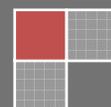


2011

Photochemical Water Oxidation

The Beneficial Interaction of SrTiO_3 Nanoparticles and TiO_2 Nanotubes Utilizing a Co_3O_4 Spinel Catalyst

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1.0 ABSTRACT

Current energy infrastructure in the United States and around the world will not be sufficient to meet growing future demand. The motivation for this research was to create better components for a photochemical water oxidation device. The properties of titanium dioxide (TiO_2), strontium titanate (SrTiO_3), and cobalt oxide (Co_3O_4) were explored in depth. It was found that SrTiO_3 could not be used to replace TiO_2 as a substrate for quantum dot solar cells due to the higher rate of recombination in SrTiO_3 . However, a heterostructure of SrTiO_3 and TiO_2 created physical charge separation that led to increased photovoltaic properties. Using PLD as the deposition technique for the SrTiO_3 , as opposed to the previously explored hydrothermal process, onto a TiO_2 nanotube substrate it was found that both the photocurrent and photovoltage could be increased to a maximum at a SrTiO_3 film thickness of 155nm.

A simple yet robust air brush technique was used to deposit Co_3O_4 dispersed in conductive carbon paint on FTO to create an electrode for electrochemical testing of the catalyst's water oxidation activity. This method of deposition was capable of producing turn-over frequencies ($\text{mol O}_2/\text{mol Co}/\text{hr}$) similar to those produced by a three dimensional nickel foam electrode with Co_3O_4 chemisorbed to the surface. This cathode also produced turn-over frequencies of the same order as the in-solution photoactive Clark electrode Ru(II) bipyridine assay which this electrode was meant to replace.

Ongoing and future work will be to combine this photoactive $\text{SrTiO}_3/\text{TiO}_2$ nanotube heterostructure with the cobalt oxide water oxidation catalyst to produce a photochemical water oxidation device. Two potential issues that have arisen are a back transfer of electrons from the

heterostructure to the Co_3O_4 hindering the activity of the overall system and the opacity of the Co_3O_4 layer impeding front side illumination of the sample. One way to address the first issue is to use a wide band gap semi conductor like ZnS which has been used to block back transfer of electrons in quantum dot solar cells. The second issue could be addressed via backside illumination of transparent electrodes such as FTO instead of titanium metal.

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3.0 INTRODUCTION

Current energy infrastructure in the United States and around the world will not be sufficient to meet growing future demand. Some predictions say that more than 10 terawatts (TW) of new power will be needed over the next forty years to maintain current lifestyles.¹ The World Coal Institute has reported that if current rates of consumption are maintained, current reasonably recoverable coal reserves will run out in 130 years, natural gas in 60 years, and oil in 42 years.² The World Nuclear Association reports that at current consumption rates in conventional reactors, only 80 years of reasonably recoverable world uranium remains.³ With breeder technology this lifetime could potentially be extended to a couple hundred years. While these numbers may indicate some security, none of them compensate for the continually increasing demand for energy. In the long term picture, coal, natural gas, oil, and nuclear will all be exhausted. This leaves us asking where we will turn to, to find energy?

The only long term solution is renewable sources of energy such as wind, hydrothermal, and solar power. Of these options, solar represents the largest potential source of power with 1000 watts of power hitting each square meter of the Earth's surface. That amounts to 82,000 TW total, with total world energy consumption reaching only 15 TW. Despite the vast amount of power solar can provide, it is inherently diffuse, which makes it difficult to use in many situations, particularly mobile applications such as vehicles. Finding a process to store solar energy in a chemical fashion – a form of artificial photosynthesis – could solve all our energy needs. In one such process, sunlight is absorbed and converted to an electrochemical potential, which is then used to drive the splitting reaction of water to oxygen and hydrogen. Hydrogen is

an energy carrier which could be used to replace fossil fuels in mobile applications where direct solar isn't feasible.

The reasons why hydrogen provides one of the most promising replacements to fossil fuels will be detailed below. In order to improve the photochemical water oxidation system described above, improvements in both solar cell technology and water splitting catalysts must be achieved. Over the past two years the effects of strontium titanate (SrTiO_3) on titanium dioxide, as a light absorbing semi-conductor metal, have been explored. The nanoparticulate cobalt oxide spinel (Co_3O_4) has also been examined for its activity as a novel water oxidation catalyst. Together these two arms of research have been utilized to attempt to create a water splitting system powered by light.

3.1 WHY HYDROGEN?

Most types of renewable energy are too diffuse (i.e. their energy densities are too low) to be useful in many applications. Wind farms, solar towers, and nuclear plants are all suitable replacements for coal-fired and natural gas power plants. However, to power a 150 horsepower car off of sunlight alone would require a little over 110 m^2 of land at a solar energy conversion rate of 100%. In comparison, the top surface area of a Toyota Prius is a little under 8 m^2 .⁴ The inherent intermittency of solar and wind power also makes them ill-suited for mobile applications. While nuclear power isn't intermittent, it is unlikely that mini reactors are going to power the cars of the future. Thus, a method for storing the energy produced by these renewable sources is a necessity and several options are available: biofuels, batteries, and hydrogen.

