

Remote Access Laboratory Guide



Dye-Sensitized Nano-crystalline Solar Cell

In this exercise, you will:

- Understand the basic concepts of energy conversion, fossil fuels, and solar cells.
- Describe how a dye-sensitized solar cell (DSC) works, and the benefits of TiO_2 .
- Understand the chemical properties and UV-Vis spectra of dyes used in DSCs.
- Fabricate a simple DSC capable of converting sunlight into electricity.
- Determine the current-voltage and power output characteristics of solar cells.



Background

Fossil fuels are limited, non-renewable resources comprised of biomass that has been deposited over millions of years. Photosynthesis is the main process that creates biomass and its main inputs are water, carbon dioxide, and sunlight. From these ingredients, the cellular machinery of plants builds sugars and other carbohydrates. So, fossil fuels are essentially stored solar energy – energy stored in the form of chemical bonds created by plants that lived millions of years ago. Burning fossil fuels breaks those chemical bonds and releases the stored energy as large amounts of heat. The products of combustion are carbon dioxide and water. If carbon dioxide is released into the atmosphere at a faster rate than it is removed (e.g., by growing plants, by dissolving in sea water, or by other mechanisms), then the concentration of carbon dioxide in the atmosphere will increase over time. Measurements indicate that human activities, such as slash and burn farming and the burning of fossil fuels, have a large effect on the composition of the atmosphere. Rising carbon dioxide levels produce an increased greenhouse effect, which over time may alter the global climate. Recently, as consumers and governments have become aware of the true costs of burning fossil fuels, there has been renewed interest in solar power generation. During the day, 800-1000 W/m² of solar power reaches the surface of the earth. Converting even a fraction of this into usable power could dramatically decrease our dependence on non-renewable resources. Therefore, researchers are continuously looking for novel ways of harnessing solar radiation as a clean and abundant energy source. In addition to driving down the cost of making conventional silicon solar cells, scientists are developing new types of photo-voltaic devices. These include ones made from polycrystalline and amorphous silicon, other inorganic semiconductors and nanoparticles (e.g., CdSe), and even organic polymers. While the newer constructions are generally less efficient than their silicon counterparts, they hold the promise of being much less expensive to manufacture.



Background

Conventional silicon-based solar cells were developed over forty years ago by Bell Labs. Typically, they employ a p-n junction, as illustrated in Figure 1. Absorbed light creates free electrons and holes in the silicon materials. These charge carriers are collected by electrodes attached to the top and bottom surfaces of the semiconductor. The resulting current flow can drive an external load or be stored in a battery for future use. Conventional solar cells are widely used for electrical power generation. For example, they power satellites and provide electricity in remote locations that cannot be reached by the distribution grid. However, since they must be constructed from extremely pure silicon, conventional devices are often too expensive to be competitive with other forms of electricity generation.

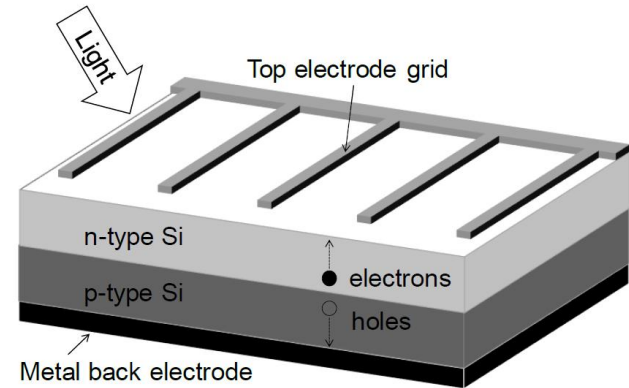


Fig.1: Typical silicon solar cell. Current is collected by leads attached to the electrodes.

On the other hand, the relatively low cost of generating electricity from fossil fuels does not reflect the true cost of such activities. The price of electricity generated in coal-fired power plants includes the costs associated with: (i) mining the coal; (ii) buying and operating the equipment needed to burn it to drive generators; and (iii) distributing the electricity over transmission lines to end users. But the price does not accurately reflect unknown costs which may be related to the build-up of carbon dioxide and other pollutants in the atmosphere.



