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Improving the efficiency of solar cells by upconverting sunlight using field enhancement from optimized nano structures

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ABSTRACT

Spectral conversion of the sunlight has been proposed as a method for enhancing the efficiency of photovoltaic devices, which are limited in current production by the mismatch between the solar spectrum and the wavelength range for efficient carrier generation. For example, the photo current can be increased by conversion of two low-energy photons (below the band gap of the absorber) to one higher-energy photon (i.e. upconversion). In this paper, we will review our ongoing activities aimed at enhancing such spectral-conversion processes by employing appropriately designed plasmonic nanoparticles. The nanoparticles serve as light-concentrating elements in order to enhance the non-linear upconversion process. From the theoretical side, we approach the optimization of nanoparticles by finite-element modelling of the plasmonic near fields in combination with topological optimization of the particle geometries. Experimentally, the nanostructures are formed by electron-beam lithography on thin films of Er^{3+}-containing transparent materials, foremost TiO_2 made by radio-frequency magnetron sputtering, and layers of chemically synthesized $NaYF_4$ nanoparticles. The properties of the upconverter are measured using a variety of optical methods, including time-resolved luminescence spectroscopy on erbium transitions and spectrally resolved upconversion-yield measurements at ~1500-nm-light excitation. The calculated near-field enhancements are validated using a technique of near-field-enhanced ablation by tunable, ultrashort laser pulses.

1. Introduction

Much of the energy from the Sun is lost in photovoltaic devices because of the spectral mismatch between the sunlight and the absorption region of the solar cell. In the present paper, we will review recent activities in the SunTune project, aimed at improving the efficiency of solar cells by upconverting the low-energy (long-wavelength) part of the sunlight [1–4]. A specific optically active system, embedded in an appropriate host, allows for the absorption of two photons each with energy below the band gap of the absorber and subsequent emission of one photon above the band gap, which is directed into the solar cell for increased current production. Combining upconversion processes with crystalline-silicon-based solar cells raises the theoretical efficiency from ~30% [5] to ~40% [6]. Different material systems have been proposed, and as discussed in greater detail in Ref. [7], the most efficient host materials have a low phonon energy in order to minimize non-radiative (multi-phonon) decay channels, with prominent examples being β-$NaYF_4$, Gd_2O_2S and BaY_2F_8. The active ions are often chosen among the lanthanides, as these offer rich spectra of atomic-like transitions that can be used for upconversion in different spectral regions. Much effort has been dedicated to Er^{3+} in various hosts [8–11], partly because this ion provides upconversion in a spectral region of high importance for crystalline-silicon solar cells.

As upconversion requires merging the energy from two low-energy photons into one photon of higher energy, it inherently exhibits a non-linear dependence on intensity. Since the upconversion process typically occurs with fairly low probability at intensities corresponding to those of sunlight on the surface of the Earth (~1 kW/m^2), different approaches to enhancing the efficiency of upconversion have been examined. In addition to the obvious solution of external concentration,

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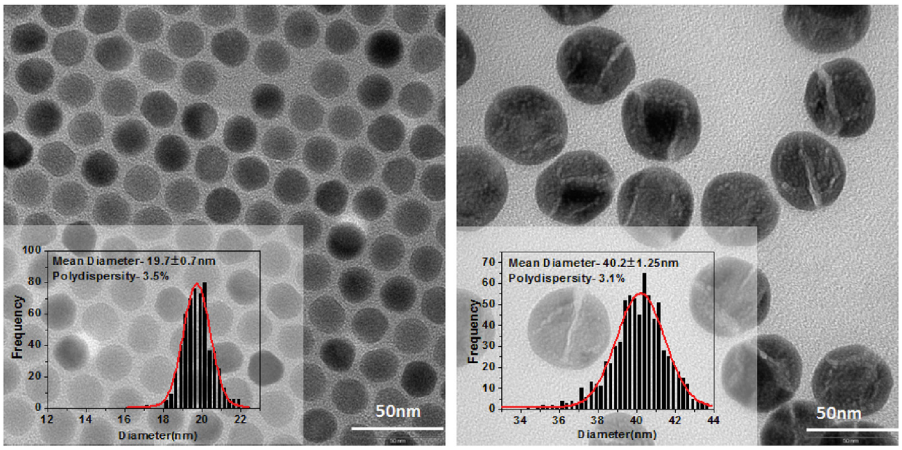

Fig. 1. Er^{3+}-doped β-$NaYF_4$ core nanocrystals of mean diameter 19.7 nm (left panel) and 40.2 nm mean diameter core-shell nanocrystals grown with two-step epitaxial growth of β-$NaLuF_4$ around the core (right panel).

many groups have considered nano-optical engineering as a tool for local field enhancement. An approach based on embedding the up-converter inside a Bragg stack was recently proposed [12], and several groups have employed variations of plasmonic near-field enhancement [13–17]. Along these lines, we recently demonstrated that a single layer of plasmonic gold nanodiscs, produced by electron beam lithography (EBL) on an Er^{3+}-doped TiO_2 film, could enhance the upconversion luminescence by a factor of 7 [1].

