed through the load and counter electrode. This reaction is represented by



Calculations which consider the spectrum of the light utilized by the dye indicate that nanocrystalline solar cells of at least 10% efficiency could be realized at a cost of \$0.60 per watt, which may be competitive with conventional electricity generation [3,13,14]. These cost estimates illustrate the promise of the new devices but further research and development is needed to find ways to seal the cell and allow it to withstand the test of time so that it can be used in large area commercial solar cells.

In the meantime, students can follow a simple procedure that will demonstrate the operating principles of the nanocrystalline solar cell and those of photosynthesis [15,16]. The objectives of the experiment are (a) to extract the natural dye, (b) to deposit the TiO_2 nanocrystalline ceramic film on conductive glass, (c) to determine how the physical and electronic coupling of an organic compound to an oxide semiconductor can occur via complexation and chelation, and (d) to determine the current – voltage and power output characteristics of the assembled photo-electrochemical cell and to compare this output to the chemical processes occurring in photosynthesis found in green plants.

4. Experimental procedure

4.1. General 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 conductive glass is available and the TiO_2 layer deposition 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 h lab period [16]. It is also suggested that the iodide electrolyte be prepared before the lab period.

4.2. Deposition of TiO_2 film

Depositing the nanocrystalline TiO_2 film requires the preparation of a solution containing commercial colloidal TiO_2 powder, the masking of a cleaned conductive glass plate, and the application and distribution of the solution on the conductive glass plate, followed by the sintering of the resulting thin film layer. The resulting 7–10 μm thick TiO_2 film has a porous, sponge-like structure that enhances both the light absorption and electron collection efficiency in a similar way as the thylakoid membrane found in green plants [2,3]. A commercially available glass plate coated with a conductive layer of fluorine doped SnO_2 is cut (2.5 cm \times 2.5 cm) and then coated with a TiO_2 film using the TiO_2 solution. The glass is TEC 10, or TEC 15 obtained from Hartford Glass Co. Inc., P.O. Box 613, Hartford City, IN 47348, USA, Fax 765-348-5435, or Pilkington, Libbey Owens Ford, 811 Madison Ave., P.O. Box 799, Toledo, OH 43697-0799, USA.

The TiO_2 solution is prepared by the incremental addition of 20 ml of nitric or acetic acid solution to 12 g of colloidal TiO_2 powder in a mortar and pestle while grinding (Degussa P25 TiO_2 , 3500 Embassy Parkway, Akron, OH, 44333, USA or Degussa AG, D-6000, Frankfurt 11, Germany). Each 1 ml addition of the dilute acidic solution (pH = 3–4 in de-ionized water) proceeds only when the previous mixing and grinding has produced a uniform and lump-free paste. As an alternative to the acid solution, 0.2 ml of acetylacetone can be added to 1 ml of water and added to the TiO_2 powder followed by the addition of 19 ml of water, again in 1 ml increments while grinding [3,17].

A volt-ohm meter should be used to check which side of the glass is conductive, and 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 in order 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. The tape should extend from the edge of the glass to the table at a 45° angle to secure the glass. This tape will form a 40–50 μm deep mold or channel into which the TiO_2 solution can flow and, at the same time, masks a strip of the conductive glass so that an electrical contact can later be made. Place three drops of the water-based TiO_2 solution uniformly on the plate (approximately 5 μl per cm^2) then slide a glass stirring rod over the plate to spread and distribute the material (see Fig. 2). The film is then allowed to dry in air for 1 min. The tape is then carefully removed and the film is

