

# Quantum Dot-Sensitized Solar Cells

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## Introduction

Solar energy is a very important energy topic in the United States and around the world. Advances in solar cell technology make solar energy more affordable every year. According to the U.S. Energy Information Administration, the cost of solar photo voltaic capacity has decreased from approximately \$300 per watt in 1956 to less than \$5 per watt in 2009. Furthermore, with expected advances in technology U.S. solar photo voltaic generating capacity is projected to increase from 30 megawatts in 2006 to 381 megawatts in 2030. Similarly, there are plans for large increases in the amount of solar energy being put into use in other countries. According to the U.S. Energy Information Administration, in Japan the government has set a target for 30 percent of all households to have solar panels installed by 2030. Quantum dot solar cells have the potential to produce high efficiencies with a relatively cheap cost to construct them. Furthermore, quantum dots have the capability of multiple electrons being excited from one photon of light (in comparison to organic dyes which generally only have one electron excited per single photon)

## Quantum Dot Theory

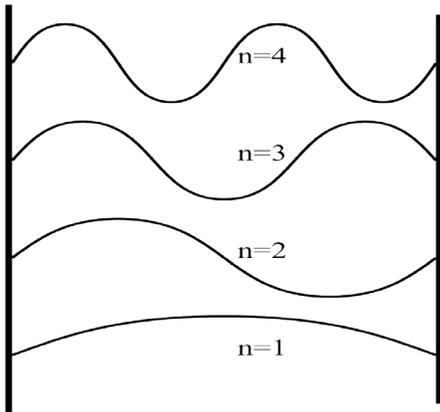
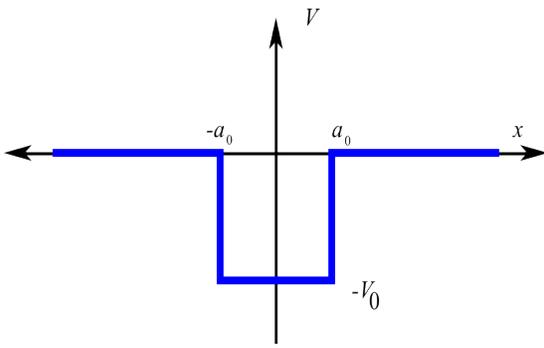


Figure 1

Quantum dots or nanocrystals are very small semiconductors, having a diameter that ranges from 2 to 10 nanometers. The electrons in a quantum dot behave like particles in a finite spherical square well. To understand quantum dots more let us first look at a one dimensional particle in an infinite well. Assuming  $L$  is the width of the well, then the potential  $V(x) = 0$  if  $0 \leq x \leq L$  and  $V(x) = \infty$  otherwise. A particle in this potential is free except at  $x = 0$  and  $x = L$  (at the boundaries), where it cannot escape because of the infinite potential. The result of the infinite potential at the boundaries means that we should have nodes there. We end up with sinusoidal standing waves in the well as shown in Figure 1.

The closed formula for the wavelength is  $\lambda = 2L/n$ . Since when inside the well the particle is completely free, the de Broglie formula  $p = h/\lambda$  holds where  $h$  is the planck's constant and the energy,  $E = p^2/2m$  where  $p$  is the momentum and  $m$  is the mass of the particle. Combining the equations, we end up with  $E = n^2h^2/8mL^2$ . Since the energy is a product of specific constants, a particle in a square well can only have specific energy levels.

In a quantum dot the electron is trapped in a three dimensional finite spherical square well. Since it is 3 dimensional, the wave function of the electron has a radial, polar angle  $\theta$ , and azimuthal angle  $\phi$  component,  $\psi(r, \theta, \phi)$ . The wave function can be separated into radial and angular components  $\psi(r, \theta, \phi) = R(r)Y(\theta, \phi)$ . However, we do not have a dependence on the angular components for our energy levels, only radial dependence. After separation of variables our radial equation becomes  $-\hbar^2/2m(d^2u/dr^2) + Vu = Eu$  where  $u(r) = rR(r)$



**Figure 2**

For a finite spherical well  $V(r) = -V_0$  for  $-a < r < a$  and  $V(r) = 0$  for  $|r| > a$  where  $2a$  is the width of the well and  $V_0$  is a positive constant as in Figure 2.

In this case the energy,  $E < 0$ .

For  $r < -a$ ,  $V = 0$  and the radial equation becomes  $-\frac{\hbar^2}{2m}(d^2u/dr^2) = Eu$  and  $d^2u/dr^2 = -(2mE/\hbar^2)u = k^2u$  where  $k = \sqrt{(-2mE)/\hbar^2}$  and  $k$  is real and positive. The general solution is  $u(r) = A\exp(-kr) + B\exp(kr)$  where  $A$  and  $B$  are arbitrary solutions.  $A\exp(-kr)$  blows up as  $r \rightarrow -\infty$  so, the only physically allowable solution is  $u(r) = B\exp(kr)$ , for  $r < -a$ .

For the region  $-a < r < a$ , the equation becomes  $-\frac{\hbar^2}{2m}(d^2u/dr^2) - V_0u = Eu$  and  $d^2u/dr^2 = -q^2u$  where  $q = \sqrt{(-2m(E+V_0))/\hbar^2}$ . Even though  $E < 0$ ,  $|E| < |V_0|$  therefore  $q > 0$ . The general solution is

$u(r) = C\sin(qr) + D\cos(qr)$ , for  $-a < r < a$ ,  $C$  and  $D$  are arbitrary constants.

For  $r > a$ ,  $V(r) = 0$  and the general solution is  $u(r) = F\exp(-kr) + G\exp(kr)$  but  $G\exp(kr)$  blows up as  $r \rightarrow \infty$  so, the only physically allowable solution is  $u(r) = F\exp(-kr)$ , for  $r > a$ .

