Final Report for DOE/EERE

Project Title:	Solar upconversion with plasmon-enhanced bimolecular complexes
Project Period:	01/01/12 – 09/30/16
Reporting Period:	01/01/12 – 03/29/15 (*PI maternity leave 9/14/14-12/14/14)
Reporting Frequency:	Quarterly
Submission Date:	11/18/15
Recipient:	Stanford University 496 Lomita Mall Durand Building Room 125 Stanford, CA 94305
Website (if available)	
Award Number:	DE-EE0005331
Awarding Agency:	DOE EERE – Next Generation II
Working Partners:	Bosch, RTC (through 10/01/2014)
Cost-Sharing Partners:	Bosch, RTC (through 10/01/2014)
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Submitted by:	N/A
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DOE Project Manager:	Susan Huang and Lenny Tinker

Signature **Date**

Project Objective:

Upconversion of sub-bandgap photons is a promising approach to exceed the Shockley-Queisser limit in solar technologies. However, due to the low quantum efficiencies and narrow absorption bandwidths of upconverters, existing systems have only led to fractional percent improvements in photovoltaic devices (~0.01%). In this project, we aimed to develop an efficient upconverting material that could improve cell efficiencies by at least one absolute percent. To achieve this goal, we first used thermodynamic calculations to determine cell efficiencies with realistic upconverting materials. Then, we designed, synthesized, and characterized nanoantennas that promise >100x enhancement in both the upconverter absorption cross-section and emissive radiative rate. Concurrently, we optimized the upconverer by designing new ionic and molecular complexes that promise efficient solid-state upconversion. Lastly, with Bosch, we simulated record-efficiency semi-transparent cells that will allow for ready incorporation of our upconverting materials.

While we were not successful in designing record efficiency upconverters during our three years of funding, we gained significant insight into the existing limitations of upconverters and how to best address these challenges. Ongoing work is aimed at addressing these limitations, to make upconversion a cost-competitive solar technology in future years.

Significant Accomplishments:

1. We developed a thermodynamic model to accurately predict the photovoltaic efficiency enhancements that can be expected with upconverting materials. Our calculations show that upconverters can increase cell efficiencies by over one absolute percent (significant for commercial applications) with improved quantum yield. Our results highlight the interplay of absorption and quantum-yield in upconversion, indicate the need for significantly improved upconversion efficiencies compared to existing materials, and provide a platform for optimizing future solar upconverter designs. *(lead: Stanford)*

2. We developed optical models of several state-of-the-art commercial and research thin-film solar cells incorporating upconversion layers. Models were built for amorphous Si, CIGS, GaAs, and Cu_2O cells, including the full cell layer structure and incorporating the interface texture. These features allowed us both accurately predict the cell efficiency improvements with an upconverter, and also optimize the cell design to achieve the maximum benefit from upconversion. Efficiency increases due to upconversion range from 1.5% to 5% (absolute percent), and are higher for higher-efficiency cells, such as GaAs. *(lead: Bosch)*

3. We designed, fabricated, and characterized a metal-dielectric “nanocrescent” that promises >100x enhancements in both the upconverter absorption cross-section and emissive radiative rate. The structures can be fabricated in high-yield at relatively low cost, and form the basis for future upconverting solids. *(lead: Stanford)*

4. We fabricated and characterized large-area (cm-scale) ordered crescent arrays. These arrays can be integrated with an upconverting material in several ways and stamped onto the back of semi-transparent cells; such work will be the subject of on-going research. Importantly for solar applications, the resonance of these arrays is easily tunable simply by changing the etch conditions of the original crescents. This will facilitate incorporation of these arrays with a variety of upconverting materials. *(lead: Stanford)*

5. We developed a new 3D characterization technique, which we term cathodoluminescence (CL) tomography. This technique enables the first three-dimensional visualization of structural, optical, and spectral properties of materials with nanometer-scale resolution. We anticipate that this new imaging technique will enable a deeper understanding of light-matter interactions in almost any inorganic or organic materials system, from probing luminescence centers in upconverting materials with atomic-scale resolution, to visualizing excitonic diffusion in organic photovoltaic devices. *(lead: Stanford)*

6. We used both mechanical strain and chemical dopants to tune the host lattice of lanthanide nanoparticles to modify their upconversion efficiency, demonstrating a 2x increase in upconversion for Yb,Er:NaYF4 nanoparticles. *(lead: Stanford)*

7.We designed a new scheme for broadband upconversion, based on hot-carrier extraction from plasmonic systems. This scheme promises solid-state upconversion efficiencies exceeding 25% (out of a maximum of 50% for a two-photon process). *(lead: Stanford)*

8. Using time-dependent density functional theory (TDDFT) code, we identified strategies to red-shift the absorption of molecular upconverters and to broaden the absorption peak to enable the capture of more photons for lower band gap cells. *(lead: Bosch)*

Deliverables and Go/No Go Criteria:

A go-no go milestone for year 3 was demonstrating at least a 3% absolute increase in quantum yield for upconverting cores with plasmonic nanocrescents over baseline quantum yield of at least 3%. Unfortunately, this milestone was not met, so it was agreed that funding should be used for other projects in year 4.