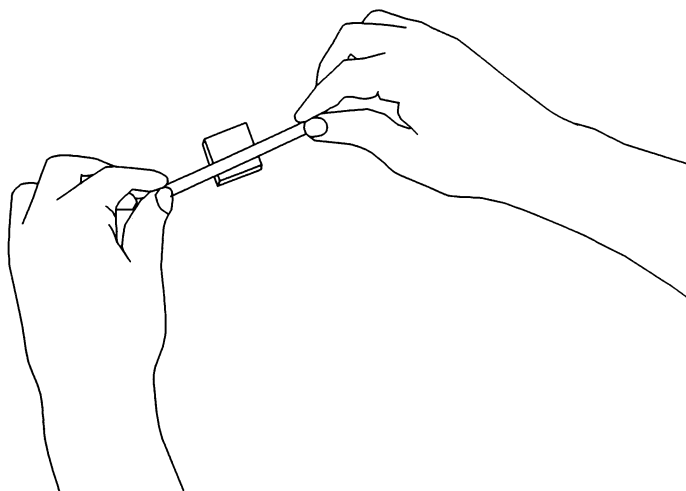


Fig. 2. Motion used to coat the titanium dioxide on the conductive glass plate.

annealed and sintered in an air stream at 450°C for 30 min. A hot air gun or tube furnace may be employed to heat the film (Leister Model Hotwind S, or Steinel Type 3449), 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 min. The TiO₂-coated conductive glass is allowed to slowly cool to room temperature, and can be stored in air for later use.

4.3. Staining of the titanium dioxide with the dye

Fresh (or freshly thawed) blackberries, raspberries, or pomegranate seeds are crushed in 0.5–1 ml of water, filtered and used as a anthocyanin dye solution [15,16]. For the simplest procedure, the TiO₂ film can be placed on the top of crushed berries to which a tablespoon of water has been added (see Fig. 3). The water obtained from soaking red Hibiscus tea leaves at room temperature may also be used, but produces varying results depending on the source of the material. A requirement for the dye structure is that it posses several =O or –OH groups capable of chelating to the Ti(IV) sites on the titanium dioxide surface (see Fig. 4). A mixture of cyanin 3-glycoside and cyanin 3-rutinoside are the main anthocyanin pigments from California blackberries (*Rubus ursinus*) and have been found to be suitable fast-staining dyes for sensitization [15,16]. The cyanin may also be 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 [15,16]. Cyanidin (cyanin without the sugar may also be extracted and used [19,20].

Soak separate TiO₂-coated glass plates for 10 min 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

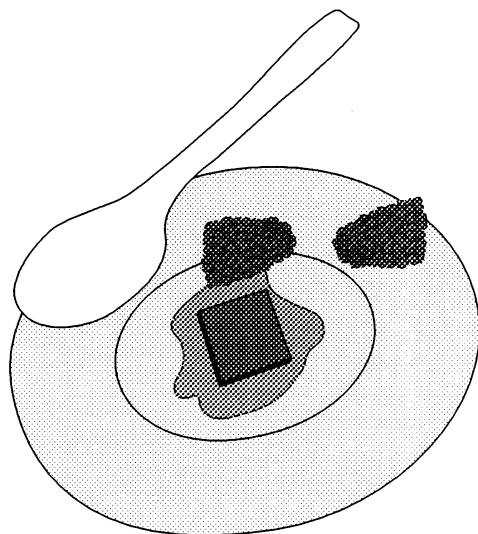


Fig. 3. Placement of the titanium dioxide coated conductive glass plate in the cyanin containing solution.

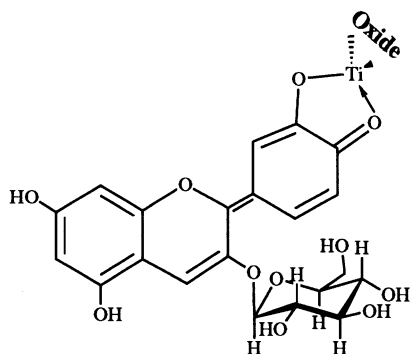


Fig. 4. Proposed structure of the cyanin dye adsorbed to one of the titanium metal centers on the titanium dioxide surface.

for 5 more minutes. Adsorption of cyanin to the surface of TiO_2 and complexation to Ti(IV) sites is rapid, forming a complex capable of electron injection (Fig. 3). The dark purple stained film is then washed in water, and then ethanol or isopropanol. The stained and washed TiO_2 film should then be gently blotted dry with a tissue. If the cyanin stained electrode is not used immediately, then it should be stored in acidified de-ionized water ($\text{pH} = 3\text{--}4$, acetic acid) in a closed dark-colored bottle.

