

Cadmium Sulfide and Titanium Dioxide Thin Film Nanostructures for Nanocrystal-
Based Solar Cells

Jason Lane, Scott Gordon, Justyna Widera
Office of Educational Programs, Faculty and Student Team (FaST)
Correspondence: jasonlane@mail.adelphi.edu

Adelphi University

Brookhaven National Laboratory
Upton, NY

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ABSTRACT

Cadmium Sulfide and Titanium Dioxide Thin Film Nanostructures for Nanocrystal-Based Solar Cells

Scott Gordon, Jason Lane, Justyna Widera (Department of Chemistry, Adelphi University, Garden City, NY 11530), and Charles T. Black (Center for Functional Nanomaterials, Brookhaven National Laboratory, Upton, NY 11973).

New solar cell architectures leverage nanostructured materials in attempting to achieve high light-to-electricity conversion efficiencies using low-cost materials and processes. One such example is a dye sensitized solar cell, wherein light is absorbed by an organic dye sensitizer (rather than by a semiconductor, as in a traditional solar cell), and the photogenerated charge transports out of the device through a nanostructured percolating titanium dioxide (TiO_2) network. Because organic dyes have a limited spectral absorption range, they are not readily suited to capture all incident solar energy. Inorganic semiconductor quantum dots represent an alternative solar cell sensitizer with potential advantages because their spectral light absorption can be controlled by their size and composition. In principle, one can design a device having a spectral absorbance range well-matched to the incident solar spectrum by using an array of differently sized quantum dots – thereby providing a pathway to higher performance efficiencies. We use solution-phase chemistry to synthesize cadmium sulfide (CdS) quantum dots with precise diameter control over the range of 2 to 10 nanometers, and corresponding control of peak optical absorption from 320nm to 365nm. We produce CdS particles using a reverse micelle method using a surfactant (AOT in heptane) allowing further integration into thin film devices using solution processing. We have characterized the optical properties of thin films of both CdS and TiO_2 nanocrystal using ultraviolet-visible spectroscopy in order to determine their absorbance. We have measured the nanocrystal film

morphologies (size, structure, and thickness) using scanning electron microscopy and profilometry in order to understand the effects of different methods of film deposition (spin coating versus doctor-blading). Spin coating of both CdS and TiO₂ nanocrystals yields uniform, three-dimensional nanocrystalline thin films. We have fabricated nanocrystal thin film devices by sandwiching nanocrystalline films of either CdS or TiO₂ between a transparent indium-tin oxide electrical contact and an aluminum contact deposited by thermal evaporation. In both CdS and TiO₂ nanocrystal devices, the device current increases with applied voltage. Under simulated solar illumination, the conductance of both CdS and TiO₂ devices increases, consistent with excitation of photogenerated carriers in the semiconductor nanocrystal film network.

1. INTRODUCTION

There has been a growing worldwide movement to reduce fossil fuel consumption. An alternative power solution must be developed that would be affordable, sustainable, efficient, clean and renewable [1]. By implementing the burgeoning science of nanochemistry, we hope to create an alternative energy source that is as cost effective as it is eco-friendly.

Solar power has been one of the most commercially available and renewable energy solutions. While other methods are still in developmental stages, silicon based solar cells are readily accessible, although the price of these devices remain high enough to discourage potential clients. Cheaper devices have been developed, which use a photosensitive dye to initiate a photoelectrochemical reaction to produce electricity. These Dye Sensitized Solar Cells (DSSC) rely on the absorbance of a dye [1], rather than an enhanced p-n junction between two silicon crystals. The energy influx of a DSSC is dependent entirely upon the dye, the device's lone method of sensitization. Dyes possess a limited absorption range, and do not cover the broad spectrum of the sun's light, wasting nearly all energy that is not at that specific absorbance range.