Background

In this experiment, you will construct a dye-sensitized solar cell (DSC), similar to those pioneered by Michael Grätzel at the Swiss Federal Institute of Technology in Lausanne, Switzerland. This particular type of device is actually a photo-electrochemical cell, which means that a photo-induced chemical reaction causes electrons to travel from one substance to another. The device construction and operation are illustrated schematically in the Figure 2.

DSCs consist of a nanostructured semiconductor film coated with organic dye molecules. The nanostructure intimately contacts an electrolyte solution that contains a iodide-triiodide mediator. The film and solution are sandwiched between two electrodes, which allow for electrical connections. Importantly, one electrode (the one coated with nanocrystals) must be transparent, while the other should be coated with a carbon catalyst to facilitate reduction of the iodide-triiodide mediator.

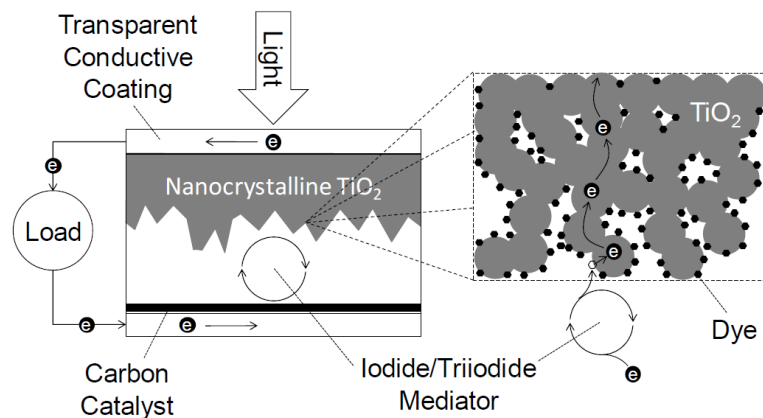


Fig. 2: Structure and operation of a dye-sensitized solar cell.



Background

Titanium dioxide (TiO_2) is a common white pigment that can be found in every-thing from paint to paper products. TiO_2 exists in several crystal forms including rutile, anatase, and brookite structures. These forms differ in the spatial arrangement of titanium and oxygen atoms in the crystals. Since the anatase form of TiO_2 is a semiconductor with a band gap of 3.2 eV, it primarily absorbs UV light rather than visible light. Anthocyanin dyes, on the other hand, are organic molecules that absorb visible light extremely well. This gives them a deep red-purple color. When certain anthocyanin dyes come in contact with TiO_2 , they can complex with the surface of the nanocrystals. This is depicted in the figure below.

The dye molecule acts as a ligand and forms bonds with titanium atoms on the TiO_2 surface. In this case, since two bonds are formed between the ligand and metal, the anthocyanin dye molecule is said to chelate the titanium atom. This is a particularly strong type of interaction and it makes the dye very difficult to remove from the surface of the semiconductor. Therefore, chelating anthocyanin molecules cannot be rinsed off by solvent or the electrolyte solution during operation of the solar cell. The close proximity of the dye molecules to the TiO_2 surface allows the dye to sensitize the semiconductor: when the dye molecules absorb visible light, they can transfer photo-excited electrons to the TiO_2 .

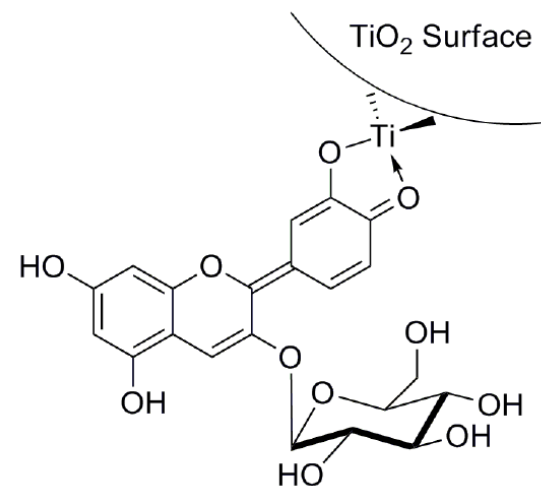


Fig. 3: Structure of anthocyanin dye attached to TiO_2 surface.