As an option for advanced classes, a second type of dye can be obtained from green chlorophyll. This is accomplished by using the naturally occurring enzymes that cleave the phytol tail and convert chlorophyll into a chlorophyllide possessing

carboxyl groups that are capable of chelating to the surface of the TiO_2 particles. Natural dyes derived from chlorophyll and Cu have achieved significant energy conversion efficiencies (2.6% and 9.4 mA/cm^2), but these results require pigment purification, and the co-adsorption of other compounds on the TiO_2 surface [17,18]. As a simplified procedure, fresh, young green leaves are ground in a mortar and pestle 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 $4 \times 4 \text{ mm}$ pieces of unground leaves are placed within the container. An unstained (white) TiO_2 film is also placed within the bottle, and additional acetone is added to the bottle until the film is completely covered by the solution. The solution is left to react for 24 h in a dark place in order to allow time for the enzymes to react with the chlorophyll as well as for the attachment of the dye to the TiO_2 . After 24 h, the electrode should be stained to a light green–yellow color. Before solar cell assembly, this stained electrode should be washed in acetone or alcohol and gently blotted dry. If the stained electrode is not used immediately, then it should be stored in the acetone and chlorophyllide solution until the electrode is ready to be assembled into the light detector device. Paper chromatography can be used to compare the purity of the crude extract with the enzyme processed materials.

4.4. Carbon coating the counter electrode

While the TiO_2 electrode is being stained in the berry juice or chlorophyll solution, the counter electrode can be made from another ($2.5 \text{ cm} \times 2.5 \text{ cm}$) piece of conductive SnO_2 coated glass. A graphite (carbon) 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 given by eq. (6). No masking or tape is required for this electrode, and thus the whole surface is catalyst coated (see Fig. 5). 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. This is accomplished by distributing a drop of a 10 mM (in Isopropanol) hexachloroplatinic acid solution on the counter electrode using a clean glass rod, and then annealing the plate at 450°C for 5 min.

4.5. Assembling the solar cell device and measurement of the electrical output characteristics

The cyanin-stained TiO_2 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 TiO_2 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 quickly placed on the table such that the film side is face up, and the

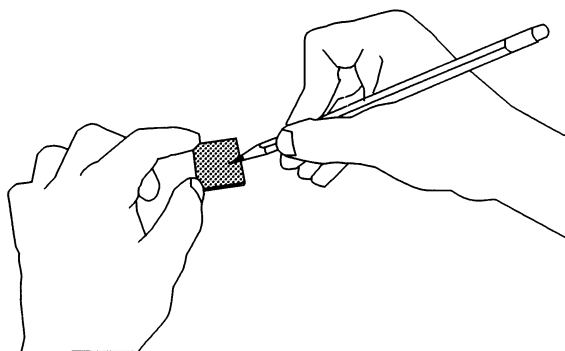


Fig. 5. Coating of the counter electrode with a carbon catalyst layer.

catalyst-coated counter electrode is placed on the top so that conductive side of the counterelectrode faces the TiO_2 film. The two opposing glass plates are offset so that all of the TiO_2 is covered by the counter electrode, and the 4 mm strip of glass not coated by TiO_2 is exposed (see Fig. 6). The two exposed sides of the device will serve as the contact points for the negative and positive electrodes so that electricity can be extracted to test the cell. Two binder clips are used to gently hold the plates together at the other edges. The Iodide electrolyte solution is 0.5 M potassium iodide mixed with 0.05 M iodine in water-free ethylene glycol. 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. In order to protect the cell from damage by excessive UV light, a cover cut from a polycarbonate plastic sheet 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, and 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. 7). Point by point current and