Since the wavelength at which quantum dots absorb light can be controlled by their size and composition, a device with absorbance ranges closer to the emittance pattern of the sun can be made by using an array of differently sized quantum dots [2]. These unique nanohybrids, known as Quantum Dot Sensitized Solar Cells (QDSSC) are expected to offer higher efficiencies.

Our research focuses upon the electrical and morphological characterization of two materials proposed to be used in the new generation of solar cells: cadmium sulfide nanoparticles and titanium dioxide nanocrystals.

Cadmium sulfide nanoparticles are an attractive choice because of their easy synthesis and their ability to be accurately tuned to a specific absorption wavelength [3]. They have been tested in a variety of applications for a large number of years, and along with Cadmium Selenide, Cadmium Telluride, and Lead Sulfide, they are among the most discussed sensitizers for QDSSC's in literature [4, 5, 6].

Titanium dioxide is almost exclusively used as the semiconductor in QDSSC research, because it has a desirable band gap and is easy to synthesize and process to form transparent thin films for electronic devices. Its very porous 3D structure makes it able to fit a large amount of sensitizing materials [7].

In the present work, synthesis procedures for both CdS nanoparticles and TiO₂ solutions are described. The process of creation of thin film devices containing those materials is outlined. The electrical, spectral, and morphological tests of these materials were carried out in order to better understand these basic components of a QDSSC.

2. MATERIALS AND METHODS

All chemicals were used as received from Sigma-Aldrich with the exception of the P25 TiO₂ powder, which was a generous gift from the Degussa Corporation. ITO glass slides were purchased from Thin Film Devices (20Ω/square).

2 grams of P25 TiO₂ powder were dispersed into either 10 ml ethanol or 10 ml 0.035M aqueous acetic acid until a homogenous dispersion was obtained. 7 drops of surfactant Triton X-100 were added to the solution and thoroughly mixed until uniform.

4 to 5 drops of TiO₂ solution were spun (using a Brewer Science Inc. CEE200 spin coater) onto ITO coated conductive glass plates (15mm x 15mm) at varying rates (from 1000 rpm to 6000 rpm for 45 seconds) and then sintered on a hot plate at 450°C for 15 minutes. An aluminum top contact roughly 80 to 90 nm thick was created on top of the TiO₂ thin films by thermal evaporation (using a Kurt J. Lesker Company PVD75). For optical characterization, TiO₂ solution was spun onto quartz plates and sintered at 450°C for 15 min.

To create CdS nanoparticles, 0.0617g of CdNO₃ and 0.0480g of Na₂S were dissolved in separate containers containing 1mL ultra pure water. 0.1M dioctyl sodium sulfosuccinate (AOT) solution in heptane was created beforehand. Microsyringes were used to inject 36 µL of the CdNO₃ solution and 36 µL of the Na₂S solution into separate 5 mL aliquots of the 0.1 M AOT in heptane solutions. In order to get the best emulsion, these aqueous solutions were injected into AOT in heptane aliquots as rapidly as possible. 36 µL is the amount calculated to obtain particles of approximately 5 nm diameter in size by setting the proper ratio of amounts of water and surfactant ($w_o = 4$) corresponding to the proper size of the created reverse micelles. These respective Cd/AOT/heptane and S/AOT/heptane solutions were allowed to sit for 30 min before being mixed together and allowed to sit for an additional 30 min before spectral testing. These solutions were protected from exposure to light to prevent the degradation of the particles and the shifting of their absorption peaks. UV-VIS measurements of CdS nanoparticles solutions were performed in order to confirm their absorption ranges.

4 to 5 drops of the CdS nanoparticles solution were spun onto ITO coated conductive glass plates (15mm x 15mm) at varying rates (from 3000 rpm to 6000 rpm) for 45

seconds. An aluminum top contact roughly 80 to 90 nm thick was created on top of the CdS nanoparticles layer by thermal evaporation.