Hydrogen is the best of these options because it is a renewable energy carrier. Biofuels, such as corn ethanol, require valuable farming land that is needed to produce food. Batteries are materials and processing intensive, requiring metals for cathodes, an electrolyte, and housing. They also suffer from short lifetimes (new electric vehicle battery packs are only guaranteed for 8-10 years) and low energy densities. Li-ion batteries, for example, have a volumetric energy density of 0.36 MJ/L, as opposed to the 10 MJ/L for liquefied hydrogen.⁵ Batteries also require long recharging periods while hydrogen can be refueled in an automobile like gasoline. Hydrogen can be produced from the limitless supply of water using solar power via electrolysis or photolysis. It can then be burned in modified internal combustion engines, rather than in expensive fuel cells.

3.2 PHOTOCHEMICAL WATER SPLITTING

There are four components necessary in a photochemical water splitting system: (1) a light harvester, (2) a charge separator, (3) a water oxidation catalyst, and (4) a hydrogen reduction catalyst (Fig. 1). Solar power is harvested and converted to excited electron and hole pairs at the anode. These must be separated quickly to prevent recombination. The electrons travel through an external circuit to the cathode, where the reduction catalyst is located and hydrogen is produced. The holes must migrate to the oxidation catalyst, where water is split into hydrogen ions and oxygen.

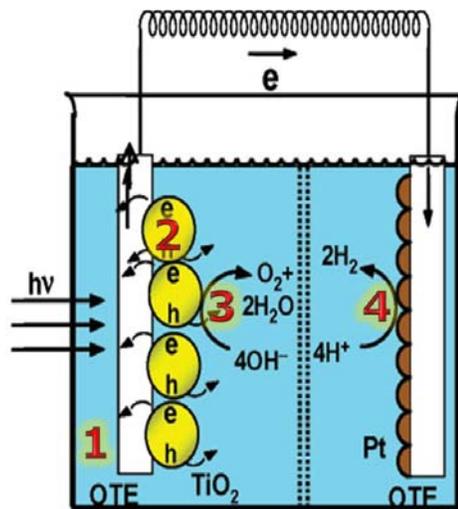


Figure 1. Photochemical Water Splitting⁶

3.3 TITANIUM DIOXIDE

The photocatalytic activity of titanium dioxide (TiO₂) has been known since the early 20th century with papers dating back to 1938.⁹ The ability of TiO₂ to photo-oxidize water was first reported in 1972 using UV-light and a platinum electrode.¹⁰ It was found that when light of wavelengths less than 415nm (~3.0 eV) irradiated the TiO₂ electrode, water oxidation occurred. The reduction reaction, or hydrogen evolution reaction, occurred at the platinum electrode. The overall reaction proceeds as follows:¹¹



Where h⁺ represents positive “holes” left by excited electrons. Reactions 3 and 4 occur at the TiO₂ electrode while Reaction 5 occurs at the platinum electrode.

Due to the high recombination of the generated electron/hole pairs in TiO₂, it is difficult to produce hydrogen from distilled water.¹² Fujishima and Honda originally reported a quantum efficiency of only 0.1 percent.¹³ It has been discovered, however, that certain physical characteristics of TiO₂ increase its photocatalytic activity. The anatase phase of TiO₂ has been found to be more photoactive than the rutile phase. The main reason for this is the reduced rate of recombination in comparison to rutile due to the 10-fold greater rate of hole trapping in the anatase phase.¹⁴ The anatase phase also has a larger band gap than the rutile phase (E_{BG} = 3.2 eV versus E_{BG} = 3.0 eV) as well as the more negative position of the anatase’s conduction band edge.¹⁵ It has also been found that the charge transfer through oriented TiO₂ nanotube

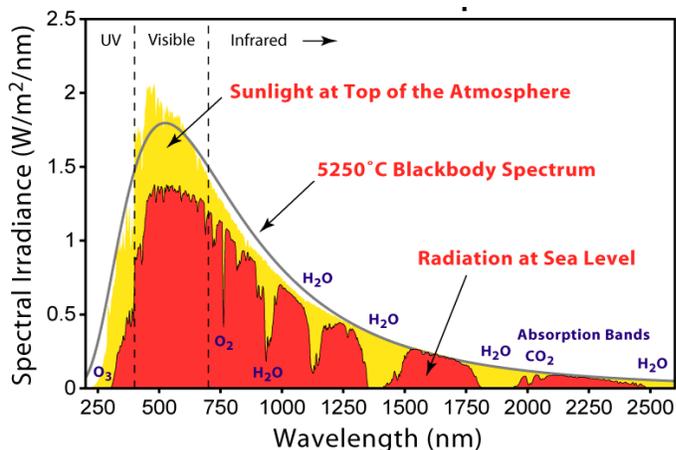


Figure 3. Solar radiation spectrum

frameworks, as opposed to TiO₂ nanoparticle assemblies, is faster.¹⁶ Thus nanotubes can be used as a basis to build more efficient photochemical water splitting systems.