The boundary conditions are that  $u$  and  $du/dr$  are continuous at  $-a$  and  $+a$ . Since the potential is an even function, and the sine and cosine functions have symmetry, sine is odd and cosine is even, we can consider the solutions separately (assume the solutions are either odd or even). In this case we can impose the boundary conditions on  $a$  and the same would be true for  $-a$  since  $u(-r) = \pm u(r)$

Looking at the cosine (even) solutions first:

Continuity of  $u(r)$  at  $r = a$ ;  $F\exp(-ka) = D\cos(qa)$  (1)

Continuity of  $du/dr$  at  $r = a$ ;  $-kF\exp(-ka) = -qD\sin(qa)$  (2)

Dividing (2) by (1) we get  $k = q \tan(qa)$

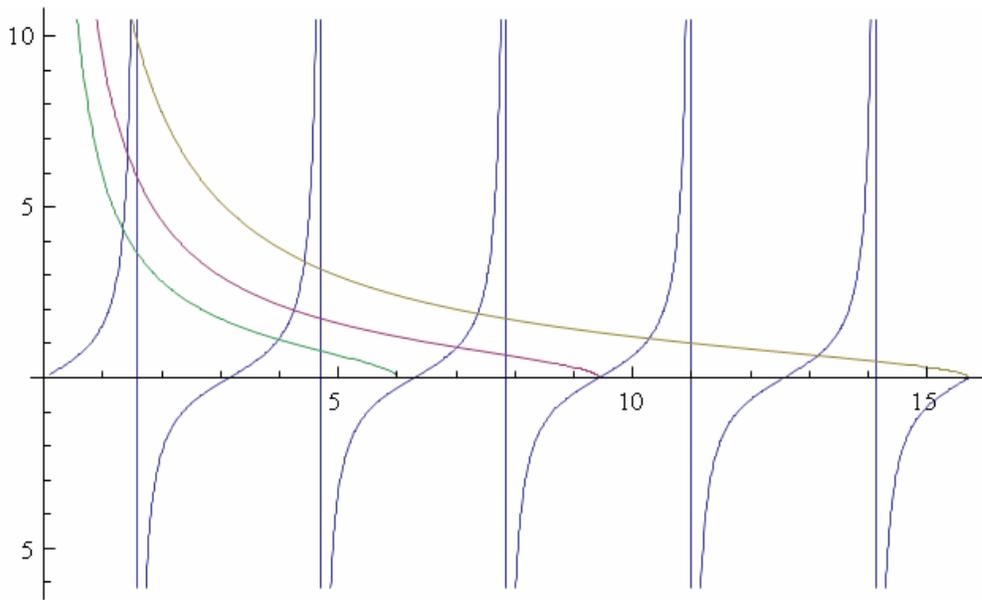
Since  $k$  and  $q$  are both functions of energy,  $k = q \tan(qa)$ , is a formula for the allowed energies.

Making the equation look nicer, let  $z = qa$  and  $z_0 = a\sqrt{(2mV_0)/\hbar^2}$  Recall,  $k = \sqrt{(-2mE)/\hbar^2}$  and  $q = \sqrt{(-2m(E+V_0))/\hbar^2}$ .  $k^2 + q^2 = 2mV_0/\hbar^2$  Thus  $k^2a^2 + q^2a^2 = 2mV_0a^2/\hbar^2 = z_0^2$ . Therefore  $ka = \sqrt{(z_0^2 - z^2)}$  (3)

Since  $k = q \tan(qa)$ ,  $ka = qa \tan(qa)$  and substituting for  $z$  gives,  $ka = z \tan z$  (4)

Equating (3) and (4) gives,  $z \tan z = \sqrt{(z_0^2 - z^2)}$ , and  $\tan z = \sqrt{(z_0^2/z^2 - 1)}$  (5)

Figure 3 shows a graph that gives the solution to the equation by plotting  $\tan z$  and  $\sqrt{(z_0^2 - z^2)}$  on the same grid.



**Figure 3**

The blue corresponds to  $\tan z$  and the purple is for  $\sqrt{(3\pi/z)^2 - 1}$ , yellow is for  $\sqrt{(5\pi/z)^2 - 1}$ , and green is for  $\sqrt{(6/z)^2 - 1}$ . The horizontal axis gives us the  $z$  values. For  $z_0 = 6$ , the allowed energies occur at  $z = 1.35$  and  $4.01$ .