Background

The operation of a dye-sensitized solar cell can be described as follows (refer to Figure 2):

- Light enters through the transparent conductive electrode. Most of the visible light passes through the TiO_2 and strikes the anthocyanin dye molecules which form a complex with the TiO_2 surface.
- The dye molecules absorb the light. The energy from the absorbed photons effects electronic transitions in the dye, resulting in a photo-excited (high-energy) state.
- Photo-excited dye molecules inject electrons into the nanocrystalline TiO_2 . This leaves the dye molecules in a partially oxidized state.
- The iodide-triiodide mediator transfers electrons to oxidized dye molecules. The result is that the dye molecules are reduced back to their original state while the mediator becomes oxidized.
- Electrons that were injected into the TiO_2 percolate through the nanocrystalline network and are collected by the top electrode.
- After passing through an external circuit, and possibly being used to drive an electrical load, the electrons reach the carbon coated counter electrode.
- The carbon acts a catalyst to transfer electrons back into the oxidized mediator, which has diffused from the dye- TiO_2 surface through the electrolyte solution and to the back electrode. Thus, the mediator is reduced back to its original state and the electrical circuit is completed.



Background

The following relationships and terminology relate to the characterization of solar cells:

- Current density (J) is the current (I) divided by the area (A) of the device.

$$J(\text{mA} / \text{cm}^2) = \frac{I(\text{mA})}{A(\text{cm}^2)}$$

- The open circuit voltage (V_{OC}) is the voltage produced under illumination when no current is flowing (i.e., leads disconnected or under infinite resistance).
- The short circuit current (I_{SC}) is the current that flows through an illuminated solar cell when there is no external resistance (i.e., when the electrodes are simply connected or short-circuited). The short-circuit current is the maximum current that a device is able to produce. Under external load, the current will always be less than I_{SC} . Short circuit current can be converted to short circuit current density (J_{SC}) by dividing by the area of the device. Power (P) is current multiplied by voltage (V) or power density is current density multiplied by voltage.

$$P(\text{mW}) = I(\text{mA}) \times V(\text{Volts}) \text{ or } P(\text{mW} / \text{cm}^2) = J(\text{mA} / \text{cm}^2) \times V(\text{Volts})$$



Background

- The maximum power point is the point (V_{mpp} , I_{mpp}) on the I-V curve where the maximum power is produced. This point can also be identified on J-V curves as (V_{mpp} , J_{mpp}).
- The power conversion efficiency (PCE) is the ratio of power produced by the device (at its maximum power point) to the total amount of power available in the incident light. The PCE can be calculated from device parameters as follows, where $P_{in} = 100 \text{ mW/cm}^2$:

$$Efficiency = \frac{P_{out}}{P_{in}} = \frac{J_{mpp} V_{mpp}}{P_{in}} = \frac{J_{SC} V_{OC} FF}{P_{in}}$$

- Here, the fill factor (FF) is the ratio of a photovoltaic cell's actual maximum power output to its theoretical power output if both current and voltage were at their maxima, I_{SC} and V_{OC} , respectively. This is a key quantity used to measure cell performance. It is a measure of the “squareness” of the I-V curve.
- On the next slide Figure 4 contains a typical current density-voltage curve. Terminology introduced above is illustrated.