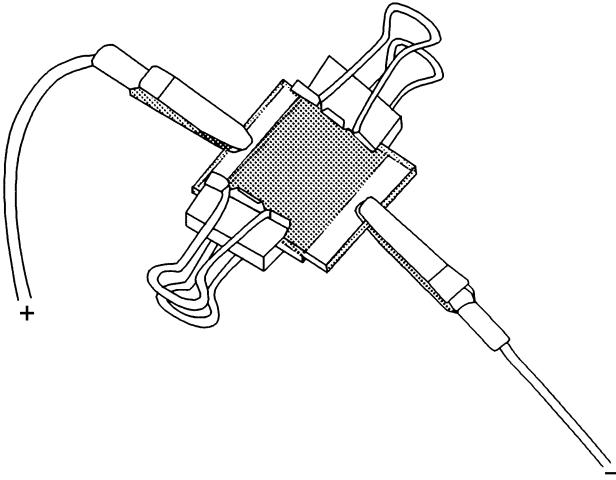


Fig. 6. Assembled solar cell. Light enters through the titanium dioxide coated glass plate.

Two Possible Current - Voltage Characteristics Set-Ups

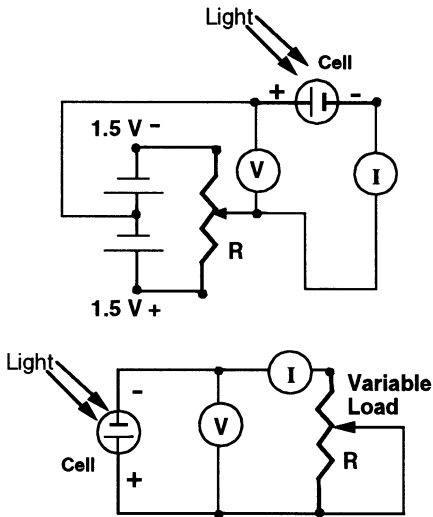


Fig. 7. Light detector or solar cell current–voltage characteristic measurement set-up. The solar cell is represented as a diode or battery.

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 result in the production of enough electrical output to power a small motor (Maxon 2522.846.12.112.000, Maxon Interelectric Co. AG, CH-6072 Sachseln/OW, Switzerland, FAX + 41 41 60 1650, or Mabuchi RF-330TK-07800, Mabuchi Motors, 3001 West Big Beaver Rd., Suite 520, Troy, MI, 48084, USA). A polarized 10000 micro-Farad capacitor can be charged using the solar cell(s) and then rapidly discharged through the motor in order 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. They are revived by washing the electrodes with ethanol (or acetone for the chlorophyll based cell), blot drying in air with a tissue, re-assembling the cell, and re-applying fresh electrolyte.

5. Results

Shown in Fig. 8 is the typical I - V (current–voltage) curve for the sunlight-illuminated cyanin (Blackberry juice) sensitized cell of active area 4 cm^2 . Similar results are also obtained with the Chlorophyll based dyes. Using the volt – ohm meter, the open circuit, or maximum, voltage produced under direct sunlight should be

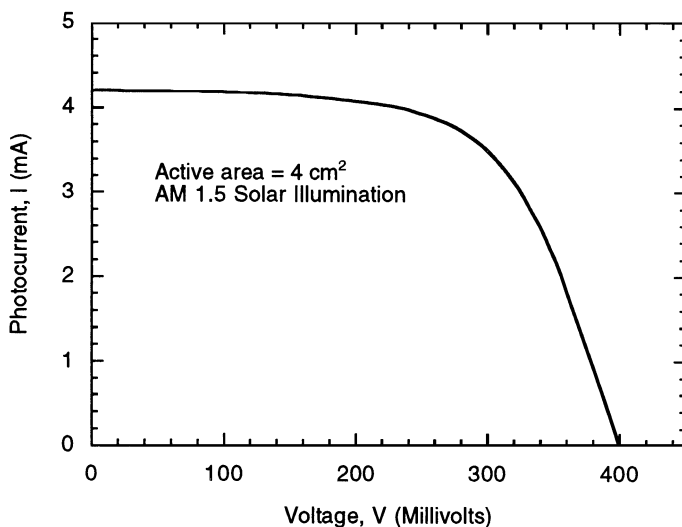


Fig. 8. Typical current–voltage curve for a blackberry juice sensitized solar cell of four square centimeter area.

