

Final Report: Renewable Energy Development Fund Project “Solid State Titania Solar Cell”

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Introduction: This report will describe the work that has been completed on the RDF project titled “Solid State Titania Solar Cell”. In this project we investigated a novel approach to dye sensitized solar cells that will allow this technology to be brought to the marketplace. Specifically we looked at quantum dots as the cells sensitizer, and at non-volatile hole-transport layer materials. Sensitizers and electrolytes are the two technological barriers to developing this technology as a renewable energy product.

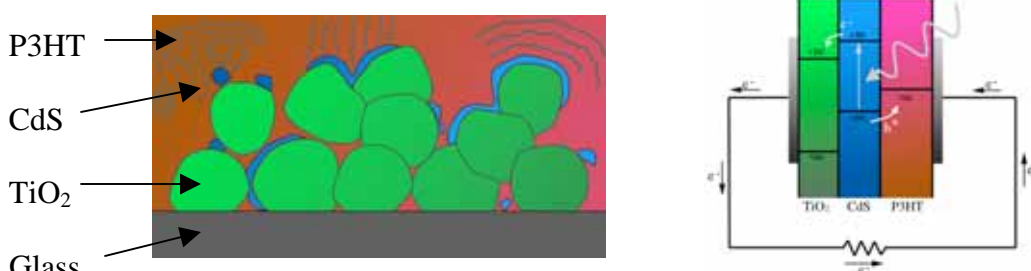


Figure 1: cartoon diagram of the cells geometry and an energy diagram showing how the solar cell functions.

Titanium Dioxide films investigated: The high surface area TiO₂ films play a very important role in all permutations of the “Gratzel” cell. The porous nature of these films leads to a very high surface area. This high surface area allows for more light-harvesting units to occupy a given square area of device, this leads to more photons being absorbed. Because the light-harvesting unit sits right at the surface of the TiO₂, this allows for an electron transfer event leading to charge separation. We employed Scanning Electron Microscopy (SEM) to characterize these films. We are able to control film thickness and pore size.

Zinc oxide columns have also been investigated as an alternative electron transport layer. They have been sensitized with CdS and the resultant films have been characterized. Also the interaction of these films with the various organic hole conductors was investigated.

Initial sensitization experiments have been conducted: We have grown CdS quantum dots directly in the porous TiO₂ films. We used a method called Successive Ionic Layer Adsorption Reaction (SILAR). This reaction may be monitored by electronic absorption spectroscopy. With each successive reaction cycle, the quantum confined semiconductor nanoparticles grow a certain amount. As the crystals grow, the quantum confinement is relaxed and the band gap shifts to lower energy. This is manifest as a red shift of the absorbance spectra. We have done High Resolution Transmission Electron Microscopy in order to characterize these structures. We also investigated other methods to introduce the metal calcogenide to the TiO₂. For many reasons our goal was to completely cover the TiO₂ surface with the sensitizer. Not only will this enhance the absorption of solar

photons, it will reduce the harmful charge recombination events that hamper solar cell efficiency.

Colloidal cadmium sulfide quantum dots were synthesized from cadmium oxide, oleic acid and elemental sulfur in 1-octadecene at 250 °C following a procedure established by Peng *et al.* [REF: W. W. Yu and X. Peng; Angew. Chem. Int. Ed., 2002, 41(13), 2368-2371]. These quantum dots represent a comparative example to the SILAR grown case. In the past we used transient absorbance spectroscopy and photoluminescence spectroscopy to show that the SILAR grown CdS does indeed transfer its excited state electron to the TiO₂. By comparing and contrasting the two quantum dot systems we will be able to draw conclusions as to how dot morphology and growth conditions affect the ability to effectively sensitize TiO₂ to the solar spectrum.

We have also investigated different metals for deposition. We have grown Lead Selenide (PbS) quantum dots onto the TiO₂. PbS is a semiconductor material that has a very small band gap and is attractive for several reasons with respect to solar energy conversion. It was found out that these films were stable. A cell was fabricated with this sensitizer and did show a real photocurrent.

Synthesis of Thiophene-Based Oligomers for Hole-Transport Material

Three six rings thiophene-based oligomers were selected as synthetic targets because of their electronic and physico-chemical properties. DH6T was chosen as it is a very well known conducting materials with high carrier mobilities as demonstrated in the literature. The two other oligomers were designed in order to investigate different band-gap organic electronic materials. To understand the solid state behavior of the **DBATn** compounds in the solid state we investigated the thin film properties of the various molecules with X-ray diffraction (XRD) and single crystal X-ray structure determination.