TiO₂ is able to oxidize water because of the position of its band gap around the chemical potential of the reaction. However, because the band gap is so large it can only absorb light in the ultraviolet region. This is problematic because a very limited amount of the sun's solar energy reaching the surface of the Earth is in this region (Fig. 3¹⁷). A significant portion of the solar energy hitting the Earth is in the visible spectrum. The potential for water splitting is low enough that photons in the visible region have enough energy to drive the reaction, even with the necessary overpotentials (Fig. 4). In order to extend the absorption of TiO₂ into the visible region many different approaches have been attempted, but can be broken into two main categories: doping and sensitizing /coupling. Sensitizing/coupling was the main focus of the research done in the past two years, and some of the approaches already investigated will be elucidated below. An additional benefit of this method is that it decreases the amount of recombination in TiO₂ via physical charge separation.

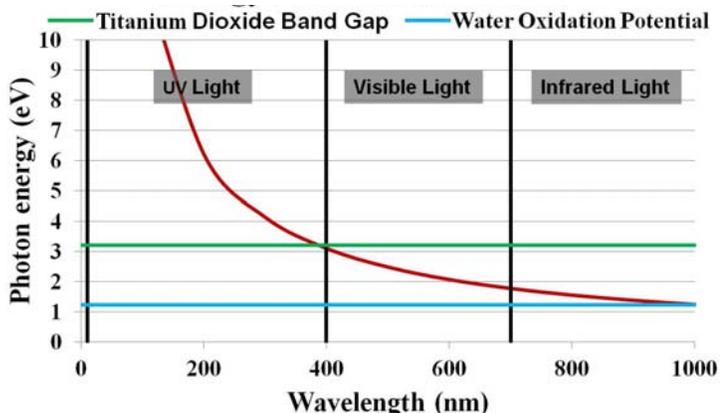


Figure 4. Energy of Incident Photons

3.4 TITANIUM DIOXIDE SENSITIZING/COUPLING

Sensitizing refers to the attachment of a narrow band gap material that extends the absorption range of composite material. Coupling is the attachment of another semi-conductor to the surface of TiO_2 to increase charge separation, thereby reducing recombination, and increasing efficiency. In some cases the addition can satisfy both of these components such as with quantum dots. This enhancement occurs because of the positions of the conduction and valance bands of TiO_2 and the sensitizing material. The conduction band of the sensitizing material must be at a more negative potential than the conduction band of TiO_2 . The photons are absorbed by the sensitizer, producing electron/hole pairs. The electrons will fall down to the less negative potential of the TiO_2 conduction band, while the holes will stay in the valence band of the sensitizer. This physical separation of electron and hole is what reduces the amount of recombination (Fig. 5). The decreased band gap of the sensitizing material is what allows for absorption of visible light.

Since the breakthrough in efficiency was demonstrated by O'Regan and Gratzel in 1991, there has been a major push to utilize dyes as sensitizer in solar cells.¹⁸ Interest in ruthenium(II) complex dyes has existed since the early 80's¹⁹ and utilization of $\text{Ru}(\text{byp})_3^{2+}$ has continued since then²⁰. However these ruthenium and other transition-metal dyes are fairly expensive and metal-free dyes, such as porphine and melocyanine dyes, have been sought after to replace them. Of

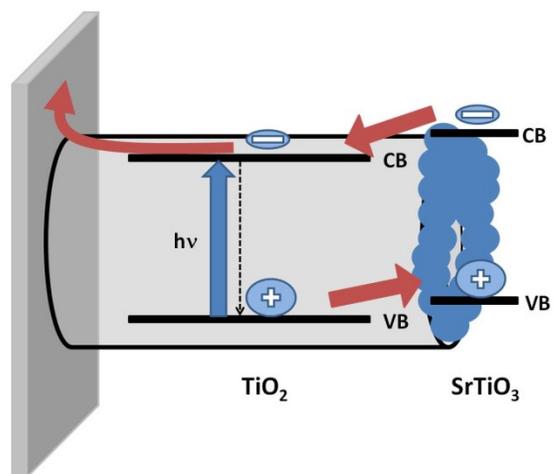


Figure 5. Graphical representation of TiO_2 and SrTiO_3 band gaps with flow of electrons and holes

particular note is Eosin Y, which as a sensitizer to various titanium dioxide substrates has produced quantum yields higher than 10% at 420 nm.²¹ The instability and generally high cost of this method of sensitization has led to exploration of other possible sensitizers.