between 0.3–0.5 V. Switching the meter to current (mA, 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 3–4 mA. The maximum product of current and voltage (obtained near the “knee” of the curve) is divided by the incoming solar power (approximately 800–1000 W/m²) to obtain the sunlight-to-electrical energy conversion efficiency which is between 1% and 0.5% for anthocyanin or chlorophyllide based cells. One can often revive a dead cell by disassembling it, washing both electrodes in ethanol, and then washing, drying and assembling 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 TiO₂ coated glass can be recycled by wiping off the stained TiO₂ with a tissue dampened with isopropyl or ethyl alcohol. The conductive transparent tin dioxide layer will withstand this, but some 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.

6. Discussion

Students are asked to sketch a diagram of the electron transfer events and write chemical equations based on the polarity and behavior 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 compounds found in photosynthesis. Students 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 the enzymatic processing of the chlorophyll. Since the TiO₂ and dye serve the same roles as the silver halide grain and colored dyes used in photography, a parallel can also be made between these two photochemical dye sensitized systems. Materials science and semiconductor physics are emphasized during the deposition of the sintered TiO₂ nanocrystalline ceramic film. Chelation and complexation is evident from the attachment of the dye to the surface of the TiO₂ semiconductor particles. Environmental chemistry can be linked to these concepts via the regenerative cycle found in the cell and expressed in eq. (2).

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/m² standard spectrum) where light absorption can occur [1]. 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. 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 [3]. The literature references can be read to improve the understanding of the operation principles, along with the nanocrystalline solar cell fabrication procedure.

7. 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. Human kind is now faced with another of life's resource challenges. There may be undesirable costs for our use of ancient chemicals and fossil fuels. Like the early chemosynthetic and photosynthetic organisms, we are now faced with dwindling resources and new opportunities. Like the oxygen-producing blue green algae, however, we may fall victim to the waste products of our own success. If we do not learn to balance and cycle the energy, materials and resources given to us, then we may be forced to bury ourselves like the anaerobic communities who long ago retreated from the light. Cycles of energy and materials have existed on the Earth for billions of years. In the past few hundred years, we have come to dominate and control many of these cycles. Like no other life form, we have changed the physical state of the planet. Our search for artificial photosynthesis is, therefore, not merely to present ourselves with alternatives for powering our society, but it is a search for our place in the biosphere.

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Appendix: Student's Glossary

Absorption, light The conversion of light into other forms of energy upon traveling through a medium, thereby weakening the transmitted light beam. Absorption is one of the possible fates of light when it interacts with matter which also includes emission, scattering, reflection or transmission.

Adsorb To bind a substance to a surface, the surface adsorbs the substance.
Examples: Dye on TiO_2 .

Anaerobe A microorganism that can live in the absence of oxygen.

Atmosphere The gaseous envelope that surrounds the Earth's solid surface, and is the barrier between space and the land/sea.

Atom The smallest particle of an element that has the chemical properties of that element. A nucleus and its surrounding electron clouds. *Example:* A single atom of the element titanium, Ti.

Billion 1 000 000 000, or 10^9 .

Biosphere All the life on a planet. The living part of the Environment on Earth consists of bacteria, fungi, viruses, plants, and animals (including humans).

Carbohydrate An energy containing compound usually of the general formula $C_x(H_2O)_y$. *Examples* $C_6H_{12}O_6$ (glucose); $C_{12}H_{22}O_{11}$ (sucrose); starch.

Catalyst A substance that increases the rate of a reaction without being consumed in the reaction.