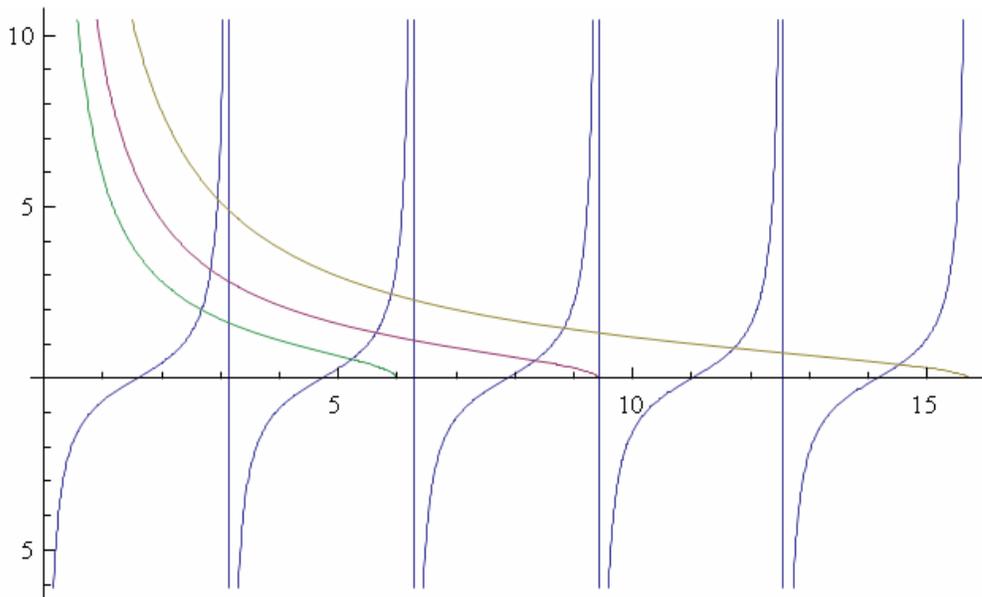
Looking at the odd/sine solutions,

$$\text{Continuity of } u(r) \text{ at } r = a; F \exp(-ka) = C \sin(qa) \quad (6)$$

$$\text{Continuity of } du/dr \text{ at } r = a; -kF \exp(-ka) = Cq \cos(qa) \quad (7)$$

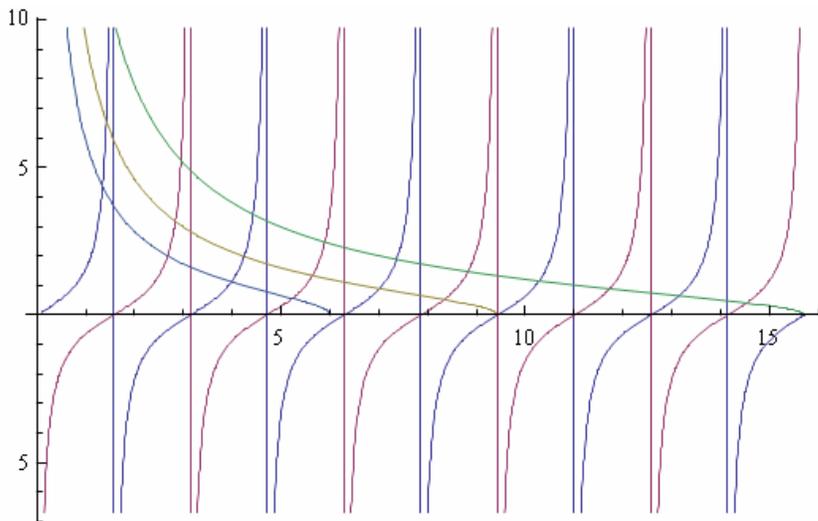
Dividing (7) by (6) we get  $k = -q \cot(qa)$

Going through the same substitutions as before, the final equation becomes  $-\cot z = \sqrt{(z_0/z)^2 - 1}$ . Figure 4 shows the solutions



**Figure 4**

For  $z_0 = 6$ , the allowed energies occur at  $z = 2.704$  and  $5.222$ . Figure 5 shows a graph with both the odd and even solutions



**Figure 5**

## Creating Quantum Dots

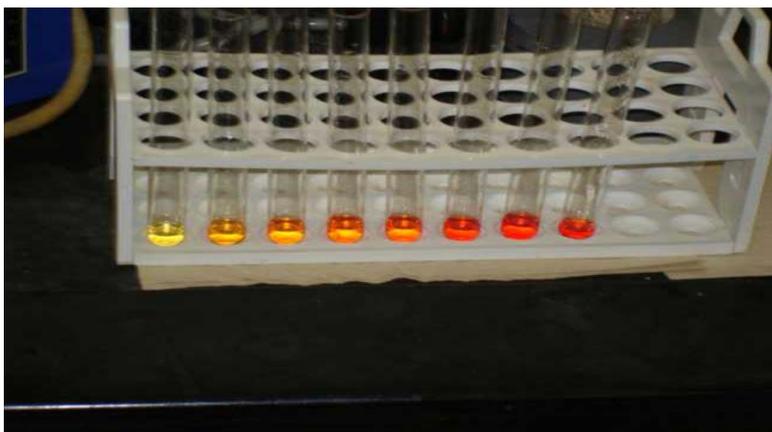
The research on thin-film semi-conductor solar cells at Cornell College has led our physics and chemistry students down some interesting paths: from raspberry juice to organic dyes, we now present our research purveying the potential energy source of quantum dots as sensitizers in titanium dioxide solar cells. The production of quantum dots is relatively simple and cheap, and the adjustable absorption spectrum of these nanoparticles is easily controlled. The most difficult part of the research will be attaching the quantum dots to the TiO<sub>2</sub> nanoporous layer of the solar cell to absorb energy from photons and transfer that energy to electrons to create an electric current.

Quantum dots provide an ideal location for this conversion of energy due to their small size (on the order of a few nanometers) and chemical makeup – completely inorganic, and therefore quite stable (<http://pubs.acs.org/doi/full/10.1021/jp802572b?cookieSet=1>). Diameters of the quantum dots range from 2-10 nm, which means that the energy levels of an excited electron (excitron) within the QD are discrete – as opposed to continuous, as the energy levels would be in a “bulk” semiconductor. In addition, the size of the quantum dot varies the band-gap, or the difference in energy between an excited electron within its “hole” and an excited electron outside its hole. This means that energy absorbed by electrons in a quantum dot from high-energy photons can be transferred out of the QD via the excited electron, and the electron “hole” can be filled with a lower-energy electron. In a solar cell, titanium dioxide provides a pathway for the excited electron to leave the quantum dot, while the electrolyte (usually an iodide solution) provides a wealth of lower-energy electrons to fill the holes left behind by the excitons. Thus, the flow of electrons creates a current.