The current activities are directed towards optimizing such enhancement factors by employing optimization of the geometry and topology of the nano-particles. The performance of plasmonic systems has previously been tuned by numerically scanning parameters defining the size, shape, and arrangement of different metal nanoparticles [1,18,19] and metallic grating couplers [20]. While the nature of parameter-based search-methods is simple and easy to understand, less freedom is given in the tuning process. In the current project, density-based topology optimization [21] is used to obtain designs tailored to enhance the electric field at wavelengths within the absorption band of erbium, without imposing any unnecessary geometric constraints on the design. Using this method, multiple excitation wavelengths, incidence angles as well as several design realizations are considered simultaneously in the optimization process, aiming for a robust, broadband, optimized nanoparticle design.

2. Approaches to fabrication of materials

The SunTune project focuses on Er^{3+} as the upconverting ion, hosted in two different matrices. Thin films of TiO_2 are very well suited for basic investigations of the upconversion process and the flat samples facilitate nanostructuring by EBL. However, the deposition rates are fairly low, and a better choice for industrial applications are thus up-converting nanoparticles produced by chemical methods.

In the following subsections, we will review the fabrication methods for the two complementary hosts, and we will describe the possibilities and limitations of using EBL for defining the geometry of plasmonic nanoparticles. Finally, in a separate subsection, we will review upconversion applied for organic solar cells.

2.1. Upconverter materials

Fabrication of Er^{3+}-doped TiO_2 thin films was carried out by a radio-frequency magnetron sputtering system from AJA Orion ATC [1,22,23]. The targets were commercially produced (Able Targets) by mixing powders of TiO_2 and Er_2O_3 in desired ratios to achieve 1.3 at% to 6.1 at% of Er^{3+} ions [23]. The deposition was performed under 3 mTorr pressure of Ar with 2% O_2 at 350 °C temperature. The sputtering power was set to 100 W for a steady deposition rate of around 0.1 Å/s to develop films with different thicknesses. Films ranging from 5 nm to a couple of hundred nanometers were fabricated showing surface roughness around 0.5 nm for thinner films and up to 5 nm, as measured by ellipsometry (Sentech SE850 PV Spectroscopic Ellipsometer) and atomic force microscopy (AFM) imaging (Bruker Edge). Cross-sectional images of the films were obtained by transmission electron microscopy (TEM) images (FEI Talos F200X) of samples prepared by focused-ion-beam milling, in order to analyze the compactness and the continuity of the films even for the thinnest samples. The crystallinity of the films was analyzed with X-ray diffraction using Cu Kα radiation, in the Bragg–Brentano geometry (Bruker D8 Discover). Rutherford back-scattering spectrometry was performed on several films to ensure the stoichiometric composition of the host TiO_2 and the concentration of the dopant Er^{3+} ions [23].

As an alternative host, we are investigating Er^{3+}-doped $NaYF_4$ nanoparticles fabricated by chemical synthesis of core-shell (Er:$NaYF_4$-$NaLuF_4$) nanoparticles deposited by drop-cast-assisted spin coating on fused quartz substrates. Synthesis of Er^{3+}-doped β-$NaYF_4$ nanocrystals was performed by a solvo-thermal method with some modifications [24] within a size range of 8.0 ± 0.7 nm to 40 ± 1.4 nm and with Er^{3+}-dopant concentrations in the range of 4 mol % to 20 mol %.

The 20 mol % Er^{3+}-doped β-$NaYF_4$ nanocrystals were used as a core for fabrication of optically inert shells of β-$NaLuF_4$ around the structures by mixed sequential injection and independent injection of precursor concentrations [25–27]. After the reaction, all the samples were washed with ethanol and suspended in toluene solvent at room temperature.

The sizes of the core and core-shell nanocrystals were measured by transmission electron microscopy (Technai G2 Spirit Twins). We synthesized core nanocrystals with diameter of 19.7 ± 0.7 nm and introduced shells of $NaLuF_4$ with thicknesses from 0.8 ± 0.8 nm to 10.3 ± 1.3 nm, see Fig. 1. X-ray diffraction techniques (Rikagu diffractometer) verified the phase and crystalline size of all samples, which was in good agreement with TEM measurements. Inductively-coupled-plasma optical-emission spectroscopy (ICP-OES) showed a 17.2 mol % Er^{3+} concentration with small (± 2 mol %) variations over all samples.

Once the particles were synthesized, drop-cast-assisted spin coating of the structures were performed to fabricate thin films on quartz substrates. The films were prepared by introducing a drop of solution on the quartz substrates and spinning afterwards with a speed of 3500 rpm for 40 s in a spin-coater. The thickness of the films was varied by tuning the concentration of the colloidal solution to form monolayers to multilayers with a couple of hundred of nanometres thickness.

Fig. 2 (a) shows the compact and homogeneous coverage of the