A Fabrication Procedure for a CdTe Quantum Dot Printable Hybrid Solar Cell

Kyle D. Gilroy
Department of Mechanical Engineering,
Temple University, Philadelphia, PA 19122

Mohammad S. Islam
Department of Mechanical Engineering,
Temple University, Philadelphia, PA 19122

Robert A. Hughes
Department of Mechanical Engineering,
Temple University, Philadelphia, PA 19122

Svetlana Neretina
Department of Mechanical Engineering,
Temple University, Philadelphia, PA 19122

Brandon Lee
Department of Mechanical Engineering and Mechanics,
Drexel University, Philadelphia, PA 19104

Ying Sun
Department of Mechanical Engineering and Mechanics,
Drexel University, Philadelphia, PA 19104

A Fabrication Procedure for a CdTe Quantum Dot Printable Hybrid Solar Cell

Kyle D. Gilroy, Mohammad S. Islam, Robert A. Hughes and Svetlana Neretina
Department of Mechanical Engineering, Temple University, Philadelphia, PA 19122

Brandon Lee and Ying Sun
Department of Mechanical Engineering and Mechanics, Drexel University, Philadelphia, PA 19104

Abstract: Solution-based CdTe quantum dots were fabricated following the synthetic protocols devised by Bawendi and co-workers. The nanocrystals, which are spherically shaped, are derived from colloidal solutions having oleic acid and trioctylphosphine as stabilizers. The quantum dots produced exhibit a strong photoluminescence where the wavelength of the luminescence was varied by altering the extraction time from the reaction vessel. Absorbance measurements on the various aliquots exhibit maxima extending from 540 to 663 nm. Transmission electron microscopy indicates that the CdTe nanocrystals are indeed spherical where the ensemble shows a narrow size distribution. Energy dispersive x-ray spectroscopy confirmed that cadmium and tellurium are present in a 1:1 ratio. Ink formulation begins by first precipitating the CdTe nanocrystals through centrifugation to produce a fine powder, dissolving the powder in toluene, and then combining the solution produced with the photoactive organic semiconductors P3HT and PCBM. Solar cell fabrication proceeded by first applying the ink mixture to an ITO-coated glass substrate using a Dimatix Materials Printer DMP-2800. Following a high temperature anneal of the ink, the solar cell device fabrication was then completed by applying layers of Poly(3,4-ethylenedioxythiophene), poly(styrenesulfonate) (PEDOT:PSS) and a top gold electrode. The work demonstrates the viability of fabricating a printable solar cell architecture based on CdTe-based quantum dot inks.

1. Introduction

One of the foremost challenges facing next generation photovoltaics is to advance designs which deliver flexible, low-cost alternatives to the rigid-substrate silicon-based architectures which presently dominate the marketplace[1-4]. The emergence of companies such as Nanosolar[5,6] and Konarka[7], which offer high-volume printable solar cell fabrication processes, reflect both the allure and promise of fabricating low-cost, efficient solar cells using conventional printing-press technologies. Inkjet printing offers a printing technology which is promising but has, thus far, remained untapped in terms of use in commercial photovoltaic technologies. While the inkjet process lends itself to the fabrication of organic solar cells[8], the formation of hybrid cells which combine both an organic polymer and inorganic nanoparticles have proved more efficient in prototype architectures[9,10]. With theoretical calculations indicating that quantum dot solar cells have the potential to reach a maximum thermodynamic conversion efficiency of up to 66%[11], the development of hybrid photoactive ink formulations which are compatible with inkjet printing processes presents one of the key challenges in advancing this technology. Thus far, hybrid cells have, for the most part, relied on the II-VI semiconductor cadmium-selenide (CdSe) for the inorganic component[12,13], while the closely related compound cadmium-telluride (CdTe) has received little attention despite the fact that it is the foremost photovoltaic material for the thin film solar cell industry[14-16]. Here, we present our studies

focused on fabricating a photoactive CdTe ink formulation which is compatible with the inkjet printing process.

2. CdTe Quantum Dot Ink Fabrication of the Hybrid Solar Cells

Synthetic protocols for the fabrication of CdTe quantum dots were first devised by Bawendi and co-workers[17]. In the present study, we closely follow the methodologies of Kloper *et al.*[18], but where slight variations to their procedures are made. Ink fabrication utilized polymers commonly used in organic solar cells[19-21].