Absorption spectra were recorded using a PerkinElmer Lambda 950 UV/Vis spectrometer with samples placed behind the integrating sphere and tested against a blank quartz slide. Electrical characterization was carried out using an Agilent 4156C precision semiconductor parameter analyzer attached to a bench top electrical probe station with bottom side illumination from a Xenon lamp based solar replicator (roughly $100\text{mW}/\text{cm}^2$) passed through a fiber optical cable, which cuts off most of the UV wavelengths. Positive probe contact was made to the ITO layer through a silver conductive paint contact and negative probe contact was made directly to the top aluminum contact. SEM images were obtained using a Hitachi S-4800 Scanning Electron Microscope.

3. RESULTS

3.1. Properties of CdS thin film devices. Figure 1 shows the UV-VIS absorbance spectra of multiple samples of freshly synthesized CdS nanoparticles ($w_0 = 4$) with an absorbance peak of 315 nm.

Figure 2 shows the dependence of the measured current passing through the ITO/CdS/Al device against an applied voltage. The current measured when the device was exposed to the simulated solar illumination (roughly $100\text{ mW}/\text{cm}^2$) is about 2.5 times higher at 0.5 and -0.5 Volts than the current measured in the dark. The shape of the I vs. E curve is symmetrical in the potential ranges from 0 to 0.5 Volts and from 0 to -0.5 Volts for both the light and dark tests.

3.2 Properties of TiO₂ thin film devices. Figure 3 shows the relationship of the measured current passing through the ITO/TiO₂/Al device against an applied voltage. The current measured when the investigated device was exposed to the simulated solar illumination (roughly 100 mW/cm²) is about 10 times higher at 0.5 Volts and 1 Volt than the current measured in the dark. The current measured under a negative voltage bias does not show as big of a current difference between the light and dark tests.

Figure 4 shows the absorbance spectra of a TiO₂ film casted onto a quartz plate. The sample was placed behind the integrating sphere and referenced against a blank quartz plate. A characteristic absorbance peak appears at 260nm.

Figure 5 shows SEM images of ethanol based TiO₂ film casted onto an ITO coated glass plate. Charge buildup problems prevented higher resolution images. However, image A shows almost uniform coverage of the ITO coated glass plate with some surface irregularity. The created film was generally smooth and without any visible cracks. Higher magnification image B shows the highly nanoporous nanocrystalline 3D structure of the TiO₂ thin film.

4. DISCUSSION AND CONCLUSION

Absorbance spectra of the freshly synthesized CdS nanoparticles are consistent with prior spectral characterization of CdS nanoparticles synthesized in a similar fashion [3]. However they are blue shifted, most likely due to a lower w_0 water to surfactant ratio. By changing the w_0 , different sized nanoparticles with different absorption peaks can be made [3]. Nonetheless, the absorption spectra shows that the technique outlined is reproducible such to make a large quantity of high quality AOT-protected CdS nanoparticles with little effort.

The electrical characteristics of the fabricated CdS thin film devices show conduction of current through the CdS layer, which is promising even though there is a large amount of surfactant protecting the CdS nanoparticles. The symmetry of the I vs. E curves comparing the positive and negative biases lead to the conclusion that Ohmic contacts are made to the CdS layer by both the ITO and the aluminum layer. Schottky contact would be preferred for a solar application for such a device [8] by using a high work function metal such as gold or platinum. However, this device ITO/CdS/Al displays photodetective characteristics by passing more current when exposed to the simulated solar illumination. At -0.5 and 0.5V the ITO/CdS/Al device passed 2.5 times more current under simulated solar illumination than the same device tested under dark conditions. This photodetection is a result of the generation of more charge carriers within CdS conduction band due to the absorption of photons when the investigated device was under the simulated solar illumination.

Overall, the TiO₂ films produced from ethanol based dispersions had better characteristics than the dilute acetic acid dispersion, which has been noted by McHale [9]. The ethanol based dispersion produced more uniform and consistent thin films when spun on ITO coated glass.