Quantum dots are a group of semiconductor nanoparticles that have tunable band gaps. These materials have proven to be viable alternatives to dyes for harvesting visible light. In particular, cadmium sulfide (CdS) and cadmium selenide (CdSe) have been shown to be capable of injecting electrons into TiO₂^{22,23}. The advantage of quantum dots is that their band gap can be selected by controlling the growth time in wet synthesis²⁴ or by controlling the number of dips in the SILAR method²⁵. One can then imagine a cell, decorated with quantum dots of all different sizes, that absorbs efficiently all across the visible spectrum. While this goal has not yet been reached, work here has shown it is possible to lay down a monolayer of single-size quantum dots, via a linker molecule, to increase the absorption of a thin film of TiO₂ nanoparticles.

Other semiconductor metals, such as strontium titanate (SrTiO₃), have been coupled to TiO₂. SrTiO₃ has been shown to be an effective electrode in water splitting application by itself.²⁶ However this research has shown that much higher recombination occurs in SrTiO₃ than in TiO₂, thus making it more suited as a coupling material. SrTiO₃ can only provide a process for electron-hole separation as it absorbs light in the same region as TiO₂. The conduction band and valance band of SrTiO₃ are 200 mV more negative than the corresponding TiO₂ bands, thus allowing for the separation described in Figure 5. Our group has demonstrated previously that a SrTiO₃-TiO₂ nanotube array composite prepared by a hydrothermal method has better photovoltaic properties than TiO₂ nanotube arrays alone.²⁷ The hydrothermal reaction proceeds with a strontium precursor reacting with the TiO₂ to form SrTiO₃. As the reaction time was

increased, the photovoltage increased due to the higher conduction band of the SrTiO₃, but the photocurrent decreased significantly due to the consumption of the underlying TiO₂ nanotube substrate. The replacement of TiO₂ in the nanotubes was undesirable and a focus of this research was the use of an alternate technique, pulse laser deposition, to deposit SrTiO₃ onto TiO₂. Despite the improved photovoltaic properties sensitized/coupled TiO₂ has, a co-catalyst to facilitate the water splitting reaction is often used.

3.5 WATER OXIDATION CATALYSTS

The low activity of TiO₂ for water oxidation (WO) necessitates the addition of co-catalysts to increase the reaction kinetics. In some cases the sensitizing agents mentioned in the previous section, which increase the efficiency with which the TiO₂/sensitizer heterostructure absorbs light, also increase the heterostructures overall activity for WO. For instance, many ruthenium-based compounds have been found to also be active for WO^{28,29}. A common metal oxide used for WO is iridium oxide (IrO₂) which is also highly active. In 2007 colloidal IrO₂ was self adsorbed onto a conductive indium tin oxide (ITO) substrate. Measurements taken in 0.1 M KNO₃ found that IrO₂ had a turn-over-frequency (TOF) of 2.3-2.5 * 10⁴ mol O₂/mol IrO₂/hr which is 16-fold higher than the TOF for a Ru-red/Pt-black system under the same conditions.³⁰ Due to the high cost of iridium and ruthenium, other common-earth metals have been sought out for WO activity.

Nature can often serve as a strong model for scientific endeavor because years of evolution have already perfected methods we as scientists want to utilize. In nature an inorganic catalyst composed of calcium and manganese(IV) acts as the center for energy conversion in the photosystem II process.³¹ The prevalence of this catalyst in nature makes it an obvious target for

reproduction as a catalyst to be used in man-driven electrolysis of water. This catalyst's structure forms a distorted cube, which was successfully mimicked in the

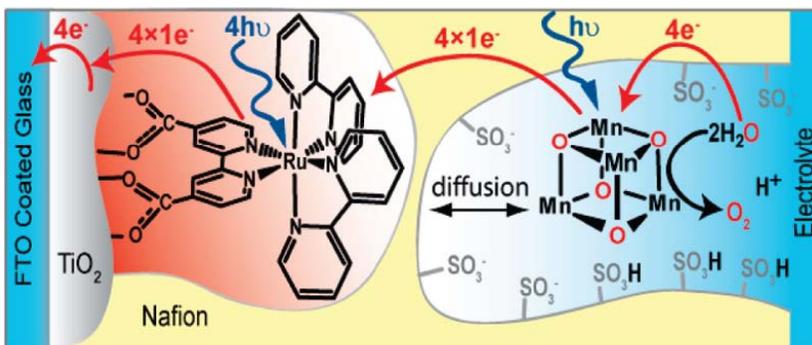


Figure 6. Photochemical system for Mn-oxo cubane³⁴

Mn-oxo cubane ($[\text{Mn}_4\text{O}_4\text{L}_6]^+$ where $\text{L} = (\text{MeOPh})_2\text{PO}_2$) and shown to be active for water oxidation. With this precedent, further development of cubic like catalysts led to the naturally common spinel structure. The cobalt oxide spinel (Co_3O_4) was used as a cathode material for lithium ion batteries³². However, it was also found to be active for water oxidation and there has since been research into mixed spinels to find higher activities.³³ The low cost and simplicity to synthesize Co_3O_4 are favorable attributes.