Celsius scale, C A temperature scale on which the freezing of water is at zero degrees and its normal boiling point is 100° . $T(\text{Fahrenheit}) = (9/5) \times T(\text{Celsius}) + 32$.

Charge The intrinsic property of matter that is a measure of the strength with which one body can interact electrostatically with another body. The charge is characterized by the polarity (either positive, +, or negative, -) and the magnitude or strength. The flow of charge constitutes an electrical current.

Chemical formula A collection of chemical symbols and subscripts that shows the composition of a compound or substance. *Examples:* H_2O ; TiO_2 ; SnO_2 ; $C_6H_{12}O_6$.

Chemosynthesis The biological process of energy utilization in which simple chemicals like hydrogen or H_2S are used to produce organic molecules used by living organisms. It is believed that this form of life occurred on the early Earth before photosynthesis and exists today at the deep ocean vents and deep within the Earth itself.

Chlorophyll The organic dye used by living plants in photosynthesis to convert light energy into chemicals such as carbohydrates and sugars. It is a compound composed of the elements carbon, hydrogen, oxygen, nitrogen and magnesium.

Chloroplast The sub-unit within a plant cell where photosynthesis takes place via the action of light energy on chlorophyll.

Colloidal suspension A collection of tiny particles in a liquid which may take a long time to settle out (if ever). *Example:* milk, TiO_2 solution.

Compound A specific combination of elements, found in a specific ratio. It can be separated into elements by using chemical techniques.

Counter electrode The electrode at which the electrochemical circuit is completed.

Crystal A solid in which the atoms, ions or molecules lie in a orderly array. *Examples:* $NaCl$; diamond; silicon; graphite.

Current, I The rate of supply of charge. Current is measured in amperes (A).

Dye A chemical pigment molecule or compound that will absorb light.

Electrochemical cell A system consisting of at least two electrodes in contact with an electrolyte.

Electrode A solid that makes contact with the electrolyte in a electrochemical cell so current may flow.

Electrolyte An ionically conducting medium.

Electron A subatomic particle with a charge of negative one (-1). The smallest division of negative electricity.

Electron injection The process of electron transfer occurring between a sensitizer and a semiconductor.

Element A substance that cannot be broken down into simpler components by mere chemical means. A substance consisting of atoms of the same atomic number. *Examples:* silicon; hydrogen; titanium; oxygen; hydrogen.

Energy The capacity of a system to do work or supply heat. Kinetic energy is the energy of motion; potential energy is the energy arising from position. Light can affect the potential energy of a compound.

Enzyme A biological catalyst.

Efficiency, Energy The fraction of one form of energy that can be converted into another form.

Evaporate To vaporize completely.

Experiment A test carried out under carefully controlled conditions in order to answer a question.

First law of thermodynamics Energy is neither created or destroyed, but rather it is converted from one form to another. The internal energy of an isolated system is constant.

Fixation, chemical To convert an elemental substance to one of its compounds. Example: CO₂ to sugars.

Gas A fluid form of matter that fills the container it occupies and can be compressed into a much smaller volume. *Examples:* CO₂; water vapor; methane.

Glass A non-crystalline inorganic mixture of various metallic oxides fused by heating. Most glasses are made of silica (SiO₂), boric or phosphoric oxides. Silica or silicon oxide based glasses transmit light.

Greenhouse effect The blocking of the heat radiation from the Earth's surface by some atmospheric gases (notably, carbon dioxide, water and methane). Since some heat is not lost into space, the Earth's temperature is higher than that of the Moon or Mars. The natural Greenhouse Effect insulates the Earth from the cold of space. Increased Greenhouse Effect could, however, lead to environmental problems such as climate changes, floods, hurricanes and crop failures.

Halide A compound containing an element such as chlorine, Cl, bromine, Br, or iodine, I. Any element from group 7 of the periodic table.

Hole Site in a crystal where an electron is missing. It is thus positively charged, and sometimes mobile.