2.1 Materials: Tellurium Powder (Te, 99.997%, 300 mesh), Cadmium oxide (CdO, >= 99.99%), Oleic Acid (OA, technical grade 90%), Trioctylphosphine (TOP, technical grade 90%), 1-Octadecene (ODE, technical grade 90%), Toluene (anhydrous, technical grad 99.8%), 1 Ethanol (anhydrous, technical grad 99.5%). All materials were purchased from Sigma-Aldrich.

2.2 CdTe Synthesis: A precursor solution, comprised of 0.1 mmol Te powder dissolved in 0.25 mL TOP, was heated to 80 °C and stirred until it turned yellow in color. Next, 2.25 mL ODE was added to the solution and gently stirred. The resulting solution was set aside while a second solution, consisting of 0.0256 g CdO dissolved in 200 µL OA and 10 mL ODE, was prepared. This second solution was heated to 300 °C, at which point the solution changed from yellow to transparent. Further heating to 310 °C led to the precipitation of Cd nanoparticles which caused the solution to turn black. Thirty seconds after this color change, 5 mL of the Te precursor solution was injected into the flask, causing it to instantly turn red, which is a signature characteristic of CdTe nanoparticle formation. Aliquots, extracted every minute, were rapidly injected into 5 mL of ambient toluene, the effect of which was to immediately quench the reaction.

2.3 CdTe Purification: In order isolate the CdTe nanoparticles, a 1:3 CdTe:Ethanol solution was centrifuged at 2000 rpm for 5 min, followed by the removal of the supernatant. This procedure was repeated twice. The CdTe remaining at the bottom of the centrifuge tube was then dried under a flow of argon gas to yield a fine powder. For this purification procedure, 17 mL of solution typically yielded 100 mg of CdTe powder.

2.4 Ink Polymer Synthesis: Ink solutions were prepared by first adding 90 mg of the CdTe powder suspended in 0.23 mL of toluene to 0.0225g poly-3(hexylthiophene) (P3HT) and 3.7485g oDCB and then stirring the resulting ink solution for 2 hours. The ink produced has a viscosity of 1.72 cP, a surface tension of 25.51 nN/m and a density of 1.3884 g/cm^3.

3. CdTe Quantum Dot Characterization

The CdTe quantum dots produced were characterized using photoluminescence, absorption spectroscopy (JASCO UV-VIS spectrometer), transmission electron microscopy (JEOL JEM-1400 TEM) and energy-dispersive x-ray spectroscopy (EDS).

3.1 Photoluminescence: Figure 1 shows images of solutions containing CdTe quantum dots illuminated with visible (Fig. 1A) and ultraviolet (Fig. 1B) light. The six vials shown are aliquots removed from the reaction vessel at various time intervals. As expected, the quantum dots show the intense photoluminescence characteristic of quantum confinement.

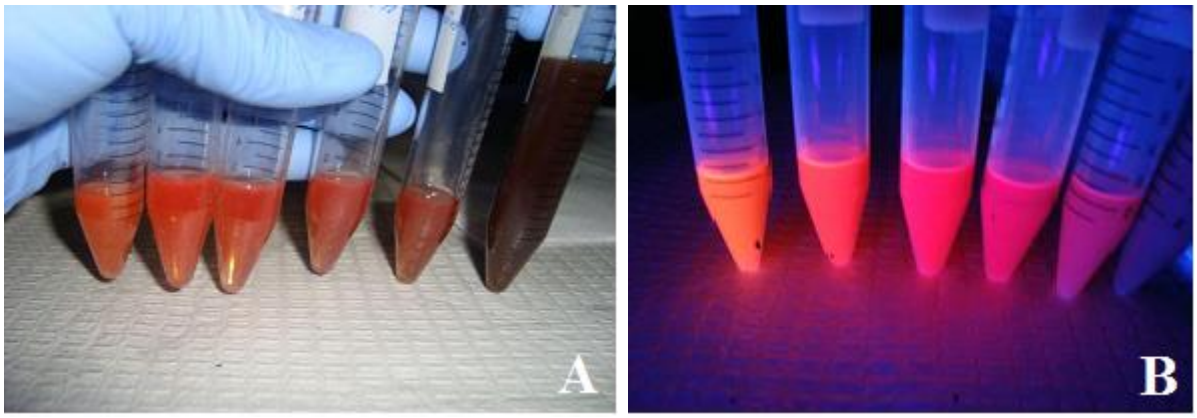

Figure 1: Images showing solutions containing CdTe quantum dots illuminated with (A) visible and (B) ultraviolet light. The extraction times, from left to right, are 0.5, 1, 1.5, 2, 2.5, 3 and 3.5 min, respectively.