In order to investigate the extent of control we can have on the conduction band energy level, we have designed a new series of compounds. The new structures are based on the same thienylene-vinylene scaffold, but with various terminal amine substitutions (Figure 3). In the **DPATn-x** series, we selected three substituted triaryl amines as the capping group for the thienylene-vinylene bridge. Three substitution on the phenyl groups attached to the amine are planned: (a) a dimethylamino electron donor group (**DPATn-NMe₂**), (b) a neutral unsubstituted phenyl (**DPATn-H**) and (c) and nitro electron withdrawing group (**DPATn-NO₂**). The dimethylamine and nitro moieties are at the extremities of the electron donating or withdrawing scale, which should allow us to probe the full range achievable for the variation of the energy level of the final solid state HTL.

We also conducted mathematical modeling of these organic species using NREL's supercomputing facility. These molecules represent an ideal test case for our mathematical modeling effort. Having the molecules and having already measured their electronic properties they make a good standard.

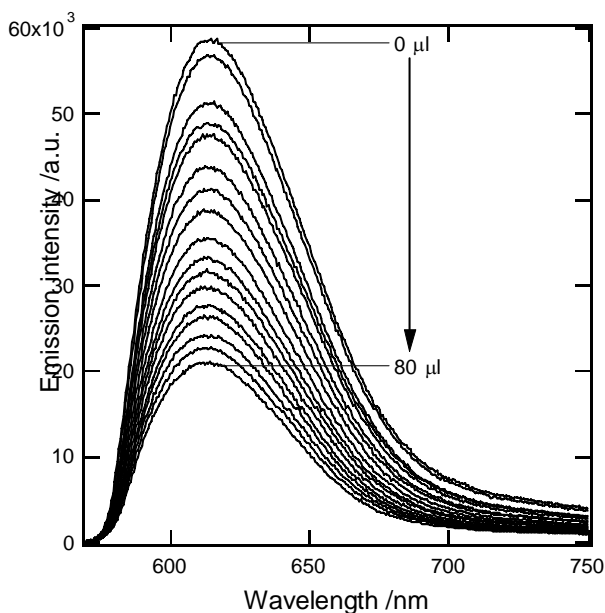
During the course of this project we conducted investigations into other materials that could behave as the electron transport layer in our proposed solar cell. One such alternative material is a biologically derived conjugated polymer. Whereas titanium dioxide is a cheap and safe material, the new material we are looking at are extracted from woody plants. This fact has a significant impact on the ecological "footprint" of cell production. Essentially the carbon that will be used in the fabrication of the solar cell

will have been extracted from the earth's atmosphere. This is an entirely new concept and to our awareness we are the only research group pursuing such an approach to solar cells. Our first question was "what is this material's electronic structure?" In order to begin to answer this we took the solutions of said material and did Photoluminescence (PL) spectroscopy on them. We can see that this bio-polymer has a very strong, blue PL signature. This is rather important. We propose that this material we have here may be a viable candidate for an OLED device.

I suggest that it may in fact behave like a pi-conjugated semi-conducting material. Its PLE and PL spectrum show it to be a large band gap material, like TiO_2 . In terms of a solar cell, this absorption has a poor overlap with the terrestrial solar spectrum. We suggest optimizing the spectral absorbance in the same manner as the dye cell, by sensitizing the bio-material to solar radiation with a dye. So the next challenge is to show charge transfer between material and a sensitizing candidate. For the sake of the empirical determination of the charge transfer event, we shall select a dye molecule that has a detectable photoluminescence signal. The PL signal from a solution of this dye will be monitored as aliquots of bio-polymer solution are added. If the PL is quenched, evidence of a potential charge transfer event will have been established.

PL Quenching with Regioregular Poly[3-hexylthiophene]

Quenching of the quantum dots photoluminescence is indicative of charge transfer



from the excited dot to the quenching media. We performed solution PL quenching of InP quantum dots with regioregular poly[3-hexylthiophene] (P3HT).

This PL quenching experiment provides us with good evidence that the quantum dots will be able to transfer their excited state hole to the solid-state hole conductor. This establishes that the proposed cell configuration is a viable candidate for solar energy conversion. The quantum dots absorb the solar photons (charge generation), the electron is transferred to the TiO_2 and the hole can transfer to the polymer (charge

separation).

Interaction between mesoporous titanium dioxide films and conductive polymer:

One focus of this project has been the solid-state hole conduction phase. In order for the "Gratzel cell" to be marketable, the liquid electrolyte needs to be replaced. One reasonable candidate for the replacement of the liquid electrolyte is the hole conductive polymer Polythiophene (P3HT). We introduced the polymer to the film in a variety of techniques and characterized said films with electron microscopy. The SEM evidence is

quite compelling in terms of polymer intercalation. Our interpretation of the results is that the polymer is coating the film in a conformal fashion.