In order to create a photochemical water oxidation system utilizing the Mn-oxo cubane, it was doped into a Nafion membrane. This membrane was layered on top of transparent fluorinated tin oxide glass covered with a TiO_2 nanoparticle film sensitized with $\text{Ru}(\text{byp})_3^{2+}$ (Fig. 6). The average TOF for this system was found to be 47 ± 10 mol $\text{O}_2/\text{cubane}/\text{hr}$ which is 10 times the baseline TiO_2 result.³⁵ This Nafion system is a poorly understood system and is not very efficient due to the dependence on diffusion within the Nafion membrane.

Currently the Co_3O_4 spinel and many other catalysts like it are tested for catalytic activity in solution.^{36,37} In this system a light absorbing dye creates the electron/hole pairs to drive photolysis, with persulfate acting as a terminal electron acceptor. This is an impractical system however because real world applications require the formation of a complete circuit. This

system is also limited by diffusion of the spinel to the dye surface, thus placing a limit on the maximum measurable turn-over frequency. For both of these reasons it is desirable to create an electrode which has intimate chemical contact with the desired catalyst. The electrode will eliminate the electron diffusion limit placed on the in-solution system by facilitating electron transport away from the spinel through an external circuit. The electrode system for testing the activity of Co_3O_4 was also a project in this research.

3.6 PULSE LASER DEPOSITION

Pulse laser deposition (PLD) was chosen as the technique to deposit SrTiO_3 onto the TiO_2 nanotubes because it is not destructive to the substrate. PLD is used primarily in the fabrication of thin films. A high energy—on the order of J/cm^2 —laser pulse repeatedly strikes the target disk and vaporizes it upon impact. This plume then rises through a high-vacuum (10^{-3} to 10^{-6} torr) chamber to the sample suspended above the target and deposits on the substrate (Fig. 7). The target materials are often metals³⁸ or metal oxides,^{39,40} which can also be doped^{41,42} with other materials. Depending on the gas used to maintain the back pressure in the reaction chamber, it is possible to generate new materials by reaction with the gas during the deposition of the target material, such as TiN ⁴³. By

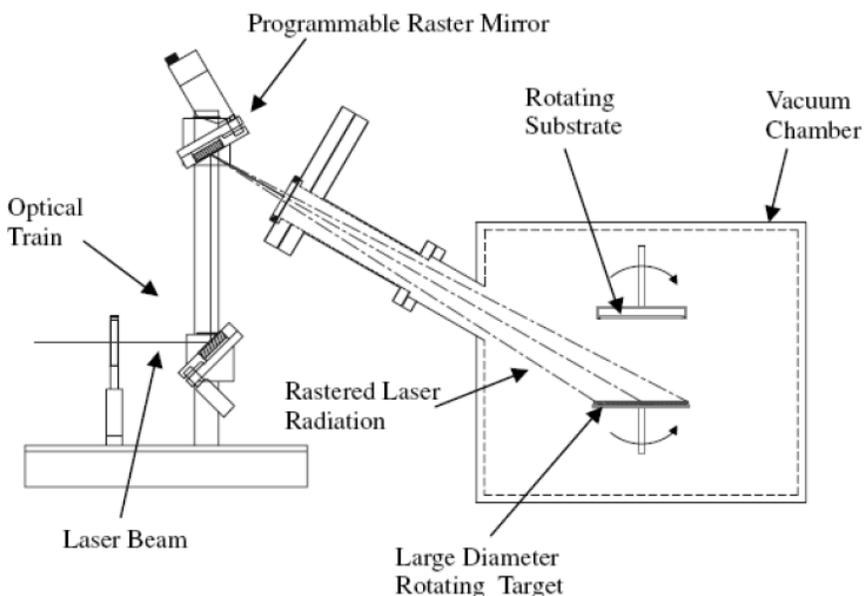


Figure 7. Graphical Representation of PLD Apparatus

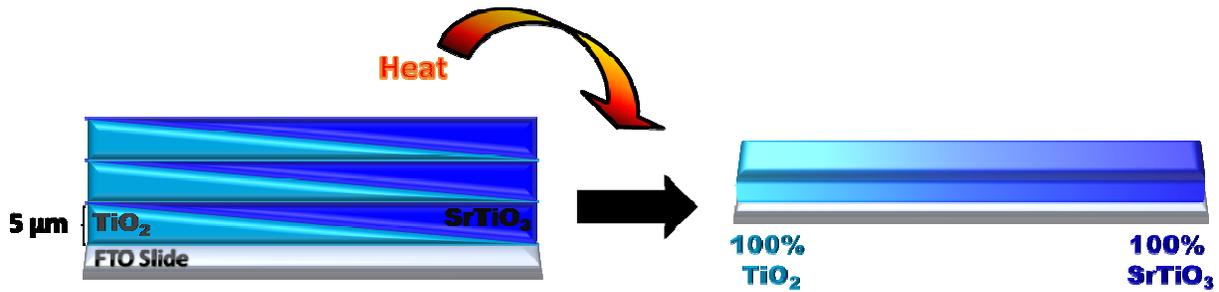


Figure 8. Representation of TiO_2 - SrTiO_3 gradient heterostructure assembly creating the SrTiO_3 - TiO_2 surface interaction without consuming the TiO_2 nanotubes both the photovoltage and photocurrent of the cell were observed to increase.

