Influence of photo-luminescent CdSe/CdS core shell quantum dots in solar cell efficiency

R Lopez-Delgado, Y Zhou, A Zazueta-Raynaud, H Zhao, J E Pelayo, A Vomiero, M E Álvarez-Ramos, F Rosei, and A Ayon.

1MEMS Research Lab, Department of Physics and Astronomy, University of Texas at San Antonio, San Antonio, TX, 78249, USA.
2Departamento de Física, Universidad de Sonora, Hermosillo, Son., 83000, México.
3Centro de Ciencias Exactas e Ingenierías, Universidad de Guadalajara, Guadalajara, Jal, 44430, México.
4INRS-EMT, Varennes, QC J3X 1P7, Canada.
5Luleå University of Technology, 971 87 Luleå, Sweden

Corresponding author email: Rosendo.lopezdelgado@utsa.edu

Abstract. We report the synthesis and characterization of CdSe/CdS core-shell quantum dots (CdSe/CdS-QDs) that exhibit absorption in the UV range of the solar spectrum and emit photons with wavelengths centered around 625 nm, a wavelength that is well suited for silicon absorption and electron-hole pair generation. We also report the fabrication and characterization of single crystal silicon (c-Si) solar cells with and without the aforementioned photo luminescent, down-shifting CdSe/CdS-QDs. The incorporation of these nanostructures triggered improvements in the performance of the devices, particularly in the open circuit voltage ($V_{oc}$) and short circuit current density ($J_{sc}$) for which the measured values showed an increase from 543 to 546 mV and from 32.5 to 37.0 mA/cm$^2$, respectively. The combined effect of the improved values led to an increment in the power conversion efficiency (PCE) from 12.01 to 13.54%. This increase represents a 12.7% improvement in the PCE of the fabricated devices. The effort described herein is considered a good fit to the generalized trend to improve the efficiency of solar cells with mass-compatible techniques that could serve to promote their widespread utilization.

1. Introduction.
In recent years, silicon solar cells have been researched with the aim of improving their power conversion efficiency by different methods. However, one of the biggest problems in the energy conversion from sunlight is the absorption range of the material constructing solar cells, since they produce energy only from a small part of the total solar spectrum [1, 2]. The wavelength distribution of the solar spectrum extends from the infrared to the ultraviolet but only a fraction is absorbed by common materials in solar cells[3, 4]. The main reasons are that only photons with energy greater than the bandgap can be absorbed by the material, and photons with energies much larger than the bandgap do not produce electron-hole pairs but only contribute to thermalization of the material, leading to losses of energy from low and high energy photons[3].
Improvements in the absorption range could be achieved by the utilization of luminescent materials, using up-conversion materials for low energy photons [5, 6] and down conversion materials for high energy photons [7, 8]. In this report, we focus on down-shifting CdSe/CdS quantum dots.

2. Experimental.
2.1. CdSe/CdS Quantum Dots Synthesis.
Core CdSe QDs were synthesized by using the hot injection approach [9]. To this end, trioctyl phosphine oxide (TOPO) (1g) and Cd-oleate (0.38 mmol, 1mL) in 8 mL of octadecene (ODE) were purged by N₂ at room temperature for 30 min. The reaction system was evacuated for 30 min at 100 °C, and then the temperature was raised to 300 °C. A mixture of trioctyl phosphine (TOP)−Se (4 mmol, 4 mL), 3 mL of oleylamine and 1 mL of ODE at was quickly injected into the Cd-oleate suspension under vigorous stirring. Ethanol was added, then the suspension was centrifuged and the supernatant was removed. The Core CdSe QDs were dispersed in toluene. Deposition of CdS layers (shell) on CdSe (core) QDs followed the procedure described in Ghosh et al [9]. Oleylamine (OLA) (5 ml), ODE (5 mL) and CdSe QDs (~2 × 10⁻⁷ mol in hexane) were degassed at 110°C for 30 min. Then the temperature was raised to 240°C with stirring. Cd-oleate dispersed in ODE (0.25 mL, 0.2 M) was added dropwise and the mixture was allowed to react for 2.5 h, followed by dropwise addition of 0.2 M sulfur in ODE with same volume and a reaction time of 1 h. The shell was further annealed for 10 min. All subsequent shells were annealed at 240 °C for ~10 min. The reaction was cooled to room temperature using ice water (0°C). Ethanol was added, the suspension was centrifuged and the supernatant was removed. The QDs were then dispersed in toluene for further characterization.