Another study that we conducted on the topic of physically integrating the hole transport material into the TiO_2 film was melting study. Here building on what we learned in the above experiments, we purposely fabricated films where excess hole conduction material was on the surface of the porous TiO_2 . Here we have drop cast the organic materials onto the TiO_2 and imaged the films as is. After collecting this 'before' image we removed the films from the microscope and heated them on a hot plate at 150 degrees centigrade. One interesting thing that we have learned from this experiment is that in the case of the molecular DBAT3 film, heating the films removes the excess material that is seen on top of the film as drop cast. It seems logical that the material 'melted' into the pores of the metal oxide film. This result is quite encouraging for our goal of filling the pores with the hole transport layer. As reported earlier in this project, this molecule was designed and synthesized to have the ability for us to 'melt' it into the pores. This is an encouraging result for our project. This result shows that unlike bought P3HT, our newly synthesized molecules are able to be melted into the TiO_2 film. This is a positive result.

One goal for this project was to improve the hole mobility of these materials. It is suggested that if we could increase the ordering of this film; then by pi-stacking, the hole mobility should be improved. One area of interest in this regard is the molecular weight of the polymer, and could the molecular weight of the polymer affect the stacking of the chains in the film. A method that can be used to size select these polymers is the Soxhlet extraction process. We were successful in obtaining several distinct fractions of different molecular weight. These fractions were characterized by Gel Permeation Chromatography (GPC). The raw product from Aldrich actually consists of a variety of different molecular weight materials. We did see a difference in the electronic properties between the two mass extremes.

Film Characterization:

Electron microscopy was employed as a means to look at these films. Normal optical microscopy is not able to resolve the nanomorphology of these films. The SEM proved to be a good route to determine how well the organics penetrate the porous metal oxide network. A new EDS detector was added to this microscope and allowed us to identify and map the elemental composition of these nanoscopic films.

A new IR photoluminescence instrument at NREL has allowed us to do a hole transfer PL quenching experiment with low bandgap PbSe quantum dots. When an aliquot of DBAT4 was added to a vial of PbSe dots, the PL signal did not decrease. This indicates that in that system the hole is not transferred to the organic. This is an illustration of the importance of band edge alignment in semiconductor heterojunctions.

The electrodes were tested for viability in a series of electrochemical IV analysis (dark and illuminated). Mott-Schottky experiments then provided two important parameters to evaluate materials as hole transport layers. Mott-Schottky slope results are proportional to the doping densities of the material. Doping density involves how many atoms in the material donate holes (p-type) or electrons (n-type) as charge carriers. X-intercept results generated from Mott-Schottky experiments are related to flat band potentials. Our results indicate that the number of monomer units does not have an

impact on the doping density of the films. However, the recently generated data does suggest that the number of monomer units does affect the band edge position. This is in reasonable agreement with the electronic absorbance shift (and the results of our quantum mechanical calculations). Whereas the electronic absorbance gave the band gap energy (a relative number), this data gives us the absolute energy with respect to vacuum.

New Experimental Approach to Study Electron Transfer and Transport:

NREL has developed a new experimental capability that can be utilized in this project. The Time Resolved Microwave Conductivity (TRMC) is a valuable addition to this work. More recently it is being applied to study charge carrier dynamics in polymer thin films, bilayer systems, donor-acceptor blends and the anisotropy in the conductivity of aligned thin films. We have been using it to study electron transfer and transport in our quantum dots sensitized TiO₂ films.

The first experiment that we conducted with this setup involved the sensitization of TiO₂ with quantum confined Cadmium Sulfide nanocrystals. As a control we also grew CdS onto a zirconium oxide film by the SILAR technique. In the control we don't expect to see charge transfer into the ZrO and the response should be that of just CdS. A clean film of TiO₂ was also interrogated. We can say that some of the signal seen in our data arises from electrons in the conduction band of the TiO₂ that have been transfer from the CdS. This TRMC experiment is a different approach to investigate this system and could give us new information about the event. For one thing this is on a very different time scale than our previous transient absorbance results. These new results are on a much longer timeframe. Secondly, unlike our TA and fluorescence quenching data, here we are probing the presence of charge carrier in the TiO₂ directly. Through this technique we may be able to learn about this materials ability to behave as an electron transport phase, and how to improve that transport behavior. Already we can see that the electron has quite a long lifetime in the conduction band. This is a good thing in terms of a functioning solar cell, the electron needs a long enough lifetime for it to reach the electrode and be collected in the circuit.

Summary: This report represents the conclusion of this RDF project. By using a sophisticated form of time resolved spectroscopy we have shown that the inorganic semiconductor does indeed transfer the excited state electron to the TiO₂. We have also used photoluminescence quenching to show that the hole is transferred from the inorganic semiconductor to the conductive polymer. This project has shown that these new materials can function in a solar energy conversion design that could be developed into a real world renewable energy generation product. The next logical step in solar cell development would be to take these bench top results that were generated by this project; and do the required engineering and fabrication research to take this technology to the pilot plant cell production level. This work could be very instrumental in the realization of affordable photovoltaic solar cells.