3.2 Absorption Spectroscopy: Figure 2A shows the normalized absorbance spectra for the various CdTe quantum dots produced. The spectra show absorbance peaks ranging in wavelength from 550 to 700 nm where there is an increasing red-shift for the progressively larger quantum dots removed from the reaction vessel at later times. Figure 2B shows the wavelength dependence of the absorbance peak as a function of aliquot extraction time from the reaction vessel. These results are in agreement with both the quantum confinement effects expected for spherical quantum dots[22] as well as those observed in previous studies[18].

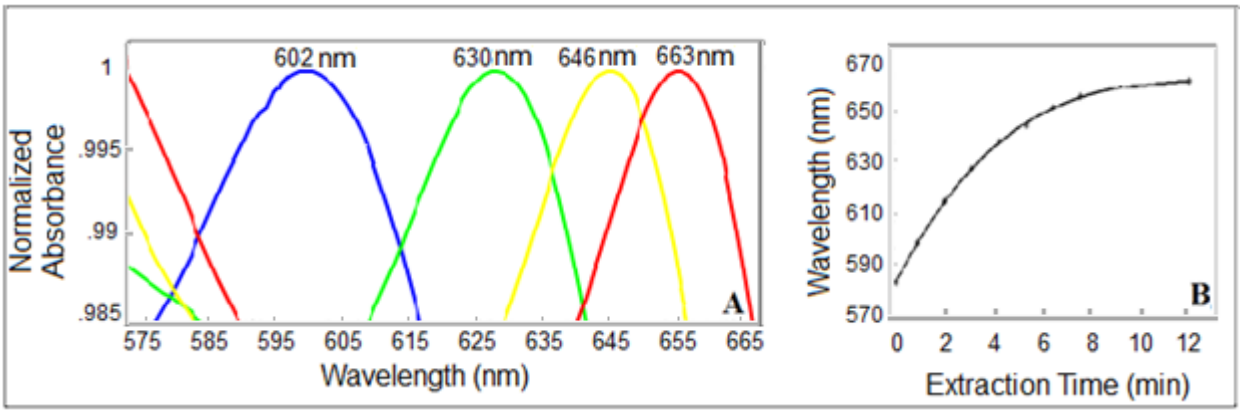

Figure 2: (A) Normalized absorbance spectra for CdTe quantum dots extracted from the reaction vessel at 1, 3, 5 and 11 min which yield absorbance maxima of 602, 630, 646 and 663 nm, respectively. (B) The absorbance maxima of the quantum dots versus the extraction time from the reaction vessel.

3.3 Transmission Electron Microscopy (TEM) and Energy-Dispersive X-ray Spectroscopy (EDS): Sample for TEM were prepared on copper grids (Carbon Type-A, 300 mesh, Ted Pella, Inc.). High resolution images indicate that the quantum dots have a high degree of monodispersity with particle diameters in the range of 4-8 nm. EDS on these quantum dots indicate the expected 1:1 Cd:Te ratio.

