Upconverting Electrodes for Improved Solar Energy Conversion

Annual Report, April 29, 2013

A. Investigators
Jennifer Dionne, Assistant Professor of Materials Science and Engineering, Stanford
Alberto Salleo, Associate Professor of Materials Science and Engineering, Stanford
Diane Wu, Graduate student, Chemistry, Stanford University
Michael Wisser, Graduate student, Materials Science, Stanford
Aitzol Garcia, Postdoctoral researcher, Materials Science, Stanford University

B. Abstract
Upconversion of sub-bandgap photons is a promising approach to exceed the Shockley-Queisser limit in solar technologies. Calculations have indicated that ideal upconverter-enhanced single-junction cell efficiencies can exceed 44%, compared to 30% without an upconverter.[1,2] However, wide-spread utilization of upconverters requires significantly improved quantum efficiency and facile device integration into photovoltaic cells. Our team is developing a high-efficiently upconverting electrode that addresses both challenges. This year, we have made continued progress in optimizing the photonic and electronic design parameters to enable high-efficiency upconversion in this electrode.

C. Introduction
The sun provides over 100 peta-Watts of power to the Earth, an amount exceeding the world's energy needs by nearly five orders of magnitude. Unfortunately, current photovoltaic technologies can harvest only a fraction of this energy, since they are unable to utilize photons with energies below the cell bandgap. For example, an ideal single junction solar cell with a bandgap of 1.7 eV wastes approximately 49% of the sun's power because it is not absorbed. Moreover, light with energy just at or above the bandgap is often transmitted as well, due to low absorption efficiencies at these energies. Addressing photovoltaic transmission losses in a scalable, cost-effective manner poses a considerable challenge to high-efficiency, low-cost solar energy conversion.

One very promising approach to address photovoltaic transmission losses is to use an upconverter. In this proposal, we are developing an efficient upconverting material using state-of-the-art synthetic, experimental, and computational techniques. A goal is to create an upconverting electrode that can i) convert low-energy transmitted photons to higher energy photons that can be absorbed the cell, and ii) electrically extract carriers from the cell.

Our proposed upconverting electrode consists of colloidally synthesized nanostructures, including upconverter-doped dielectric nanoparticles and metallic nanowires. While the upconverter-doped nanoparticles allow the cell to absorb below-bandgap sunlight, the metallic nanowires provide direct electrical contact to the cell, allowing efficient carrier extraction. This upconverting electrode can be deposited over large areas by spray-coating, allowing for facile and affordable device integration.
D. Background
The most relevant upconverters for photovoltaic device integration are those that can upconvert near-infrared light to the visible. Currently, we are focusing on upconverters composed of lanthanide dopants – specifically Yb$^{3+}$ and Er$^{3+}$ - in a NaYF$_4$ matrix. As shown in the literature, this material is one of the most efficient near-infrared to visible upconvertors to date [3-5] and several recent advances have been made in the phase, size and shape controlled synthesis of such NaYF$_4$:Yb$^{3+}$/Er$^{3+}$ upconverting nanoparticles.[6,7]

Figure 1 shows our recent calculations of upconverter cell efficiencies for existing NaYF$_4$:Yb$^{3+}$/Er$^{3+}$ upconverting nanoparticles.[8] The lowest upconverter efficiencies in the plot represent recently measured values (0.1-1% for the nanoparticle lanthanide-based system [9]); the higher upconverter efficiencies are meant to reflect the expected results with ongoing work leading to more efficient upconversion.

Though narrow absorption bandwidths and low quantum efficiencies limit existing lanthanide-based upconverters, these calculations highlight the promise of this system. For example, if lanthanide upconversion reaches quantum yields of 20%, 50%, or 100%, it is expected that the efficiency of a 1.7 eV bandgap solar cell would be boosted from 28.2% to 28.8%, 31.3%, or 34.4%, respectively.[8] Our results to date show promise for reaching these efficiencies.