## Procedure

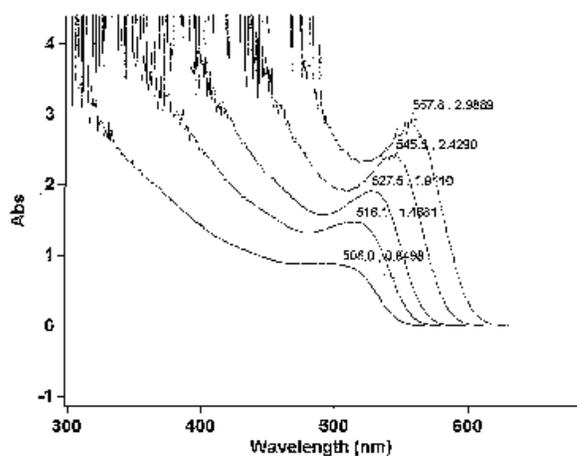
We used cadmium oxide and selenium to create cadmium selenide nanocrystals in a “wet-chemical” reaction, as outlined by UW-Madison, albeit modified to create a higher concentration of the reaction solution, as shown in Figure 6 and the video clip below.

(<http://mrsec.wisc.edu/Edetc/nanolab/CdSe/index.html#Materials>).



**Figure 6**

0.200 g selenium was dissolved in 2.8 mLs trioctylphosphine (TOP) and 7.2 mLs octadecene on a stirring hot plate (0.253 M). 0.300 g cadmium oxide was dissolved in 10 mLs oleic acid and 20 mLs octadecene at 225°C in a round-bottom flask. The selenium solution was then added to the pre-heated cadmium solution, and 5-10 mLs of the reaction solution was removed and quenched at room temperature at various intervals (10-30 seconds) until all of the reaction solution was removed from the flask. The growth of the quantum dots can be monitored visibly by the color change of the reaction solution, which remains stable post-quenching. To purify the quantum dots, all of the aliquots were recombined and the nanocrystals were precipitated with 100% (200 proof) ethanol (1 part QD solution to 2 parts ethanol). The precipitate was centrifuged, the solvent removed, and then the quantum dots were redissolved in a small amount of toluene (as little as needed to re-dissolve the dots, usually 1-2 mLs). This process was repeated, and the toluene solution was filtered through a paper filter to remove large debris.



**Figure 7**

To characterize the quantum dots, a UV-vis spectrometer was used to identify the absorption of the toluene-dissolved quantum dots. Figure 7 shows the absorption spectra of 5 different intervals of the quantum dot reaction, having been purified and analyzed separately – the change in peak absorption corresponds to a change in color as well as change in size of the quantum dots.



**Figure 8**

Figure 9 shows the purified quantum dots. It is very important to use pure (100%) ethanol when purifying the dots. 95% ethanol is not effective, as shown in Figure 8.

There is no apparent change in absorption nor contaminants of the quantum dots in toluene, having been purified with ethanol and toluene once, twice, and three times. Thus, I feel it is necessary to purify the quantum dots simply by precipitation with ethanol, re-dissolution in toluene, and finally paper filtration.



**Figure 9**

Figure 10 shows a mixture of quantum dots purified with ethanol and dissolved in toluene, with the absorption range spanning 300 to 575 nm. This shows that a mixture of different sizes of quantum dots used in a solar cell could be more efficient than a solar cell containing one size of quantum dots.

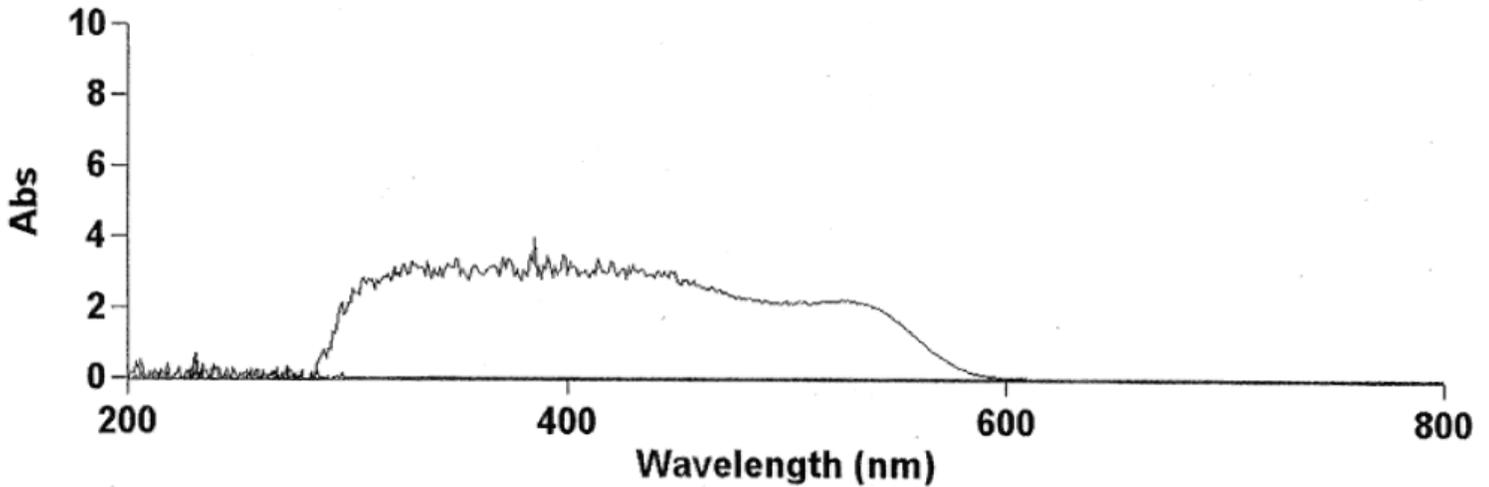


Figure 10

This is because we may be able to match the absorption spectra of the quantum dots and the emission spectra of the sun. The sun is composed of different wavelengths and frequencies of light. The sun can be approximated to behave like a black body at 5777K. The sun emits mostly in the visible spectrum (400 to 700nm) with a maximum emission around 500nm and also infrared (near infrared 700 to 1000nm and short wave infrared 1000 to 3000nm) as shown in Figure 11.