The electrical characterization of ITO/TiO₂/Al devices shows definite conduction through the TiO₂ layer. The current versus applied voltage graph shows an obvious asymmetry. It is seen that the device ITO/TiO₂/Al acts as a photodetector in positive voltage bias, as seen by the 10-fold increase in current (at 0.5 and 1.0 Volts) under simulated solar illumination compared to the dark test. This is due to the increase in the number of charge carriers as the TiO₂ absorbs photons. Additionally there is only a slight

increase in current under negative voltage bias. This behavior was rather expected on both sides of the I vs. E curve at positive and negative biases. As stated previously, the solar light source used for this characterization was passed through a fiber optic cable, which cuts off most UV wavelength and as you can see in Figure 4, TiO₂'s characteristic absorption peak appears at 260 nm [9, 11]. It can be theorized that the photodetector properties of the TiO₂ in such a device would be increased if it was exposed to such particular wavelengths in the UV range. The asymmetrical curves in Figure 4 also suggest that the TiO₂ makes good (Ohmic) contact to the aluminum but possibly (preliminary results) makes Schottky contact to ITO. More device testing and interpretation are needed to confirm this.

Lastly, SEM imaging of spun coated TiO₂ on ITO shows an almost uniform thin film, which is highly nanoporous as seen in the Figure 5B. The use of the surfactant in the dispersions plays two roles: makes the solution thicker, so it sticks to the substrate, and helps to create pores in the TiO₂ film. The high temperature of sintering removes the organic surfactant (Triton X-100) leaving the 3D nanocrystalline lattice [10].

Overall, TiO₂ seems to be a good choice of the semiconductor for Grätzel type solar cell due to its desirable electronic and morphological characteristics.

5. FUTURE WORK

Due to the preliminary nature of this project a lot of future work must be done to achieve the final goal of assembling a Quantum Dots Sensitized Solar Cells (QDSSC). Several ideas of future experiments were developed. First of all, spectrally resolved solar illumination needs to be applied to determine what wavelengths of light are responsible for the photodetection in the CdS thin film device. This will determine whether the CdS

nanoparticles and not some other component such as the AOT surfactant, are actually responsible for the photodetection.

Additionally, experiments that progress towards the creation of a QDSSC, such as trying to use linker molecules to link the CdS nanoparticles to the TiO₂ lattice [5, 11] will be carried out. One of the potential downfalls of using CdS nanoparticles is its near-UV absorption, which is not where the bulk of the sun's illumination is located. For those reasons other nanoparticles are being considered such as CdTe and PbS, which have more desirable absorption wavelengths for a solar application. Alternative synthesis procedures for these new nanoparticles will need to be considered as well, even though the relatively easy synthesis of CdS is attractive.

TiO₂ also needs further refinement to achieve highly ordered, more durable and defect free films. Using AFM and SEM will allow for a closer inspection of the morphological characteristics of the films we are currently creating.

Lastly, charge transport and charge separation studies will be useful in gauging our progress as we carry out these proposed experiments.