2.2. Silicon Solar Cell Fabrication.
Single crystal silicon solar cells were fabricated employing 4-inch, n-type, <100> silicon wafers with a resistivity of 10-20 Ω-cm employing a spin on dopant technique (SOD) that has been described elsewhere [10].

The silicon samples were cleaned using an extended 4-steps RCA cleaning process. In order to create the p-type emitter layer and the p+-back surface field (BSF) for charge collection, Boron and Phosphorous spin-on-dopant (SOD) solutions were prepared by the sol–gel method [10]. The Boron (SOD) solution was deposited on the front side of the silicon sample and the Phosphorous (SOD) on the opposite side. The samples were annealed at 120°C for 10 min to remove the organic solvents. Subsequently, the samples were annealed at 1000°C for 10 min to diffuse the dopants and create the p–n junction and the BSF. To make the electrical contacts, 200 nm of aluminum were deposited on each side of the device by thermal evaporation. A shadow mask was used on the front side to make a pattern of finger electrodes, while a blanket deposition was performed in the back side. Finally, the samples were annealed at 585°C for 10 min to promote the formation of an ohmic Al/Si contact.

After a set of solar cells were fabricated and characterized, CdSe/CdS-QDs were spin cast on the window of the solar cells. To this end, 200 μl of CdSe/CdS-QDs solution was dispersed with an angular velocity of 5000 rpm during 60s. All the samples were characterized by the same method in order to compare the performance of the device with and without the influence of the CdSe/CdS -QDs.

Figure 1. Flowchart of the fabrication of c-Silicon solar cell and CdSe/CdS-QDs deposition: 1) Extended RCA cleaning, 2) Diffusion of the emitter layer and BSF, 3) Front and back electrode deposition and 4) spin casting of CdSe/CdS-QDs.
3. Results and Discussion.

3.1. Characterization of CdSe/CdS Quantum Dots.

The UV-Vis absorption spectra of the synthesized CdSe/CdS-QDs were measured using a Varian Cary 5000 UV-Vis spectrometer, while the photoluminescence effects were recorded using an Ocean Optics Flame-S-UV-VIS spectrometer. The absorption and photoluminescence spectra of the synthesized CdSe/CdS-QDs are shown in Figure 2. It is observed that the CdSe/CdS-QDs have absorption of photons below $\sim 525$ nm while the photo-luminescence spectra consist of a broad band extending from 525 to 675 nm with a maximum around 625 nm, confirming the down-shifting effect, which is desired to improve the absorption by the silicon solar cell.

![Absorbance and Photoluminescence Spectrum of CdSe/CdS-QDs](image)

Figure 2. Absorption and photoluminescence spectrum of CdSe/CdS-QDs varying the amount of APTES.

Transmission electron microscopy (TEM) images were collected employing a JEOL 2010-F transmission electron microscope. Figure 3 shows TEM images of the synthetized CdSe/CdS-QDs as well as the size distribution histogram, where it was found that the size average is around 10 nm.

![TEM Images and Size Distribution Histogram](image)

Figure 3. TEM images of CdSe/CdS QDs and size distribution histogram.