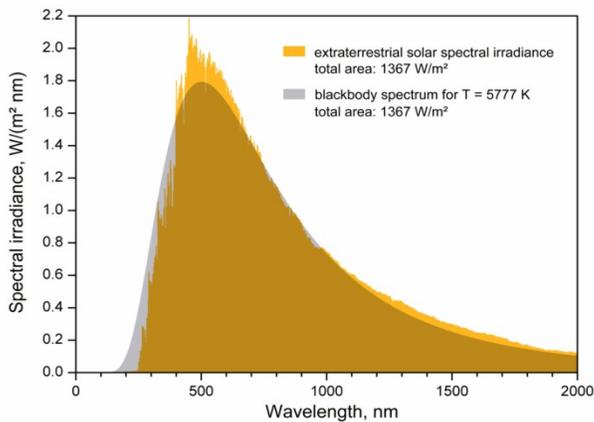


Figure 11

Image from

[http://en.wikipedia.org/wiki/File:EffectiveTemperature\\_300dpi\\_e.png](http://en.wikipedia.org/wiki/File:EffectiveTemperature_300dpi_e.png)

## Creating Solar Cells

### How Does A Quantum Dot Solar Cell Work?

In general this type of solar cell works by a photon of light traveling into the cell and striking a quantum dot particle which in turn raises the energy of some of the electrons in the quantum dots. These excited electrons get injected into the titanium dioxide and travel through it to the conducting surface of the electrode. While the electrons are traveling to the conducting surface of the electrode they leave holes in the quantum dots that need to be filled by other electrons. To fill these holes the quantum dots take electrons from the electrolyte. The electron depleted electrolyte in turn takes electrons from the counter electrode. This process creates a voltage across the cell and induces a current. Figure 12 below shows a diagram of a quantum dot solar cell.

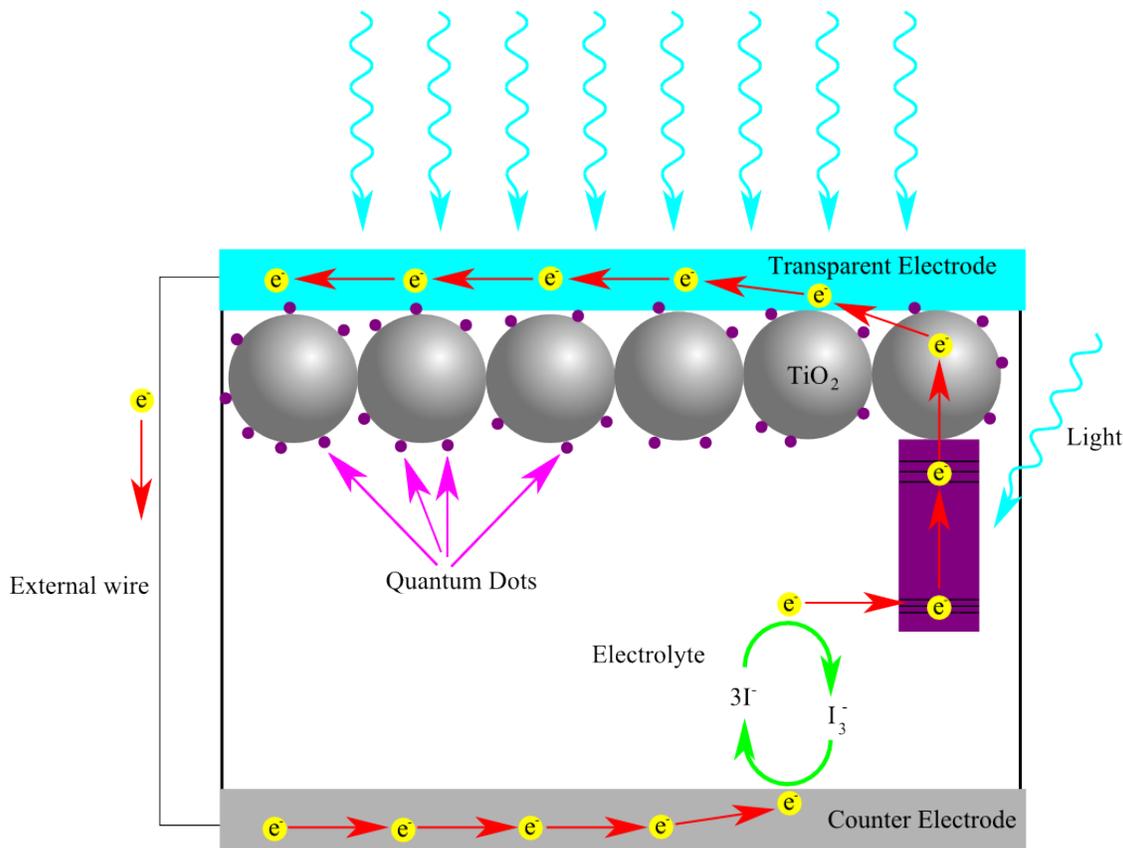


Figure 12

## Parts of a Solar Cell

There are many different parts that make up a solar cell. Furthermore, there are many parts of a cell that can be altered to affect how well the cell performs. One of the main components of the solar cell is the electrode.