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FIGURES

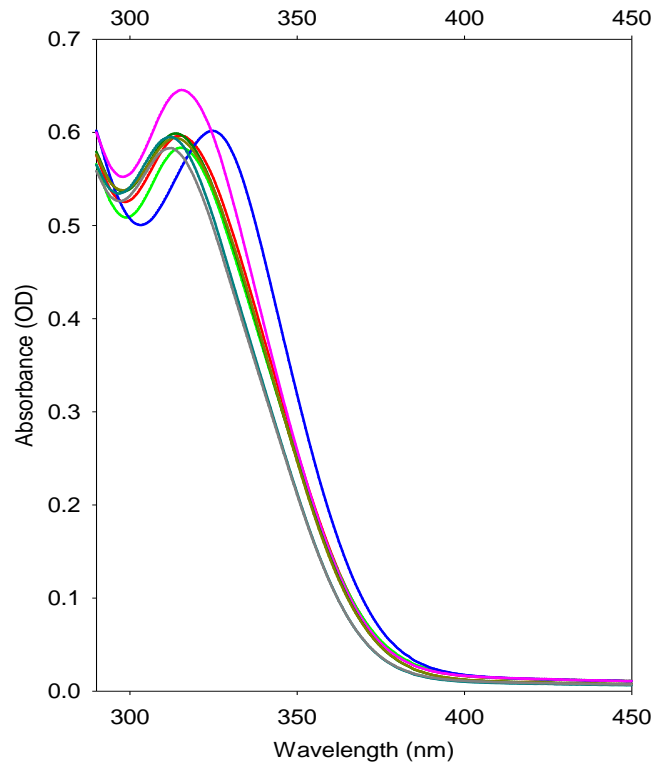


Figure 1. UV-VIS spectrum of multiple samples of freshly synthesized CdS nanoparticles. ($w_0 = 4$)

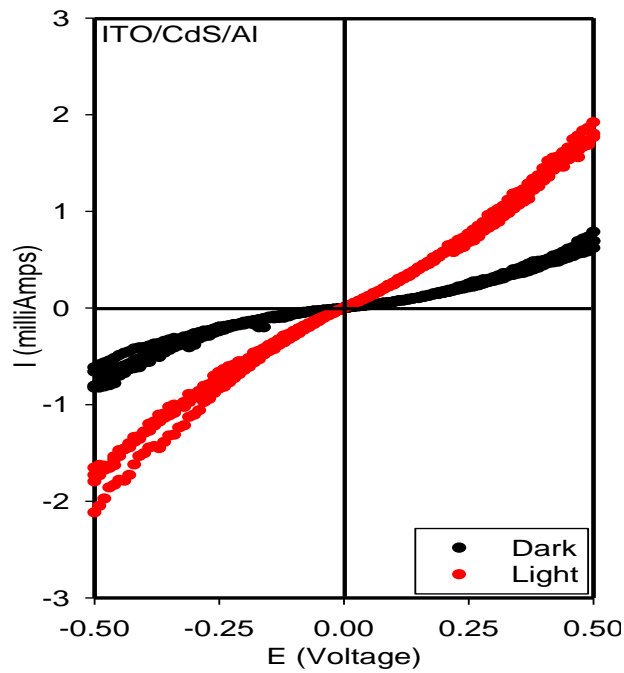


Figure 2. Current versus applied potential plot for ITO/CdS/Al devices. Measurements performed in the dark and under the simulated solar illumination.

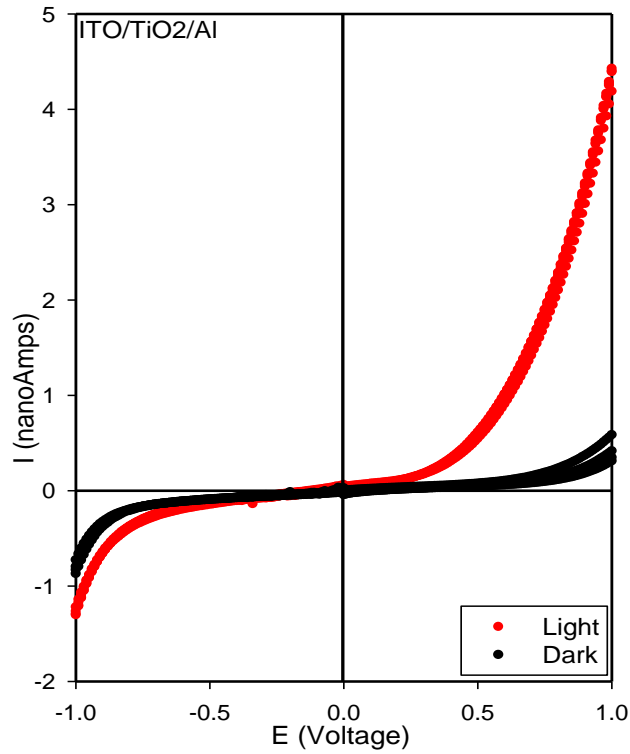


Figure 3. Current versus applied potential plot for ITO/TiO₂/Al devices. Measurements performed in the dark and under the simulated solar illumination.