3.2. Solar Cell Characterization.

A set of three c-Si solar cells were fabricated with the previously described approach. CdSe/CdS-QDs were deposited on the set of solar cells to determine their influence. The I–V characteristics of the devices were measured before and after the deployment of the CdSe/CdS-QDs. In all cases, the utilization of these nanostructures improved the performance of the solar cells as shown in Figure 4. The averages of the solar cell parameters are listed in Table 1. The application of the QDs on c-Si solar cells lead to increases in two of the three main parameters that contribute to solar cell efficiency, namely, the open circuit voltage ($V_{oc}$) and the short circuit current density ($J_{sc}$). An improvement was observed in all the solar cells after the deposition, where $V_{oc}$ showed an increase from an average of 543.38 to 545.90 mV, the $J_{sc}$ went from 32.49 to 37.03 mA/cm$^2$ and although the fill factor (FF) decreased from 68.04 to 66.96%, the combination of all these parameters led to an improvement of the power conversion efficiency (PCE) from 12.01 to 13.54% for an overall PCE improvement of 12.7%.

![I-V Characteristics of Solar Cells](image)

Figure 4. I–V characteristics of solar cells before and after the deployment of CdSe/CdS-QDs.

Table 1. C-Silicon solar cell performance parameters before and after application of CdSe/CdS-QDs.

| Solar cell performance | $V_{oc}$ (mV) | $J_{sc}$ (mA/cm$^2$) | FF (%) | PCE (%) |
|------------------------|---------------|---------------------|--------|---------|
| c-Si Solar cell set    | 543.38        | 32.49               | 68.04  | 12.01 ± 0.2 |
| c-Si Solar cell set +CdSe/CdS QDs | 545.90 | 37.03 | 66.96 | 13.54 ± 0.2 |

The External Quantum Efficiency was measured in order to study the spectral response of the fabricated c-Si solar cells with and without the deployed CdSe/CdS-QDs. The observations indicate that the photovoltaic response improved in a wavelength segment extending from the UV region to the
visible with the maximum influence between 400 and 600 nm as shown in Figure 5. These EQE improvements are thought to be responsible for the current increase measured during the I–V analysis.

4. Conclusions.
In the present work it was studied the influence of CdSe/CdS-QDs in c-Si solar cells as photovoltaic response improvers. Experimental results showed that the incorporation of CdSe/CdS-QDs as down-shifting material on the window side of a solar cell improves the photocurrent generation, which can be seen from the current density and open circuit voltage increase as well as the EQE improvement in the segment in accordance to the absorbance and photoluminescent results. Even though the FF was observed to decrease in all cases, the overall power conversion efficiency achieved after the application of CdSe/CdS-QDs was increased from 12.01% to 13.54%. This result represents an improvement of 12.7% in the photovoltaic performance. The experimental results evince that this strategy represents a promising way to improve the efficiency of existing solar cells, which could promote the proliferation of photovoltaic energy harvesting.

Acknowledgements
The authors would like to acknowledge the U.S. Army Research Office (Grant W911NF-13-1-0110), CONACYT, the Physics and Astronomy Department of the University of Texas at San Antonio and the Physics Department of University of Sonora, for the financial support.

References
[1] Hirst L C and Ekins-Daukes N J, 2011. Progress in Photovoltaics: Research and Applications. 19(4): p. 286-293.
[2] Scholes G D, et al., 2011. Nature chemistry. 3(10): p. 763-774.
[3] Huang X, et al., 2013. Chemical Society Reviews. 42(1): p. 173-201.
[4] Richards B, 2006. Solar energy materials and solar cells. 90(15): p. 2329-2337.
[5] Qu B, et al., 2016. Journal of Alloys and Compounds. 658: p. 848-853.
[6] Van Der Ende B M, Aarts L, and Meijerink A, 2009. Physical Chemistry Chemical Physics. 11(47): p. 11081-11095.
[7] Zhang Q and Huang X, 2010. Progress in Materials Science. 55(5): p. 353-427.
[8] Trupke T, Green M, and Würfel P, 2002. Journal of Applied Physics. 92(3): p. 1668-1674.
[9] Ghosh Y, et al., 2012. Journal of the American Chemical Society. 134(23): p. 9634-9643.
[10] Pudasaini P R and Ayon A A, High performance nanopillars array silicon solar cells in Design, Test, Integration and Packaging of MEMS/MOEMS (DTIP), 2013 Symposium on: IEEE.