## Electrode

The electrode is the first part of the cell we deal with in constructing a solar cell. The electrode is a glass slide that has a thin conducting layer on one side. The thin conducting layer is made of tin oxide. The electrode is special because it has to be able to conduct electricity and at the same time be transparent enough so that light can travel through it. The electrodes must be cleaned before titanium dioxide can be attached to them. We do this by rinsing the conducting side of the electrode, once in deionized water, once in methanol, and then with ethanol. From here we bake the electrode in the oven at 600° C for an hour to bake off any organic materials that may have held on through the rinsing. Once the electrodes cool they are ready to have the titanium dioxide attached to them.

## Titanium dioxide (TiO<sub>2</sub>)

The titanium dioxide is a very important part of the solar cell. It holds the quantum dots in place and gives a pathway for the electrons to travel from the quantum dots to the conducting layer of the electrode. Furthermore, the titanium dioxide has to have a large surface area so that it can hold a large number of the quantum dots in a smaller area. We use a titanium dioxide mixture that was created by students who worked on the solar cell project this past summer. We tried three different methods for attaching the titanium dioxide to the conducting surface of the electrode.

### Screen Printing

The first method we attempted was a screen printing method. This method works by placing a very finely meshed screen on top of the electrode and doctor blading the titanium dioxide paste through the screen onto the conducting side of the electrode. We quickly abandoned this method because of various problems ranging from the titanium dioxide pooling to the titanium dioxide smearing.

### Doctor Blade Method

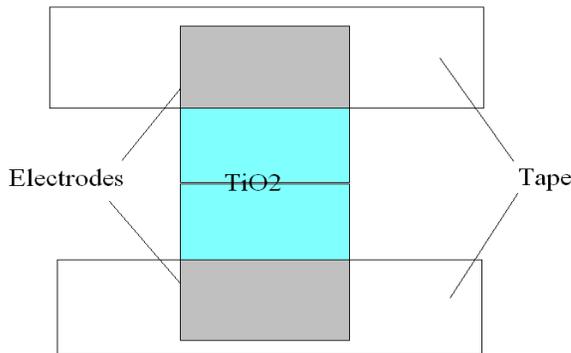
The second method we used was known as doctor blading. For this method we taped off a small rectangle so that it covers the majority of one half the electrode. We then placed a few drops of the titanium dioxide in the non-taped area and used a glass slide to smooth out the titanium

dioxide until it appeared to be uniform over the entire exposed surface.

### ***New Doctor Blade Method***

The current and preferred method we use for depositing the titanium dioxide is the new doctor blade method. For this method we place two electrodes edge to edge and tape the top half of one electrode and the bottom half of the other as illustrated in Figure 13. We then smooth out the titanium dioxide on the electrodes in the same way as we did for the original doctor blade method. We prefer this method because it produces two cells that have similar titanium dioxide depositions which aids in making the cells reproducible.

For all three methods of attaching the titanium dioxide the electrode then gets baked in the oven at 450°C for an hour. Once the electrode cools to room temperature the electrode is then ready for the quantum dots to be attached.



**Figure 13**

### **Quantum dots**

The quantum dots are the most important part of the solar cell. The quantum dots are the part of the cell that adsorbs the incoming photons of light and send out the usable energy. We tried three different methods to attach the quantum dots to the titanium dioxide. For the first method we placed the electrodes with the baked titanium dioxide in a Petri dish and deposit a few drops of the quantum dot solution on top of the electrode. We then allowed the quantum dots to adhere over night. For a second method we tried mixing the quantum dots with the titanium dioxide paste. We then took this paste and spread it over already deposited titanium dioxide. For the third method of attaching quantum dots we took an electrode with titanium dioxide deposited on it and soaked it in 3-mercaptopropanoic acid for a few hours. We then soaked the cells in quantum dots dissolved in toluene for a few hours. Once the Quantum dots are attached we need to then prepare the counter electrode.

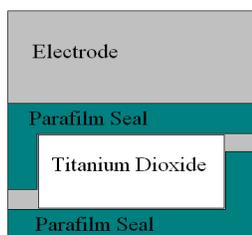
### **Counter Electrode**

The counter electrode is very similar to the electrode; however, a layer of silver nitrate must be added to the conducting side of the counter electrode. The silver nitrate catalyzes the recombination of electrons into the electrolyte from the counter electrode. To add this layer we place a few drops of the liquid silver nitrate on the conducting side of the counter electrode and spread them around evenly. We then bake the counter electrode in the oven for 50 minutes at 375° C. Once the counter electrode has cooled the cell is ready to be sealed.

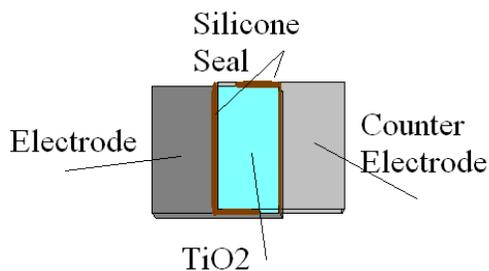
### **Sealing the Cell**

To seal the cell we tried two different methods. For the first method we cut L-shaped strips of stretched Parafilm and placed them around the titanium dioxide. We made sure to leave two small holes for adding electrolyte later. An example of this is shown in Figure 14. We then took the cell and placed it on top of a heat plate set on low heat (1 or 2) and then placed a weight on top of

the cell. We left the cell there for approximately three minutes and then allowed the cells to cool to room temperature. The current method we use for sealing the cells makes use of silicone caulk. This method works best when paired with the new doctor blade method for depositing the titanium dioxide. We start by clamping the electrode and counter electrode together in their final resting positions. We then smear the silicone caulk around the area where the electrodes meet making sure to leave two holes so that electrolyte can be added later. An example of this is shown in Figure 15. Once the cell is sealed it is ready to have leads attached to it and electrolyte added.