Background

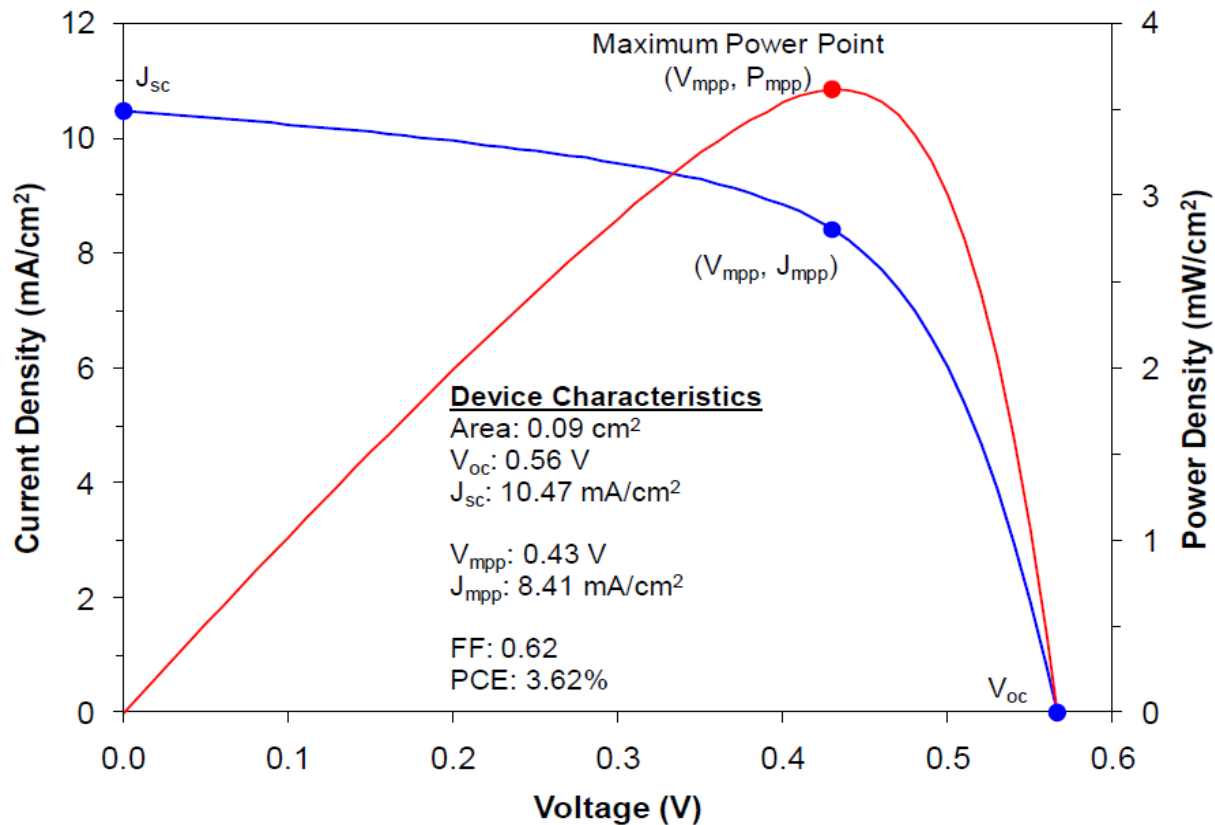


Fig. 4: Example J-V curve for a solar cell. Current density (blue line) is graphed on the left axis. Power density (red line) is graphed on the right axis.



Background

For this lab exercise, you will need the following :

- A kit that contains the supplies (conductive glass, nanocrystalline TiO₂, binder clips, KI3 electrolyte, manual, etc.) to create five titanium dioxide raspberry solar cells can be ordered from the [Institute for Chemical Education](#). The kit contains enough nanocrystalline titanium dioxide to be used many times.
- Glass Microscope Slides & Tweezers & Transparent tape
- Empty syringe and parafilm
- Very dilute acetic acid (0.1 mL concentrated acetic acid in 50 mL of water)
- Multimeter
- Hotplate
- Raspberry juice or Frozen raspberries: The anthocyanin used as the dye must complex with the titanium(IV). Testing a variety of red or blue colored plant material is a possible source for inquiry-based extensions. Blackberries, raspberries, pomegranate, and bing cherries work. Strawberries and red grapes do not work. Because of general availability and the intense color we use thawed frozen raspberries pulverized in a blender; the mixture can be refrozen and thawed many times.
- Alternative to the graphite pencil that is available in the solar cell kit: a candle
- Powerful light source
- Water wash bottle & ethanol wash bottle
- Cotton swabs
- Shipping Supplies



Procedure

The first step of this lab is to obtain two glass substrates and clean the substrates. On each of these glass substrates is an ITO layer that is conductive. The cleaning of these substrates can be done with Acetone followed by Isopropanol and DI water. Later on, the steps shown on video found at: <https://www.youtube.com/watch?v=Jw3qCLOXmi0#t=113> will be followed. Please watch the video very carefully to understand how TiO_2 paste is prepared and follow the steps concurrently.