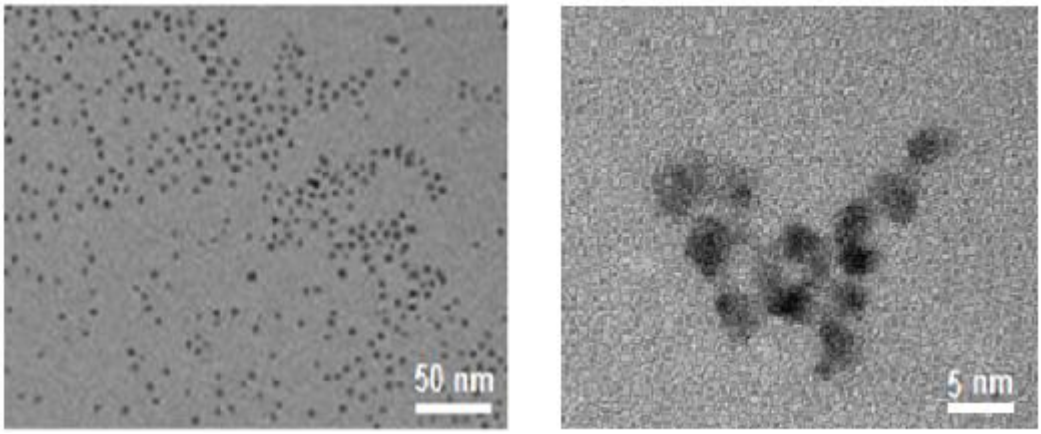

Figure 3. HR-TEM images of CdTe nanoparticle quantum dots with an average diameter of 6.3 nm.

4. Solar Cell Fabrication

A cartridge for a Dimatix Materials Printer DMP-2800 (Fig. 4A) was loaded with the CdTe quantum dot ink solution and dispensed onto a ZnO-coated indium-tin-oxide (ITO) substrate. Inkjet printing instrumentation and procedures are described in detail elsewhere. [19-21] The coating was formed from three identical layers where each layer has areal dimensions of 7 mm x 7 mm and a thickness of 20-25 nm (Fig. 4B). The layers were then annealed at 140 °C for 10 min and inspected under an optical microscope (Fig. 4C). The solar cell structure was then completed by first spin coating a polymer containing PEDOT:PSS (Poly(3,4-ethylenedioxythiophene) ploy(styrenesulfonate) (Fig. 4D) followed by the application of a gold electrode using a sputter coater (Fig 4E-F).

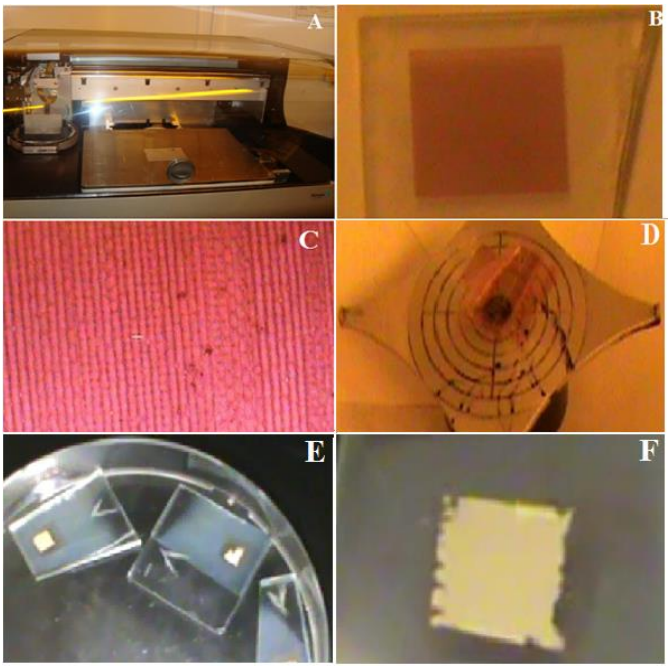

Figure 4: Optical images of (A) the Dimatix Materials Printer DMP-2800 used for Printing CdTe quantum dot ink, (B) the substrate after the ink has been printed, (c) the ink after annealing, (D) spin coating of the cell with the PEDOT:PSS polymer, (E) the final cell and (F) the top gold contact.

5. Summary

We have demonstrated the viability of fabricating a CdTe quantum dot hybrid solar cell architecture using an inkjet printing process. Crucial to this demonstration was the synthesis of monodisperse CdTe quantum dots exhibiting quantum confinement effects and their subsequent incorporation into an ink formulation. Future work will focus on assessing and optimizing the light harvesting capabilities of the solar cells produced.

Acknowledgements:

This work was funded by the Energy Commercialization Institute. KDG acknowledges the financial support of the NSF NUE grant No 1042071. We also acknowledge Dr. M. Kiani and Dr. R. Suri for providing access to their facilities.

References:

[1] A. V. Shah, H. Schade, M. Vanecek, J. Meier, E. Vallat-Sauvain, N. Wyrsche, U. Kroll, C. Droz, J. Bailet, Thin-film silicon solar cell technology, *Prog. Photovolt: Res. Appl*. **12**, 113–142 (2004).