Patents:

1. J. Dionne, A. Atre, B. Brenny, T. Coenen, A. Polman, Nanoscale optical tomography with cathodoluminescence spectroscopy, The Board of Trustees of the Leland Stanford Junior University, U.S. Pat. Doc. 027,125

Publications/Presentations:

In Press:

1) D. Wu, M. Wisser, A. Salleo, and J. Dionne, “A path upward: New upconversion schemes for improving photovoltaics,” invited perspective for the Roadmap on Optical Energy Conversion, Journal of Optics, in press (2015)
2) G. Naik and J. Dionne, “Photon upconversion with hot carriers in plasmonic systems,” in press, Applied Physics Letters (2015)
3) J. Dionne, A. Baldi, B. Baum, C. S. Ho, V. Jankovic, G. Naik, T. Narayan, J. Scholl, Y. Zhao, “Localized fields, global impact: Industrial applications of resonant plasmonic materials ” *MRS Bulletin*, in press, 2015.
4) J. Dionne, “Lights, Nano, Action! New plasmonic materials and methods to probe nanoscale phenomena” *MRS Bulletin*, 40, 264 (2015).

Published:

5) AC Atre, B Brenny, T Coenen, A Garcia-Etxarri, A Polman, J Dionne, “Nanoscale optical tomography with cathodoluminescence spectroscopy,” Nature Nanotechnology, 10, 429 (2015).
6) M. Wisser, M. Chea, Y. Lin, D. Wu, W. Mao, A. Salleo, J. Dionne “Strain-Induced Modification of Optical Selection Rules in Lanthanide-Based Upconverting Nanoparticles” Nano Letters 15, 1891 (2015)
7) J. A. Briggs, D. M. Wu, A. C. Atre, A. Garcia-Etxarri, J. A. Dionne. “Upconversion for Enhanced Photovoltaics.” Physics of Sustainable Energy III: Using Energy Efficiently and Producing it Renewably. American Institute of Physics, 2015.
8) D. M. Wu, A. Garcia-Etxarri, A. Salleo, J. Dionne. “Plasmon-Enhanced Upconversion”, J Phys Chem Lett 5, 4020-4031 (2014).
9) **J. Briggs**, **A. Atre** and J. Dionne, “Narrow-bandwidth solar upconversion: Case studies of existing systems and generalized fundamental limits,” *Journal of Applied Physics*, 113, 124509 (2013).

Presentations:

10) AC Atre, B Brenny, T Coenen, A Polman, J Dionne, “Nano-optical Tomography & Solar Upconversion: A Multi-dimensional & Multi-photon Approach to Controlling Light-matter Interactions,” Optical Society of America Incubator on the Fundamental Limits of Optical Energy, November 12-14, 2014, Washington, DC
11) AC Atre, B Brenny, T Coenen, A Garcia-Etxarri, A Polman, J Dionne, “Nanoscale optical tomography with cathodoluminescence spectroscopy,” Light-Material Interactions in Energy Conversion, DOE Energy Frontier Research Center Kickoff Meeting, September 22-24, 2014, Caltech, Pasadena, CA

12) AC Atre, B Brenny, T Coenen, A Garcia-Etxarri, A Polman, J Dionne, “Nanoscale optical tomography with cathodoluminescence spectroscopy,” Electron Beam Spectroscopy for Nanophotonics, June 2-4, 2014, Amsterdam, The Netherlands
13) D. M. Wu, S. Sheikholeslami, A. Salleo, J. Dionne. “Solution processed approaches to enhanced upconversion”, RR 8.04, Materials Research Society, Solution synthesis of inroganic functional materials, San Francisco, CA, April 21-25, 2014.
14) AC Atre, B Brenny, T Coenen, A Garcia-Etxarri, A Polman, J Dionne, “Nanoscale optical tomography with cathodoluminescence spectroscopy,” Materials Research Society, April 21-25, 2014, San Francisco, CA
15) J. Dionne, A. Atre, J. Briggs, D. Wu, M. Wisser, A. Salleo, A. Polman, “Giving Photovoltaics the Green Light: Thermodynamic, Electronic, and Photonic Considerations for efficient upconversion” Materials Research Society, December 2013, Boston, MA
16) J. Dionne, A. Atre, J. Briggs, D. Wu, A. Polman, “Photonic principles for enhanced solar upconversion”, Next Generation Photovoltaics, Erlangen, Germany, December 2013
17) A. Atre, A. Garcia-Etxarri, T. Coenen, B. Brenny, A. Polman, J. Dionne, “Nanoscale optical tomography with cathodoluminescence tomography” Next Generation Photovoltaics, Erlangen, Germany, December 2013
18) J. Dionne, “Controlling the interplay of photonics, electronics, and thermodynamics in solar upconversion”, SPIE Defense, Security, and Sensing Baltimore, MD, May 2013
19) J. Briggs, A. Atre, D. Wu, J. Dionne, “Addressing Narrow-band absorption and non-uniform quantum efficiency in upconverting systems” Materials Research Society, San Francisco, CA, April 2013
20) M. Wisser, M. Chea, D. Wu, A. Salleo, J. Dionne, “Pressure Dependence of Lanthanide-based Upconverting Nanomaterials” Materials Research Society, San Francisco, CA, April 2013
21) A. Atre, A. Garcia-Etxarri, T. Coenen, B. Brenny, A. Polman, J. Dionne “Probing visible frequency magnetism in a plasmonic nanoparticle” Materials Research Society, San Francisco, CA April 2013

Jobs Created: Two funded students have graduated. One is now employed at Sunpower, the other is taking a year off before applying for postdoctoral/faculty positions.