- I. Identify the conducting side of a tin oxide-coated piece of glass by using a multimeter to measure resistance. The conducting side will have a resistance of 20-30 ohms.
- II. With the conducting side up, tape the glass on three sides to the center of a spill tray using one thickness of tape. Wipe off any fingerprints or oils using a tissue wet with ethanol. Opposite sides of tape will serve as a spacer (see below) so the tape should be flat and not wrinkled. The third side of tape gives an uncoated portion where an alligator clip will be connected.
- III. Next the TiO_2 layer is applied to the conductive surface of the glass slide. The glass substrate is taped down (conductive side facing up) so that 4-5 mm of the edge will remain clear of any TiO_2 . The TiO_2 is placed on the substrate using a spatula and smeared over the surface using a glass rod.
- IV. Carefully remove the tape without scratching the TiO_2 coating. Leave the removed tape in a spill tray for disposal.



Procedure

- V. Heat the glass on a hotplate in a hood for 10-20 minutes. The surface turns brown as the organic solvent and surfactant dries and burns off to produce a white or green sintered titanium dioxide coating. (Note: this requires a plate that gets quite hot.) Allow the glass to slowly cool by turning off the hotplate. The sample will look quite similar before and after heating; you only know it is done if you have observed the darkening stage along the way.
- VI. Place a small amount of the raspberry juice (i.e., anthocyanin dye solution) in a petri dish and gently immerse the TiO_2 coated substrate into the solution with the TiO_2 film facing down. Note: Soak the TiO_2 film for 10 minutes in the dye solution. If white TiO_2 can be seen upon viewing the stained film from either side of the glass, then the film should be soaked longer (in 5 minute increments until the TiO_2 film is completely stained). When staining is complete, the TiO_2 should appear dark purple. Do not remove the substrate from the staining solution until you are ready to completely finish the assembly process from start to finish. The stained TiO_2 film should not be exposed to air for more than one minute. This minimizes degradation of the anthocyanin dye molecules.
- VII. Rinse gently with water to remove any berry solids and then with ethanol to remove water from the porous TiO_2 . The ethanol should have evaporated before the cell is assembled.
- VIII. Pass a second piece of tin oxide glass, conducting side down, through a candle flame to coat the conducting side with carbon (soot). For best results, pass the glass piece quickly and repeatedly through the middle part of the flame. Note: This carbon coating can also be handled with a graphite pencil. This glass slide will serve as the anode of the device.
- IX. If you used the candle option, wipe off the carbon along the perimeter of three sides of the carbon-coated glass plate using a dry cotton swab.



Procedure

- X. Assemble the two glass plates with coated sides together, but offset so that *uncoated glass extends beyond the sandwich*. With the TiO_2 side facing up, carefully place the carbon coated electrode on top of the TiO_2 film so that the carbon side faces the TiO_2 . Do not slide or rub the films against each other. Proper positioning should leave 4-5 mm of each plate exposed on alternate ends of the assembly. The exposed areas will serve as contact points for the test leads (wires with alligator clips). Clamp the plates together with binder clips.
- XI. Add a drop of a triiodide solution to opposite edges of the plate. Capillary action will cause the KI_3 solution to travel between the two plates. (The KI_3 electrolyte solution consists of 0.5 M KI and 0.05 M I_2 in anhydrous ethylene glycol.) Add another drop of triiodide solution to the other end of the device, if needed, and repeat the gentle opening and closing of the binder clips. The entire stained area of the TiO_2 film needs to contact the triiodide solution for the device to function properly. Wipe off the exposed areas of the glass contacts with alcohol in order to remove excess triiodide solution. It is very important that the contact areas be clean and free of solution. The solution can corrode the alligator clips in the next step so wipe off an excess. Fasten alligator clips and electrical test leads to the device. Attach the black (-) wire lead to the TiO_2 coated glass. Attach the red (+) wire lead to the counter electrode (carbon coated glass). Read the current and voltage measurements using your multimeter with the help of a light source.