Injection The transfer of an electron or hole into a semiconductor or solid (see sensitization).

Iodide An element present in sea water that is assimilated and concentrated by many seaweeds. The Iodide ion is essential for the proper functioning of the human thyroid gland. Alcohol solutions of iodine are used as an antiseptic. In the nanocrystalline solar cell, it functions as the mediator. The reduced form is called the Iodide ion (I⁻), and the oxidized form is the iodine or triiodide ion (I₂ or I₃⁻).

Ion An electrically charged atom or group of atoms.

Junction When a p-type and n-type semiconductor are joined, the region in which the type changes is the p–n junction. The term p and n refer to the semiconductor doping such that holes or electrons are more easily conducted, respectively.

Mediator In a photoelectrochemical cell, the mediator is the molecule that maintains, and protects, the electric charge on another substance by becoming oxidized or reduced. It is the catalyst present in the electrolyte.

Meter A SI unit of length (1 inch is 2.54 cm, or 0.0254 m).

Micro- A SI prefix meaning 10⁻⁶ of a unit.

Milli- A SI prefix meaning 10^{-3} of a unit. One mA equals one milliamperere

Million 1 000 000, or 10^6 .

Nano- A SI prefix meaning 10^{-9} of a unit. One nanometer is one billionth of a meter.

Nanocrystalline A material made up of minute regions that are each in the range of 1–100 billionth's of a meter in dimension.

Organic Pertaining to living organisms, compounds or molecules formed by living organisms, and to the chemistry of compounds containing the element carbon.

Oxidation A reaction in which an atom, an ion, or a molecule loses an electron that sometimes (but not always) involves its combination with oxygen. Titanium metal is oxidized to TiO_2 .

Photoelectrochemical cell A device in which a photo-driven reaction induces electrons to travel from one substance to another. Electricity, fuels, or new compounds may thus be produced.

Photon A particle-like packet of electromagnetic radiation that characterizes some properties of light.

Photosynthesis The process in which plants use the energy from light to synthesize organic compounds for their growth from carbon dioxide and water. Plants “fix” carbon dioxide into sugars and carbohydrates using photosynthesis. Photosynthesis occurs via a complex chain of reactions taking place within the membrane in the plant cells. (See *Fixation*).

Power The rate of supply of energy, or the rate of doing work. In electrical units, voltage times current.

Photovoltaic cell A device that converts radiant energy (photons or light) into electricity. Photo stands for photon and voltaic stands for the voltage produced from the photons. See *Solar Cell*.

Rate The change in something per unit of time. A ratio in which time appears in the denominator.

Reduction A reaction in which an atom, an ion, or a molecule gains an electron. The opposite of oxidation. Carbon dioxide (CO_2) is reduced to sugars and carbohydrates by plants and photosynthesis.

Recombination The reunion or combination of an excited electron and a hole to produce heat or light. This is an undesirable process in a solar cell, photoelectrochemical cell or photovoltaic device.

Respiration The oxidative breakdown of food molecules that releases energy from chemical bonds.

Ruthenium A chemical element with 44 electrons and protons used as a platinum substitute in jewelry, electrical contacts and in catalysts and superconductors.

Science The systematically collected and organized body of knowledge based on experiment, observation and careful reasoning and deduction. Western civilization's method of obtaining the truth about the nature of our universe.

Second law of thermodynamics A mathematical inequality asserting that it is impossible to transfer heat from a colder to a warmer system without making some other changes in the environment or universe. For every process that occurs, the entropy (or disorder) of the universe is increasing. (See *First Law of Thermodynamics*).

Semiconductor A crystalline solid with an electrical resistance that decreases as the temperature is raised. A semiconductor does not normally conduct electricity well, unless it is doped with specific impurities.

Sensitization The process by which an otherwise transparent substance is made to respond to light. This involves the transfer of energy, or electrons, by the sensitizer compound that absorbs the light.

SI The International System of units based on the metric system.