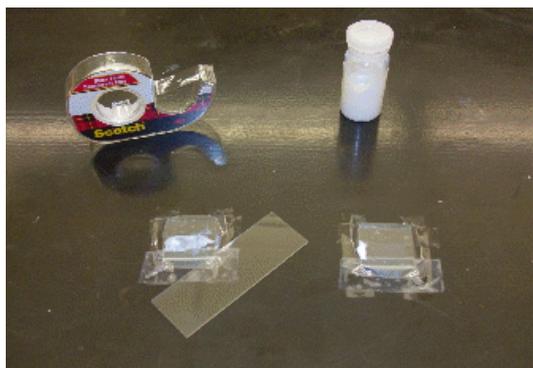


**Figure 14**



**Figure 15**

### Attaching Leads and Adding Electrolyte



**Figure 16**

To attach the leads we use silver epoxy to attach the 40 gauge wires to the electrode and counter electrode. Once the silver epoxy sets the cell is ready to have the electrolyte added. We simply drop in electrolyte with a dropper in one of the holes we previously left in the seal and the capillary effect takes over and spreads the electrolyte out over the cell. The electrolyte uses a redox reaction between triiodide and iodide to transfer the electrons from the counter electrode into the quantum dots. When the photon of light enters the cell and excites an electron in the quantum dot the quantum dot needs an electron. The quantum dot then strip an electron from the iodide (oxidizes it) which turns the iodide into a triiodide. The triiodide then travels to the counter electrode and takes an electron from the counter electrode (reduces it) which turns the triiodide back into an iodide. Once the cell has the leads attached and electrolyte added it is ready for tests to be performed on it.

### Tests

Currently I have only performed two different kinds of test on the cells. The first test that I use on the cells makes use of the digital multimeter to measure the voltage across the cells when there is a large amount of light shining on them from a modified projector. I then measure the voltage across the cells when there is only room lighting on the cells and I find the difference of these two measurements. If there is a high enough voltage across the cells I will then perform a second test which is taking an IV Curve for the cells. To qualify for a second test I compare the difference in voltages across the cells with quantum dots attached to the difference in voltage across cells that only have titanium dioxide. If the difference in voltage across the cells with quantum dots is higher than that of the titanium dioxide cells then I run the IV Curve test on them.

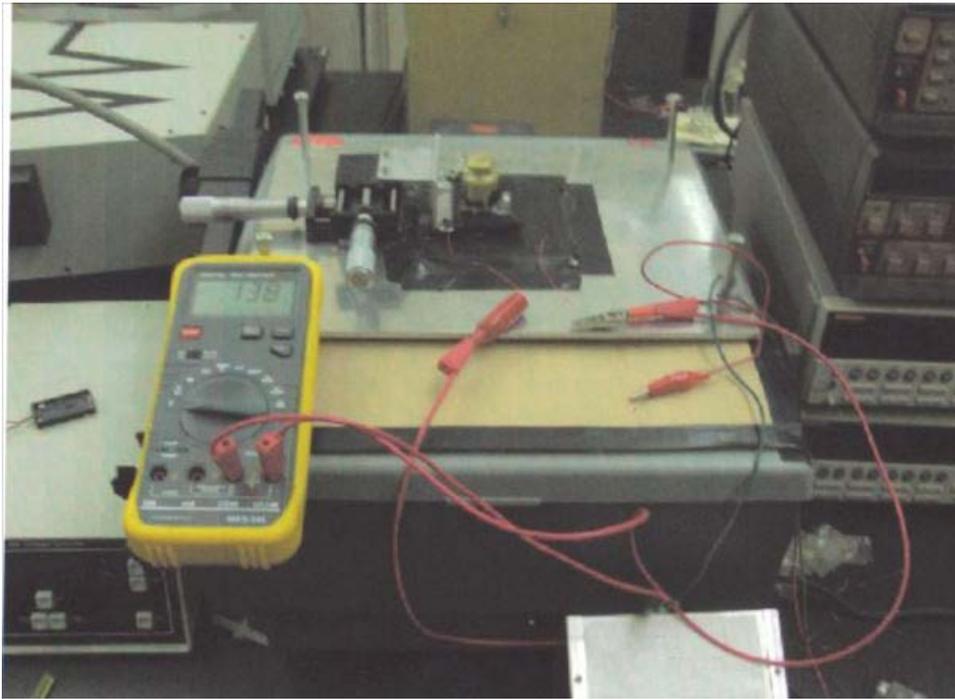


Figure 17

### IV Curve

An IV Curve is a graph of all of the possible current and voltage outputs for a cell (I usually only look at IV Curves for when the current and voltage are greater than or equal to zero.) From an IV Curve I can gather a large amount of diagnostic information about performance of the cells.

### Short Circuit Current and Open Circuit Voltage

A cell produces its maximum current when there is no resistance in the circuit, i.e., when there is a short circuit between its positive and negative electrodes. This maximum current is known as the short circuit current and is abbreviated  $I_{SC}$ . When the cell is shorted, the voltage across the circuit is zero. Conversely, the maximum voltage occurs when there is a break in the circuit. This is called the open circuit voltage ( $V_{OC}$ ). Under this condition the resistance is infinitely high and there is no current, since the circuit is incomplete. To make an actual IV Curve we use a program to record the current and voltage of these two points along with a large number of intermediate values. This results in a graph similar to Figure 18.