Video ends here, next steps involve measurements and observations that can be carried out either at your classroom or remotely using FE-SEM with the help of our scientists.



Procedure

XIII. Perform Characterization in your classroom

- The solar cell kit available from the Institute of Chemical Education comes with a potentiometer and detailed instructions regarding how to obtain current-voltage data for your students' solar cells. The data can be transferred to a spreadsheet program (e.g., Microsoft Excel) and graphs similar to Figure 4 can be constructed. The data can also be used to calculate device characteristics such as: J_{SC} , V_{OC} , and PCE.

XIV. Perform Remote FE-SEM Analysis

- The Remote Access centers offer free web access to several instruments which can be used to complement this experiment.
- *Note:* There is no need to send us samples for this experiment. We already have samples premade and ready to go. However, if you have additional samples or special requirements, we are willing to assist you in obtaining whatever images and data you require.

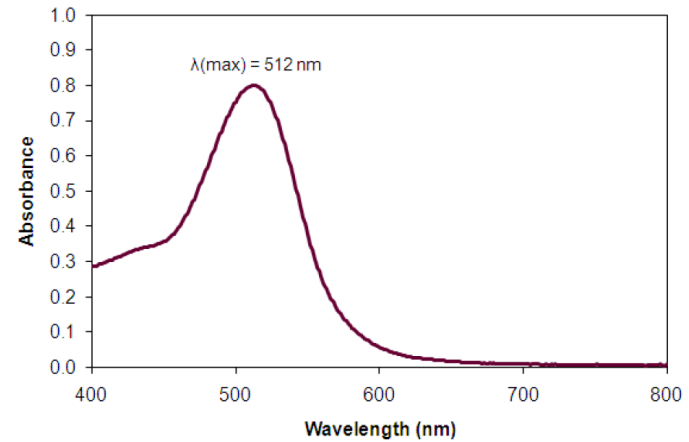
XV. UV-Vis Spectrophotometer

- The Remote Access centers also offer free web access to UV-Vis spectrophotometers in case the users require.
- Students can remotely access our UV-Vis instrument. This instrument measures the amount of light absorbed by a sample as a function of wavelength. For solar cell applications, researchers are continuously looking for new dye molecules that absorb as much light as possible. An example spectrum of blackberry extract (note: raspberry is expected to be similar) is illustrated in Figure 5 at the top of the next page.



Procedure

Fig. 5: UV-Vis spectra of filtered blackberry juice, used to stain the TiO_2 films.



Field Emission Scanning Electron Microscope (FE-SEM)

- This piece of equipment can be used to image nano-scale objects. In this experiment, the students use a film of nano-crystalline TiO_2 . The extremely small particles provide a huge surface area onto which the dye molecules to attach. The FE-SEM can be used to visualize and measure the size the TiO_2 nano-crystals. An example image is shown in Figure 6.

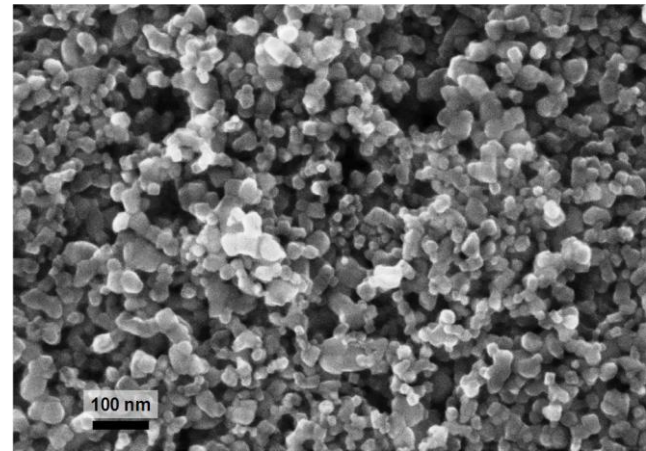


Fig. 6: FE-SEM image of nanocrystalline TiO_2 films.