PLD can be used to deposit gradient films, where the thickness of the thin film deposited is greatest at the bottom and decreases to near zero at the top. It can also be used to lay down uniform thickness films, by rotating the sample stage during the deposition. Finally it can be used to create heterogeneous mixtures by laying down alternating layers of two metal oxides, like TiO_2 and SrTiO_3 for example. PLD can deposit alternating gradient films of 5 microns as shown in Figure 8, which will then uniformly mix vertically but not horizontally after annealing. The result is a thin film which varies in mixture from 100% TiO_2 to 100% SrTiO_3 . This method can be used to test libraries of combinatorial heterogeneous thin films in an efficient manner.

4.0 THIN FILM TiO₂/SrTiO₃ AND QUANTUM DOTS

In this initial project the goal was three-fold: 1.) Become familiar with standard practices with titanium dioxide nanoparticle thin film solar cells sensitized with quantum dots. 2.) Examine the efficacy of strontium titanate as an electron transport layer in place of TiO₂. 3.) Explore the effects thin film thickness of the TiO₂ layer has on the electron injection and transport properties of the quantum dot (QD) solar cell. It was theorized that due to the more negative band gap of SrTiO₃, it should provide a solar cell with increased photovoltage as compared to the TiO₂ cell. The thickness of the electron transport layer also plays an important part in the efficiency of the solar cell. If it is too thick, it will hinder electron transport and recombination will result. If it is too thin, too little light will be absorbed by the layer decreasing the total amount of possible current that could flow.

4.1 EXPERIMENTAL

Materials and Preparation: Quantum dots were synthesized via the hot injection method.⁴⁴ The CdSe precursors utilized were cadmium oxide (CdO, Alfa, 99.998%), tetradecylphosphonic acid (TDPA, PCI Synthesis), trioctylphosphine oxide (TOPO, Acros, 99%), selenium (Se, Aldrich, 99.5+%), trioctylphosphine (TOP, Aldrich, 90%), and dodecylamine (DDA, Alfa, 98+%) – all used as supplied. 2 grams of TOPO were added to 0.3 grams of TDPA and 0.05 grams of CdO in a 150 mL round bottom flask. Depending on the size of dots desired 0.05 to 1 gram of DDA was also added; 0.5 grams were used here to synthesize medium size dots. DDA is added to slow down the reaction and better control the size of the dots. The entire procedure was conducted under nitrogen until the synthesis was complete. The round bottom is then heated

to 300°C at which point a mixture of 0.25 mL 1M TOPSe (Se dissolved in TOP) and 4 mL TOP is added via syringe into the round bottom. The reaction is then monitored until the desired color is reached and heat is removed. Once the liquid has cooled to 100°C, 10 mL of toluene is added to completely quench the reaction. The resulting solution of dots is cleaned via centrifugation and washing with toluene several times. The final clean dots are re-suspended in toluene and capped in a nitrogen purged vial.

A TiO₂ nanoparticle paste obtained from DyeSol and fluorine doped tin oxide glass (FTO) were used to create the doctor bladed TiO₂ nanoparticle solar cells. Using scotch tape to mask out the FTO slide, the thin film thickness was approximately 5 microns. These slides were annealed at 450°C for one and a half hours before use.

Mercaptopropionic acid (MPA, 99+% purity) was obtained from Aldrich to act as the linker between the TiO₂ nanoparticles and the QD. A 0.1 M solution was



Figure 9. TiO₂ thin film sensitized with quantum dots

used to sensitize the slides overnight before the slides were washed and placed in a diluted QD solution overnight again (Fig. 9).

Due to the unavailability of SrTiO₃ nanoparticles to make a direct comparison to the TiO₂ nanoparticle thin films, another type of cell had to be used. Gradient thin films of TiO₂ and SrTiO₃ were deposited via PLD in Prof. Paul McGinn's lab onto FTO and were used for the desired comparison. These films were annealed at 450°C for three hours because the as received thin films were amorphous. They were then sensitized in the same fashion as the doctor bladed cells. These gradient thin films were also used to explore the effect of thin film thickness.

Characterization: Chronoamperometric, open circuit potential, and current-voltage (IV) measurements were taken using a Princeton Applied Research PARstat 2273 potentiostat in a 2-electrode cell with a platinum mesh counter electrode, using 1 M sodium sulfide as the electrolyte. The cell was irradiated with a 300 W xenon lamp using a CuSO₄/water filter to mimic natural sunlight. The incident power of the light was maintained at 100 mW/cm².