Silicon Element 14, Si, in the Periodic table most commonly found in sand, quartz and window glass, SiO₂. Silicon is a brittle, gray colored semiconductor.

Solar cell An artificial device that can convert light energy (photons) into electrical or chemical energy.

Solid A rigid form of matter that maintains the same shape whatever the container.

Tin Dioxide (SnO₂) An oxide of the metal tin (Sn) which has the useful property of being both electrically conductive and optically transparent.

Titanium Dioxide (TiO₂) The oxide of the metal titanium used as the white pigment in paint. It is found in nature as the minerals rutile and anatase. Titanium metal is used in the production of steels and corrosion resistant metal alloys of high strength.

Thylakoid The basic unit of the chloroplast in plants. A sac-like structure consisting of stacks of membranes containing chlorophyll and enzymes.

Voltage, V A measure of difference in electrical potential between two electrodes or points (in V). The work per unit charge.

Watt The electrical unit for power representing the amount of work being done per second. The rate of energy use or production.

References

- [1] K. Zweibel, *Harnessing Solar Power: The Photovoltaics Challenge*, Plenum Press, New York, 1990, pp. 235–253.
- [2] B. O'Regan, M. Graetzel, *Nature* 353 (1991) 737.
- [3] G. Smestad, C. Bignozzi, R. Argazzi, *Solar Energy Materials and Solar Cells* 32 (1994) 259–273.
- [4] A. Hagfeldt, M. Graetzel, *Chem. Rev.* 95 (1995) 49.
- [5] M.K. Nazerruddin, A. Kay, I. Rodicio, R. Humphry – Baker, E. Mueller, P. Liska, N. Vlachopoulos, M. Graetzel, *J. Amer. Chem. Soc.* 115 (1993) 6382.
- [6] A. Truman, D. Schwartz, M. Bunce, *Chemistry in Context, Applying Chemistry to Society*, W.C. Brown Publishers, American Chemical Society, Dubuque, IA, 1997.
- [7] L. Margulis, *Early Life*, Science Books International, Inc., Boston, MA, 1982, pp. 1–73.
- [8] C. de Duve, *Vital Dust*, Basic Books, Harper Collins Publishers, New York, 1995, pp. 99–136.
- [9] H.L. Ehrlich, in: *Geomicrobiology*, 3rd ed., Marcel Dekker Inc., New York, 1996, pp. 20–64.
- [10] J. Lovelock, *Healing Gaia*, Harmony Books, New York, 1991, pp. 62–88.
- [11] L. Schipper, S. Meyer, R. Howarth, R. Steiner, *Energy Efficiency and Human Activity: Past Trends, Future Prospects*, Cambridge University Press, Cambridge, 1992, pp. 7–35.
- [12] M. Graetzel, P. Liska, *Photo-electrochemical cell and process of making same*, US Patent No. 5,084,365, 1992.
- [13] D. Coiante, L. Barra, *Solar Energy Materials and Solar Cells* 27 (1992) 79.
- [14] J.M. Ogden, R.H. Williams, *Int. J. Hydrogen Energy* 15 (1990) 155.
- [15] N. Cherepy, G.P. Smestad, M. Graetzel, J.Z. Zhang, *J. Phys. Chem. B* 101 (1997) 9342.

- [16] G. Smestad, M. Graetzel, *J. Chem. Edu.* 75 (1998) 752.
- [17] A. Kay, M. Graetzel, *J. Phys. Chem.* 97 (1993) 6272.
- [18] A. Kay, R. Humphry-Baker, M. Graetzel, *J. Phys. Chem.* 98 (1994) 952.
- [19] K. Tennakone, G. Kumara, I. Kottegota, K. Wijayantha, *Semicond. Sci. Technol.* 12 (1997) 128.
- [20] K. Tennakone, A.R. Kumarasinghe, G.R.R.A. Kuma, K.G.U. Wijayantha, P.M. Sirimanne, *J. Photochem. Photobio. A: Chem.* 108 (1997) 193.