E. Results

E.1. Upconverting Electrode
Our first year of funding enabled us to develop the first upconverting electrode, using a low-cost, scalable spray deposition technique to create hybrid films of colloidally-synthesized upconverting nanoparticles and Ag nanowires. This electrode is characterized by upconversion optical efficiencies that are 4-5 times higher than stand-alone
upconverting materials. Furthermore, the electrical properties of the electrode are competitive with ITO (~6Ω/sq).

These results are very promising for large-area upconverter electrode device integration, but higher increases in upconverted emission were desired. Towards this end, we have been researching techniques to improve upconverter quantum yield.

**E.2. Improving Upconverter Quantum Yield**

Three key factors limit the efficiency of upconverters. They are:

- *The absorption cross-section of the upconverter.* The upconverting material must efficiently absorb incident solar photons.
- *The lifetime of the intermediate state.* Since lanthanide upconversion involves sequential absorption of two photons to create a higher energy photon, the first excited electron must not decay back to the ground state before excitation by the second photon.
- *The radiative rate of emission.* To prevent non-radiative recombination, the upconverter should efficiently and quickly radiate upconverted photons after the second photon excitation.

The first factor can be addressed through photonic engineering, i.e., using plasmonic or nanophotonic resonances to increase the absorption cross-section of the upconverter. The second two factors are influenced strongly by opto-electronic ‘selection rules.’ To modify these selection rules, it is essential to tune the crystal field of the upconverter, for example by modifying the crystalline structure or phase. Our efforts from this year have focused on addressing each factor, as discussed below.

**E.2.1 Improving upconverter absorption cross-sections**

To achieve large upconverter cross-sections, our team has been investigating the upconversion efficiency of single lanthanide upconverting nanoparticles near single metallic nanorods. By carefully determining the ideal nanoparticle-nanowire separation, we can optimize the composition of our composite upconverting electrode.

As seen in Figure 2, we have synthesized colloidal, hexagonal-phase NaYF₄:Yb³⁺/Er³⁺ upconverting nanoparticles with sizes ranging from 30 to 90 nm. We have also synthesized colloidal Au nanorods with longitudinal and transverse plasmon resonances tailored to match the absorption and emission frequencies of the upconverting nanoparticle. The rod geometry enables enhancement of both the absorption and the anti-Stokes shifted emission from an upconverting nanoparticle.

Concurrently, we have developed the experimental techniques to correlate the specific geometry and orientation of the metal rod/upconverting particle pair to its emission spectra and radiative rate. Both the particles and rods are deposited on silicon nitride TEM membranes, enabling correlated optical spectroscopy and high-resolution electron microscopy. Polarization sweeps of the optical input are performed to excite both the longitudinal and transverse modes of the dispersed nanorod. Additionally, lifetime studies of upconversion and photoluminescence emission enable a direct mapping of the local density of states. Our experimental results are then compared with full-field simulations.
of both the field enhancement and the local density of optical states (i.e., lifetime). Preliminary results indicate that emission enhancements are highly dependent on the position of the nanoparticle with respect to the nanorod. Optimized upconverter-nanorod separations (<20nm) are predicted to yield radiative enhancements of $10^{-4}$.

### E.2.2. Controlling upconversion efficiency through modified selection rules

A significant problem in lanthanide-based upconversion is the long radiative lifetime, which is on the order of milliseconds. This long lifetime reflects the orbital symmetry of the upconverted energy levels; because the transition corresponding to upconverted emission is between orbitals of the same symmetry, radiative decay is technically forbidden. While slight distortions in the lanthanide host lattice enable some upconverted emission, this emission is typically very weak (as evidenced in the literature).

To modify the transition rate, our team has developed experimental techniques to dynamically tune the crystal-field and hence modify the orbital symmetry. In particular, we are investigating the efficiency of upconverting luminescence from particles in a diamond anvil cell, where pressures can range up to tens of GPa. By applying pressure to these nanoparticles, we induce distortions in the crystal field and accordingly, modify the electronic orbital symmetry.