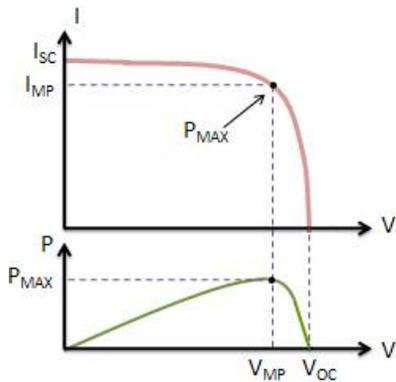


Figure 18

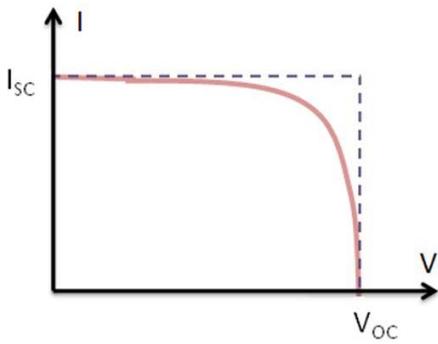


Figure 19

### Max Power

From the graph of values we can calculate the max power out of our cells. We first find the product of the current and voltage at every point. Where this product is a maximum is the max power for the cell.

An example of this is given in Figure 19.

### Fill Factor

The fill factor is a measure of the quality of a cell. It compares the theoretical power of the cell as derived from the short circuit current and open circuit voltage to the actual max power output by the cell. Figure 20 gives an example of how to calculate the fill factor for a given IV Curve.

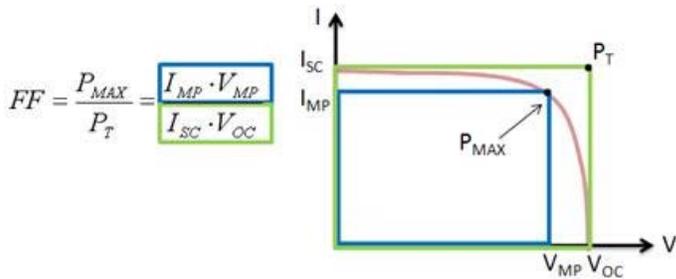
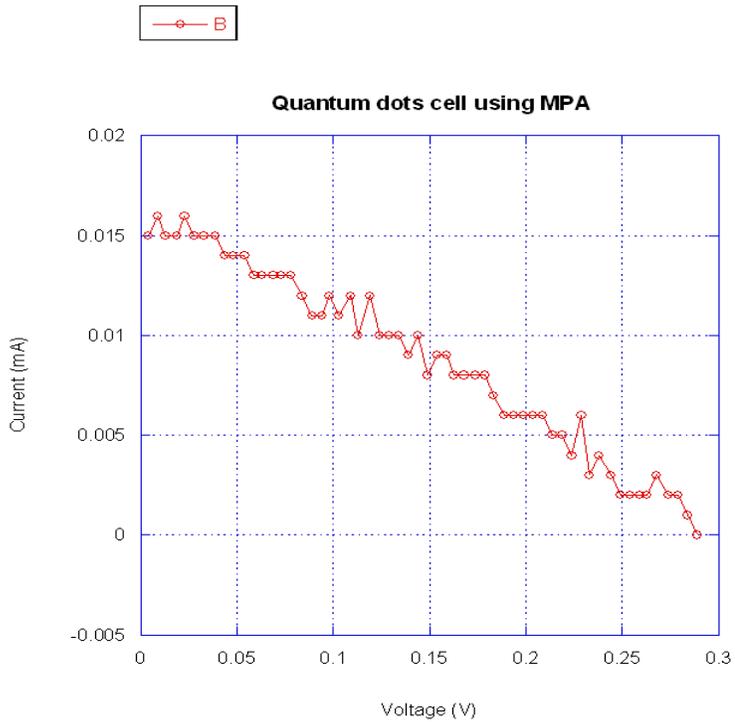


Figure 20

### Efficiency

Efficiency is the main measurement for the performance of a cell. The cells efficiency is the cells ability to convert light into electricity. To measure the cells efficiency we take the cells out into direct sunlight and use a pyroheliometer to measure the power going into the cell. Furthermore, we measure the cells short circuit current in the direct sunlight. With the cells short circuit current and area we can calculate the power output by the cell. We then take the power output of the cell and divide it by the power going into the cell and multiply by 100. This gives us the efficiency as a percentage value.

### Results



**Figure 21**

We were able to get results out of one of the cells we created. For the cell that was soaked in 3-mercaptopropanoic acid we got a substantial change in voltage when we performed the DMM test that could not be accounted for by the titanium dioxide only. We also took an IV curve for this cell as shown in Figure 21. The new doctor blade method and sealing method show lots of promise and have worked better than expected so far.

### Future Plans

While we have not thoroughly tested the effects of quantum dots in the solar cells, one method may have functioned well enough to investigate further. A plain titanium dioxide solar cell was immersed in 3-mercaptopropionic acid (MPA) overnight, then immersed in the quantum dot-toluene solution for 3 hours. The MPA acted as a ligand, or glue, to which the QDs attached to the TiO<sub>2</sub> layer, and the solar cell gave a measurable voltage when exposed to light. Further research will include reproducing the MPA-capped QD solar cell, as well as investigating other ligands to bind the QDs, such as pyridine and cysteine. Further investigation should also be made into the quantum dot synthesis itself, such as percent yield, fluorescence spectroscopy of the quantum dots (to determine actual size).

### Resources

U.S. Energy Administration

<http://www.eia.doe.gov/oiaf/ieo/solar.html>

The Encyclopedia of Alternative Energy and Sustainable Living

[http://www.daviddarling.info/encyclopedia/AE\\_I-V\\_curve.html](http://www.daviddarling.info/encyclopedia/AE_I-V_curve.html)

National Renewable Energy Laboratory National Center for Photovoltaics

[www.nrel.gov/pv/thin\\_film/docs/kaz\\_best\\_research\\_cells.ppt](http://www.nrel.gov/pv/thin_film/docs/kaz_best_research_cells.ppt)

National Instruments

<http://zone.ni.com/devzone/cda/tut/p/id/7230>