[2] M. A. Green, Solar cells: Operating principles, technology, and system applications, *Prentice Hall* **18**, 1-274 (1982).

[3] A. Shah, P. Torres, R. Tscharner, N. Wyrsch, H. Keppner, Photovoltaic technology: The case for thin-film solar cells**,** *Science* **285,** 692-698 (1999).

[4] P. Lorenz, D. Pinner, T. Seitz, Solar market powers silicon, *The McKinsley Quarterly* **1**, 1-10 (2008).

[5] T. D. Nielsen, C. Cruickshank, S. Foged, J. Thorsen, F. C. Krebs, Business, market and intellectual property analysis of polymer solar cells, *Sol. Energy Mater. Sol. C* **94**, 1553-1571 (2010).

[6] http://www.nanosolar.com/

[7] http://www.konarka.com/

[8] S. Günes, H. Neugebauer, N. S. Sariciftci, Conjugated polymer-based organic solar cells, *Chem. Rev*. **107**, 1324–1338 (2007).

[9] X. Mathew, J. P. Enriquez, A. Romeo, A. N. Tiwari, CdTe/CdS solar cells on flexible substrates, *Sol. Energy* **77**, 831–838 (2004).

[10] Y. Zhou, M. Eckab, M. Kruger, Bulk-heterojunction hybrid solar cells based on colloidal nanocrystals and conjugated polymers, *Energy Environ. Sci*. **3**, 1851–1864 (2010).

[11] A. J. Nozik, Quantum dot solar cells, *Physica E* **14**, 115- 120 (2002).

[12] I. Gur, N. A. Fromer, C. Chen, Antonios G. Kanaras, A. Alivisatos, Hybrid solar cells with prescribed nanoscale morphologies based on hyperbranched semiconductor nanocrystals, *Nano Lett*. **7**, 409–414 (2007).

[13] W. U. Huynh, J. Dittmer, A. P. Alivisatos, Hybrid nanorod-polymer solar cells, *Science* **295**, 2425-2427 (2002).

[14] A. Romeo, M. Arnold, D. L. Bätzner, H. Zogg, A. N. Tiwari, Development of high efficiency flexible CdTe solar cells, *Sol. Energy Mat. Sol. C* **90**, 3407–3415 (2006).

[15] D. L. Bätzner, R. Wendt, A. Romeo, H. Zogg, A. N. Tiwari, Development of efficient and stable back contacts on CdTe/CdS solar cells. *Thin Solid Films* **387**, 151-154 (2001).

[16] D. Cunningham, M. Rubcich, D. Skinner, Cadmium telluride PV module manufacturing at BP Solar, *BP Solar* **10**, 159 -168 (2002).

[17] C. B. Murray, D. J. Norris, M. G. Bawendi, Synthesis and characterization of nearly monodisperse CdE (E = S, Se, Te) semiconductor nanocrystallites, *J. Am. Chem. Soc.* **115**, 8706–8715 (1993).

[18] V. Kloper, R. Osovsky, J. Kolny-Olesiak, A. Sashchiuk, E. Lifshitz, The growth of colloidal cadmium telluride nanocrystal quantum dots in the presence of CdO nanoparticles, *J. Phys. Chem*. 111**, 10336-10341 (2007).**

[19] A. Teichler, R. Eckardt, S. Hoeppener, C. Friebe, J. Perelaer, A. Senes, et al. Combinatorial screening of polymer-fullerene blends for organics solar cells, *Adv. Energy Mater.* **1**, 105-114 (2011).

[20] C. N. Hoth, S. A. Choulis, P. Schilinsky, C. J. Brabec, High photovoltaic performance of inkjet printed polymer:fullerene blends, *Adv. Mater*. **19**, 3973–3978 (2007).

[21] C. N. Hoth, S. A. Choulis, P. Schilinskya, C. J. Brabeca, On the effect of poly(3-hexylthiophene) regioregularity on inkjet printed organic solar cells, *J. Mater. Chem.* **19**, 5398–5404 (2009).

[22] Y. Masumoto, K. Sonobe, Size-dependent energy levels of CdTe quantum dots**,** *Phys. Rev. B* **56**, 9734–9737 (1997).