This year, we have investigated the pressure dependence of upconverted luminescence from hexagonal-phase, 90-nm NaYF4:Er$^{3+}$/Yb$^{3+}$ nanoparticles. Particles were loaded in a diamond-anvil cell using silicone oil as the pressure medium within a stainless steel gasket. The cell also contained a small ruby, the fluorescence peak of which was used to
determine the pressure within the cell. Ruby fluorescence was achieved via excitation with an Ar-ion laser emitting at 488 nm, while a diode laser emitting at 980 nm was used to excite the nanoparticles. The ruby fluorescence and upconversion intensity were quantified using an optical spectrometer while pressure was varied from ambient up to approximately 25 GPa.

As seen in Figure 3, these particles exhibit a negative correlation between pressure and UCL intensity. Additionally, noticeable shifts in emission peak positions are observed; whereas peaks initially located at 550 nm redshift by as much as 20 meV, peaks at 654 nm exhibit 3-meV blueshifts while the 540-nm emission shows no spectral change. The peaks return to their initial positions upon pressure reduction. A decrease in the average erbium-erbium interionic distance (which would increase the prevalence of cross-relaxation) or a detuning of the energy resonance between the Yb$^{3+}$ sensitizing state and the Er$^{3+}$ emitting states are the two most likely hypotheses explaining the observed decrease in UCL with pressure. The shifts in peak positions and intensities are attributed to changes in the surrounding crystal field environments of the ions due to lattice distortion, and point toward routes of improving the crystal lattice for enhanced upconversion efficiency (i.e., through applied tension).

These fundamental studies will help us design better particles. Indeed, tensile strain can in principle be “engineered-in” the nanoparticles during synthesis by using small dopant atoms or possibly shells surrounding the particles.

**F. Progress and Future Plans**

In order to obtain a complete picture of the interaction between nanorods and upconverting nanoparticles to compare quantitatively to the simulations, we will perform measurements at the Molecular Foundry at Lawrence Berkeley National Laboratory. We have a proposal under consideration to use a calibrated confocal microscope in James...
Schuck’s group (http://foundry.lbl.gov/six/imaging/staff-P._James_Schuck.html ). By combining SEM characterization with upconverting efficiencies measured on the calibrated confocal microscope, we will be able to measure the upconversion enhancement of different known nanorod/nanoparticle configurations.

We will complete the work on the effect of crystal field on upconversion efficiency by studying the changes in upconverting properties of cubic-NaYF₄ nanoparticles. Although these particles have a lower upconversion efficiency of the hexagonal phase, the different lattice symmetry will provide insights into the effect of the nanoenvironment around the emitter and sensitizer ions on their transitions rates.

Our results on the effect of pressure on emission characteristics suggest that putting the particles under tension might increase the upconversion efficiency. In an effort to optimize the host lattice properties for upconversion, we will apply tensile tractions to the nanoparticle surfaces using polymeric fibers, and subsequently measure the changes in upconversion efficiency.

From the materials standpoint, the question remains as to where the dopant ions sit in the NaYF₄ lattice, for instance whether they are substitutional or interstitial and what is their symmetry. These structural properties are likely to play a role in the upconversion efficiency yet they are largely unknown. We will use powder X-ray diffraction, collected at SSRL, to provide us with enough diffraction peaks to conduct a Rietveld refinement and extract the distribution of locations of Er and Yb in the NaYF₄ lattice.

The work described above will allow us to optimize the upconverting nanoparticles and the nanorod/nanoparticle geometry. Ultimately we will make use of these findings when we incorporate optimized nanoparticles and nanorods in spray-coated electrodes.

G. Publications, Patents, and Presentations
• Diane Wu– Poster presentation, Spring MRS meeting 2013 (San Francisco)
• Diane Wu– Oral presentation, SPIE Optics+Photonics general meeting 2012 (San Diego)
• Michael Wisser– Oral presentation, Spring MRS meeting 2013 (San Francisco)
• Michael Wisser– Poster presentation, Lawrence Berkeley National Laboratory
• Michael Wisser, “Effect of pressure on upconverted emission in doped NaYF₄ nanoparticles”, manuscript in preparation
• Diane Wu, “Upconversion enhancement in doped NaYF₄ nanoparticles via plasmonic coupling to metal nanostructures”, manuscript in preparation

References

**Contacts**
jdionne@stanford.edu, asalleo@stanford.edu