Remote Access Connection Instructions

What makes these labs different and unique from other classroom experiments is that we have incorporated a section in each activity to remotely characterize your nanoscale samples from your classroom. Remote access to a variety of characterization tools can enhance the visualization of nano-related concepts by allowing students to see the effects of their work first hand. You can choose to mail your samples to our facility to be analyzed at a later date or you can use our samples that have been processed using the same procedure. Please use the following steps to successfully complete a remote session.

- I. Request a remote lab session specifying pertinent information such as: the day, the time, and the instrument you are interested in using by visiting our web site <http://nano4me.org/> Go to the *Educator's* tab and select the *Remote Access* tab in that section. You will see the list of partners with the instruments provided to chose from.
- II. You will be contacted by a Remote Access staff member to set up a test run to ensure you are set up properly and have the required infrastructure.
- III. Send samples or verify the in-house sample you would like us to prepare and load for characterization. Send your samples to the Remote Access center that you chose on your request.
- IV. There are two communications soft-ware packages, that will allow us to communicate instructions and answer questions during the session.
 - I. Zoom: You can obtain a free download at: <https://www.zoom.us/>
 - II. TeamViewer: You can obtain a free download at: <https://www.teamviewer.com/en/index.aspx>



Remote Access Connection Instructions

V. You will need:

- a) Computer with administrator access to install plug-ins and software
- b) An internet connection
- c) Speakers
- d) Microphone
- e) Projector connected to the same computer
- f) Web browser (Firefox preferred)

VI. During the test run you can refer to this guide to perform the following steps, but it's very important that you only proceed with these steps during your scheduled times. You may interfere with other remote sessions and potentially damage equipment if you log in at other times.

- a) Open and logon to your Zoom/Team-viewer account. You will be given the access code to enter at the time of your test and then again during the remote session.
 - If you are using the Zoom software, Remote Access staff will give you the access code.
 - If you are using the Team-viewer software, Remote Access staff will give you the ID & password.
- b) You should soon see the Remote Access desktop and at this point you can interact with the icons on the screen as if it were your desktop.
- c) Switch to full screen mode by selecting the maximize screen option in the top right corner of the screen.
- d) Upon completion of the session, move your mouse to the top right corner of the screen, and click on the X to disconnect the remote session. It will ask if you want to end the remote session. Click Yes.



References and Supplemental Material

- Greg P. Smestad and Michael Grätzel, "Demonstrating Electron Transfer and Nanotechnology: A Natural Dye-Sensitized Nanocrystalline Energy Converter," *J. Chem. Ed.* **1998**, 75(6), 752. <http://JChemEd.chem.wisc.edu>
 - Michael Grätzel, "Solar Energy Conversion by Dye-Sensitized Photovoltaic Cells," *Inorg. Chem.* **2005**, 44(20), 6841. <http://dx.doi.org/10.1021/ic0508371>
 - Michael Grätzel, "Photoelectrochemical Cells," *Nature* **2001**, 414, 338. <http://dx.doi.org/10.1038/35104607>
 - This handout is designed to work with the "Titanium Dioxide Raspberry Solar Cell" lab which is available from the University of Wisconsin Madison MRSEC. The web address is <http://mrsec.wisc.edu/Edetc/nanolab/>
 - Materials for this lab are available from the Institute for Chemical Education: <http://education.mrsec.wisc.edu/289.htm>
- The Nanotechnology Applications and Career Knowledge (NACK) Center was established at the Penn State College of Engineering in September 2008 through the National Science Foundation (NSF) Advanced Technological Education program.

Please contact a NACK representative today to assist you in increasing the awareness of nanotechnology and education related opportunities across the nation. Visit our website for an expanded contact list.

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Nanotechnology Applications and
Career Knowledge (NACK)
National Center



Pennsylvania State University
118 Research West
University Park, PA 16802



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