In order to measure the effects of thickness across the gradient thin films, two new instrumentation set ups had to be devised. These set ups were also created with the combinatorial heterogeneous thin films in mind. Using the Ocean Optics 2000 UV-Vis instrument, a cuvette on a movable platform was used to slide the test cell up and down to get incremental measurements of absorption over the length of the cell. The instrument used a 1 mm diameter light spot to take its measurements, which insured only the desired position on the plate was being tested (see picture in supplemental information 9.1.1). In order to take the photochemical measurements at differential positions on the plate, a fiber optic cable was used to focus the light source down to a single 2 mm diameter point (see picture in supplemental information 9.1.2). The incident light power measured from this optical cable was found to be 1.5 mW.

4.2 RESULTS/DISCUSSION

Examination of Strontium Titanate: The size of the dots was determined via UV-vis spectroscopy (Fig. 10). The max absorption was found to be at 540 nm which corresponds to

dots of 3.68 nm diameter. Using Beer's Law (Eq. 1), the concentration of the dots solution was found to be 8.45×10^{-6} M. Three doctor bladed TiO₂ nanoparticle cells were made to provide baselines for comparison to the PLD technique, which had never been

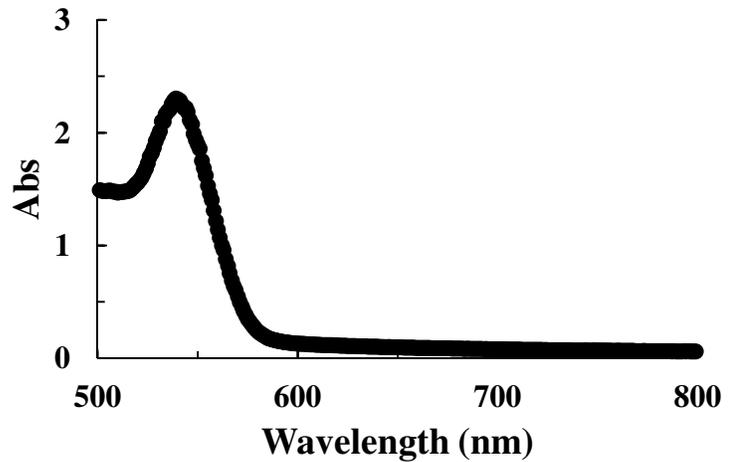


Figure 10. UV Vis Absorption curve for synthesized QD

used for this purpose before. The fill factor (FF) and quantum efficiency (η) were calculated from the IV curves (Fig. 11) utilizing the equations 2 and 3, and are tabulated in Table 1:

$$A = e * b * c \quad \text{Eq. 1}$$

$$FF = \frac{V_{\text{maxpower}} * I_{\text{maxpower}}}{V_{oc} * I_{sc}} \quad \text{Eq. 2}$$

$$\eta = \frac{V_{oc} * I_{sc}}{P_{\text{incident light}}} * FF * 100 \quad \text{Eq. 3}$$

Table 1. Properties of TiO₂ nanoparticle thin films

	FF	η
Cell 1	.321	.0436
Cell 2	.237	.0125
Cell 3	.221	.0471

Note that V_{maxpower} and I_{maxpower} come from the point on the IV curve where the cell is outputting the most power. V_{oc} is the point on the IV curve where the current flow is zero and the I_{sc} is the point where the voltage is zero. The fill factor represents how closely the IV

curve of the sample mimics the ideal case, which is a box with corners at the origin, $[0, I_{sc}]$, $[V_{oc}, 0]$, and $[V_{oc}, I_{sc}]$. The quantum efficiency represents how much of the power coming into the cell is actually converted to power out. Cell 2, which has

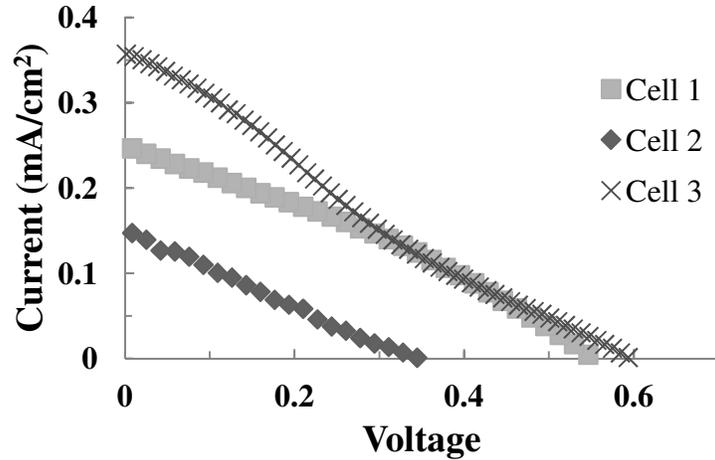
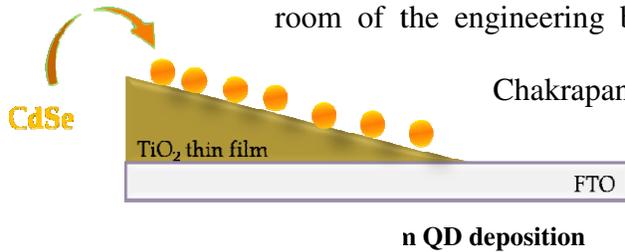