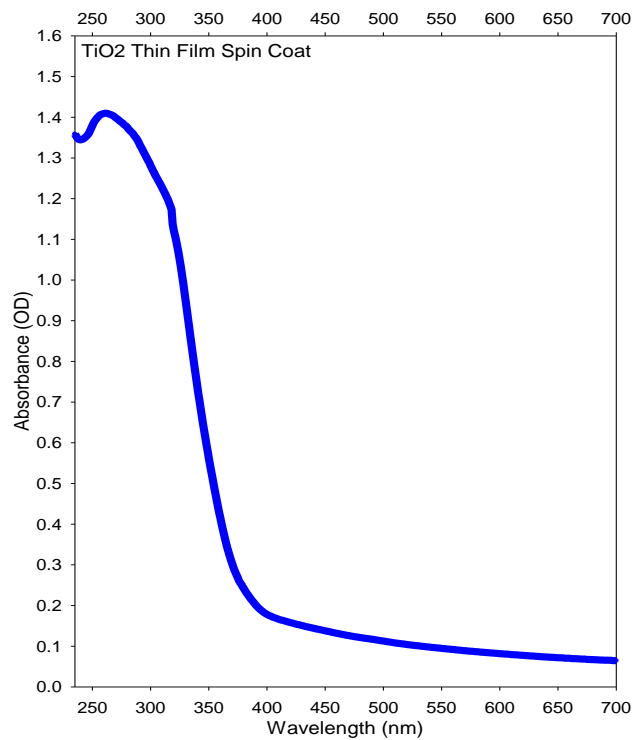


Figure 4. UV-VIS spectrum of TiO₂ thin film on quartz plate.

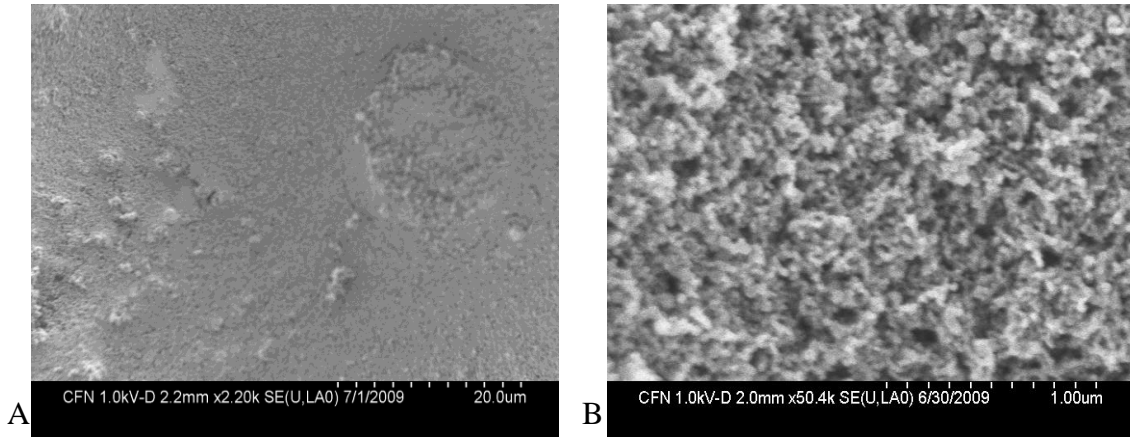


Figure 5. SEM images of a TiO₂ thin film spun coated on ITO glass plate at 3000 rpm spin rate.