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B. Abstract
Upconversion of sub-bandgap photons is a promising approach to exceed the Shockley-Queisser limit in solar technologies. Placed behind a solar cell, upconverting materials convert lower-energy photons transmitted through the cell to higher-energy above-bandgap photons that can then be absorbed by the cell and contribute to photocurrent. Because the upconverter is electrically isolated from the active cell, it need not be current-matched to the cell, nor will it add mid-gap recombination pathways. Calculations by our team and others have indicated that ideal upconverter-enhanced single-junction cell efficiencies can exceed 44% - a significant improvement over the maximum cell efficiency of 30% without an upconverter. However, widespread utilization of upconverters requires significantly improved quantum efficiency and facile device integration into photovoltaic cells. Our team is developing techniques that promise to enable high-efficiency and cost-effective upconverting electrodes that convert infrared to visible light and enable efficient extraction of current from photovoltaic cells.

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 upconverting nanoparticles composed of lanthanide dopants – specifically Yb$^{3+}$ and Er$^{3+}$ – in a NaYF$_4$ matrix. This material can upconvert light of energy $\sim$1.3 eV to 1.9-2.4 eV, a range of upconversion appropriate to enhance light absorption in thin film or organic solar cells with band gaps falling between 1.3 and 1.9 eV. Moreover, this material is one of the most efficient near-infrared to visible upconvertors to date [3-5] and several recent advances have been made in the phase, size and shape controlled synthesis of such NaYF$_4$:Yb$^{3+}$/Er$^{3+}$ upconverting nanoparticles.[6,7]

Figure 1 shows our calculations of upconverter cell efficiencies for 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...
E. Results

While previous upconversion systems have only led to fractional percent improvements in photovoltaic systems (~0.014%), our goal is to synthesize an upconverting electrode capable of improving cells by at least 1 absolute percent. To achieve this goal, we have designed, synthesized, and characterized plasmonic nanoantennas that can significantly increase the absorption cross-section and radiative rate of upconverters. Concurrently, we have optimized the upconverting material by investigating methods to overcome LaPorte selection rules in lanthanide systems.

E.1 Improving upconversion with plasmonic nanoantennas

To achieve large upconverter cross-sections and fast radiative rates, our team has investigated the upconversion efficiency of lanthanide upconverting nanoparticles near metallic nanorods. The nanorods support plasmonic resonances matched to the absorption and emission wavelengths of the upconverter, enabling improved absorption and increased radiative rates. By carefully tuning the nanorod geometry and the nanoparticle-nanorod separation, we can optimize the composition of our composite upconverting electrode.

As seen in Figure 2, we have synthesized large-area monolayer films of lanthanide upconverting nanoparticles and metallic nanorods. Our solution-processed films show enhancements of upconversion emission intensity of 3.5x when the metallic nanorods have absorption resonances matched to the lanthanide nanoparticles.

Using this optimized monolayer film as building block, we have also created three dimensional ‘superlattice-like’ composite structures that incorporate the upconverting nanoparticles, Au nanorods, and silver nanowires for efficient, cost-effective upconverting electrodes. This electrode is characterized by upconversion optical
efficiencies that are twice as high as our rod-UC nanoparticle composite films. Furthermore, the electrical properties of the electrode are competitive with ITO (~6Ω/sq).

E.2 Controlling upconversion efficiency through modified selection rules

The electronic transitions which comprise upconversion in lanthanide-based systems are exclusively between \( f \)-states. As such, these transitions are classically forbidden via the parity selection rule, yielding very slow radiative rates and thereby a decreased likelihood of radiative decay. However, the parity selection rule can be relaxed by distorting or reducing the symmetry of the involved orbitals; achieving such a result in a lanthanide-based system would lead to significantly increased radiative rates and hence increased upconverter efficiency. Our work has addressed the normally-forbidden parity selection rules by engineering the crystal fields surrounding the dopant Yb\(^{3+}\) and Er\(^{3+}\) ions so as to distort the molecular orbitals.

To explore this approach in a thorough and continuous fashion, we first used mechanical compression of the host lattice as a means to tune the crystal fields. Then, we began using synthetic techniques that generate internal strains to reproduce our mechanical measurements.

We studied two different host matrices to confidently ascribe our observed changes to orbital parity effects. These matrices are the cubic (\( \alpha \)) phase of NaYF\(_4\), which is centrosymmetric (meaning the parity selection rule applies), and the hexagonal (\( \beta \)) phase of NaYF\(_4\), which is non-centrosymmetric even without any strain induction; the structures of both materials, as well as transmission electron microscope (TEM) images of the corresponding nanoparticles, are shown in Figure 3.

![Figure 3: a,c) TEM images of the \( \alpha \)-phase and \( \beta \)-phase NaYF\(_4\);Yb,Er nanoparticles, respectively. b,d) Lattice structures of \( \alpha \)- and \( \beta \)-phase NaYF\(_4\);Yb,Er, respectively. Sites which can be occupied by either Na\(^+\) or Y\(^{3+}\) are filled in a random, 1:1 fashion.](image-url)
Briefly, we colloidally synthesized nanoparticles consisting of Yb$^{3+}$ and Er$^{3+}$ ions doped into both NaYF$_4$ lattices. After confirmation of phase purity via x-ray diffraction (XRD) measurements, the sample was then loaded into a diamond anvil cell (DAC) capable of exerting pressures as large as 25 GPa. Upconverted emission and excited-state lifetimes from the nanoparticles were monitored as the pressure inside the cell was incrementally raised to ~25 GPa and subsequently lowered back to ambient conditions. Synchrotron radiation was also used to perform *in situ* pressure-dependent XRD to extract the crystal structure and magnitude of strain induced at each pressure.