Figure 11. I-V curves for three TiO_2 nanoparticle thin films

the lowest efficiency of those cells tested, performed poorly because the fragile TiO_2 thin film had started to crumble before testing could be completed.

The PLD thin films have the advantage of being much sturdier than the nanoparticle thin films and were tested next. When submitted to the same series of tests the TiO_2 thin film performed as well as the nanoparticle films with a fill factor of 0.219 and a quantum efficiency of 0.0482%. The $SrTiO_3$ thin films, however, performed dismally. Little to no current was produced upon irradiation with 100 mW/cm^2 light. This was attributed to the increased speed with which electron/hole pairs undergo recombination in $SrTiO_3$ as compared to TiO_2 . Due to this lack of light response, the study of thickness effects was only continued with the TiO_2 gradient films.

Effect of Thin Film Thickness: The method of laser ablation deposition creates a gradient of metal oxide deposit across the surface of the FTO slide. This gradient was assumed to be approximately linear. The thickness of this wedge was found using the Profilometer in the clean



room of the engineering building. From a previous study by Vidhya

Chakrapani, it was hypothesized that regardless of the

thickness of the metal oxide, there would be

an even layer of CdSe deposited during

sensitization (Fig. 12). Thus the SrTiO₃ and the TiO₂ thin films were ideally set up to find the optimum film thickness to maximize current.

In order to confirm this hypothesis, differential UV-Vis absorption spectra were taken at 5 mm intervals on the TiO₂ and SrTiO₃ cell (Fig. 13). It was expected that this absorption should be constant over the thickness of the thin film.

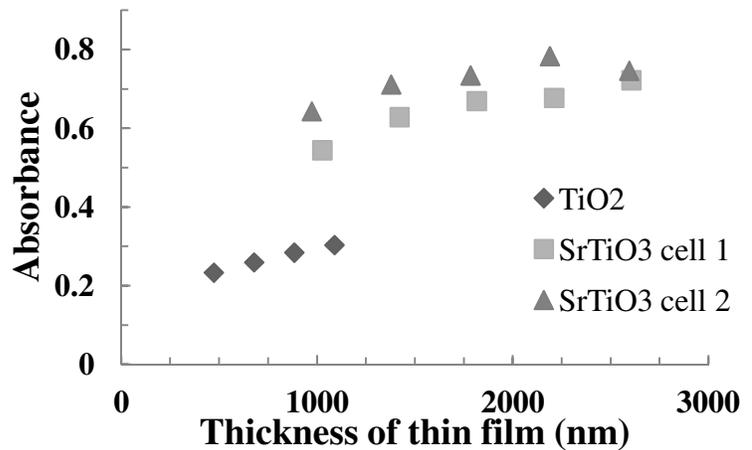


Figure 13. UV-Vis Absorption at 540 nm across film thickness

However, it was found that absorption did increase slightly with increasing thin film thickness; although the increase is fairly small. This confirmed relatively well that CdSe forms an even layer.

Chronoamperometric, open circuit potential, and IV measurements were taken every 5 mm across the surface of the TiO₂ thin film. It was expected that V_{oc} would stay constant across

the cell, but that I_{sc} would increase with increasing thin film thickness to a maximum and then fall off at high thin film thickness. The results of this analysis were inconclusive. One of the cells used showed some correlation with a peak photocurrent appearing at a thickness of 1.2 micrometers. However, the other sample cell showed little change in photocurrent across the varying thickness.

4.3 CONCLUSION/FUTURE WORK

After examining both TiO_2 and $SrTiO_3$ thin films, it can be concluded that strontium titanate is not a viable alternative to titanium dioxide as the electron transport layer of a thin film solar cell. $SrTiO_3$ only provided minimal photocurrents and proved to be a fairly unstable substrate. The thickness analysis, on the other hand, requires more attention. There could be a correlation, but the data presented here is insufficient to make any conclusion. Further thin films will need to be tested to obtain reproducible and reliable data. The thin film itself should be examined by SEM to confirm if there is a uniform layer of QDs present on the surface. Finally this process should be extended to the combinatorial heterogeneous thin films described in section 3.6. A film like this of $SrTiO_3$ and TiO_2 could be easily tested using the apparatuses developed here for the ideal mixture of the two oxides that produces the most efficient QD solar cell.

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