Figure 4 summarizes the emission changes for the α-phase NaYF$_4$:Yb,Er particles. We observe a peak in upconversion emission intensity at 2.1 GPa before further compression leads to emission quenching, originating from pressure-induced crystal information. Shown in Figure 4b, this emission maximum corresponds to nearly a 2x increase in integrated intensity. We further observed a reduction in excited-state lifetime (which includes both radiative and nonradiative components) for each emission transition with increasing pressure. Thus, at low pressures we measure an upconversion intensity enhancement alongside a lifetime reduction, the simultaneous occurrences of which definitively verify that we successfully increased the radiative rate in the α-NaYF$_4$:Yb,Er system. To our knowledge, this is the first demonstration of dynamic parity selection rule modulation.

In contrast to the α-phase results, the β-NaYF$_4$:Yb,Er particles exhibited a monotonic decrease in upconversion emission with pressure; these data are shown in Figure 5. Here, because the electronic orbitals are already non-centrosymmetric even before any strain induction, the only effect of compression is pressure-induced defect formation. Thus, the β-phase particles serve as an effective control system to isolate and highlight the beneficial influence of parity modulation.

![Figure 4](image)

*Figure 4:* a) Emission spectra from α-phase NaYF$_4$:Yb,Er upconverting nanoparticles as the applied pressure is raised from 0.4 GPa to 24.3 GPa; each peak is labeled with the corresponding emitting state. b) Integrated upconversion emission intensity as the particles are compressed then decompressed. c) Excited-state lifetimes of the three upconversion transitions throughout the pressure cycle. (Figure adapted from Ref. 9)
To elucidate the lattice distortion necessary to achieve emission modulation, we collected *in situ* XRD patterns. For the α-NaYF₄:Yb,Er particles, these patterns are shown in Figure 6a. The diffraction peaks are observed to shift to larger values of 2θ as the applied pressure is increased, suggesting the decrease in interplanar spacing we would expect with compression. Also apparent is the rapid increase in peak breadth with pressure, indicating the onset of lattice deformation. Additionally, the appearance of new peaks and disappearance of some α-phase peaks beginning near 13 GPa reveals a high-pressure phase transition. Finally, the lattice parameter of the host material can be extracted from the XRD patterns. As shown in Figure 6b, the lattice parameter changes by less than 6% throughout the cycle and by only 1% at the point where maximum upconversion emission is observed (i.e., 2.1 GPa). This result demonstrates the sensitivity of Yb,Er-based upconversion to the geometry of the chosen host lattice as well as the feasibility of reproducing these results using synthetic means.

The analogous data for the β-phase particles are shown in Figure 7. Unlike those of the α-phase particles, the diffraction peaks in Figure 7a show very little irreversible peak broadening, suggesting that any pressure-induced, large-scale deformation is elastic. Additionally, no new peaks arise throughout the cycle, indicating that no phase change occurs. Shown in Figure 7b, the particles experience a maximum strain of approximately 5%. However, at only a 1% induced strain (which occurs around 4 GPa), the upconversion emission from the particles has already decreased to half of its initial intensity. Thus, while no emission enhancement is obtained in the β-phase material, the relation between host structure and upconversion efficiency is just as sensitive and intricate as that observed for the α-phase particles.

*Figure 5: a) Emission spectra from β-phase NaYF₄:Yb,Er upconverting nanoparticles. b) Integrated upconversion emission intensity as the pressure in the DAC is increased then relaxed. c) Excited-state lifetimes of the three upconversion transitions throughout the pressure cycle. (Figure adapted from Ref. 9)*
Motivated by these results, we have been exploring substitutional doping which allows us to induce a similar amount of strain in the α- and β-NaYF₄ lattices without damaging the material (i.e., inducing deformation and/or defect formation). By replacing some fraction of the Y³⁺ ions in the NaYF₄ lattice with an isovalent ion slightly smaller or larger in size, we can induce tensile or compressive strain, respectively, in the nanoparticles.
As a proof of concept, we have synthesized β-phase NaLuF₄:Yb,Er and β-phase NaGdF₄:Yb,Er nanoparticles, which have lattices slightly smaller and larger, respectively, than that of NaYF₄:Yb,Er. We also synthesized intermediate-concentration nanoparticles, including β-phase NaLu₀.₅Gd₀.₃F₄:Yb,Er nanoparticles. So far, XRD confirms that the NaGdF₄:Yb,Er and NaLuF₄:Yb,Er lattices are roughly 1% larger and smaller, respectively, than the NaYF₄:Yb,Er lattice - exactly the result we had hoped to achieve. Figure 8 includes upconversion photographs of these particles (all taken with the same illumination power and particle concentration), indicating the potential to significantly tune upconversion intensity with slight modification of the host lattice. Upon identifying the ideal host lattice, we will incorporate these nanoparticles into the upconverting electrode.

Conclusions
Using a suite of analytic calculations, electrodynamic simulations, and state-of-the-art experimental techniques, our project has: 1) predicted the expected photovoltaic efficiency improvements with realistic upconverters; 2) improved existing upconversion processes by precisely controlling photonic and electronic processes; and 3) developed cost-effective upconverting electrodes that can convert near-infrared light to visible light and extract current from solar cells. Our innovation in upconverter materials design has yielded record-efficiency upconverting layers, though the efficiency of these films are still too small for commercial solar applications. Ongoing work is aimed at boosting near-infrared to visible upconversion efficiencies beyond 10%, and subsequently incorporating these materials into research and commercial solar cells.

G. Publications, Patents, and Presentations
Naik, G., Dionne, J., “Photon Upconversion with Hot Carriers in Plasmonic Systems”, submitted (2105)


References

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