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Strongly enhanced upconversion in trivalent erbium ions by tailored gold nanostructures: toward improving silicon-based solar cells beyond the SQ-limit

Jeppe Christiansen^{a,1}, Joakim Vester-Petersen^{b,1}, Søren Roesgaard^{a,c}, Søren H. Møller^a, Rasmus E. Christiansen^d, Ole Sigmund^d, Søren P. Madsen^b, Peter Balling^{a,c}, Brian Julsgaard^{a,c}

^aDepartment of Physics and Astronomy, Aarhus University, Ny Munkegade 120, DK-8000 Aarhus C, Denmark
 ^bDepartment of Engineering, Aarhus University, Inge Lehmanns Gade 10, DK-8000 Aarhus C, Denmark
 ^cInterdisciplinary Nanoscience Center (iNANO), Aarhus University, Gustav Wieds Vej 14, DK-8000 Aarhus C, Denmark
 ^dDepartment of Mechanical Engineering, DTU, Nils Koppels Allé 404, DK-2800 Kgs. Lyngby, Denmark

Abstract

We investigate the enhancement of 1500 nm to 980 nm upconversion in thin films of erbium-doped TiO₂:Er by tailored nanostructures, which constitutes a promising way to improve the efficiency of silicon-based solar cells. A theoretical model for the upconversion enhancement is developed to asses the applicability of photonic-enhanced upconverters for photovoltaic applications. The geometry of the gold nanostructures is found using topology optimization and fabricated by electron-beam lithography. The fabricated samples show substantial electric-field enhancements inside the upconverting film for varying angles of incidence, polarization, and intensity of the excitation laser in qualitative agreement with the developed model. Inspired by a topology-optimized design, three additional designs are re-optimized using parameter-based optimization to validate the UCL model under different illumination conditions further. The best performing sample is measured at the optimal experimental conditions, which resulted in an unprecedented measured upconversion-enhancement factor of 913 ± 51 at 1.7 W cm⁻². Through investigation of the upconversion intensity-dependence, a simplified enhancement expression is derived, valid for arbitrary excitation intensities. As a result of this, we can determine the concentration factor of the mean electromagnetic energy density, which allows a determination of the upconversion.

Keywords: Upconversion of sub-bandgap photons, effient solar cells, photonic enhancement, topology optimization

1. Introduction

Photon upconversion [1, 2, 3, 4], the photoluminescence process in which the emission wavelength is shorter than the excitation wavelength, has exciting applications in many fields such as bio-imaging [5, 6], anti-counterfeiting [7, 8], and in improving the efficiency of solar cells [9, 10, 11]. Different mechanisms are known to be able to upconvert light, but among the most promising is upconversion from trivalent lanthanide ions embedded in a glass or crystalline host material. The multitude of 4f-4f electronic transitions in the lanthanide series allows for a wide range of upconversion wavelengths, and the real intermediate states provide the opportunity to upconvert incoherent and less intense light. However, the active 4f-4f transitions in lanthanide ions are dipole forbidden, causing low absorption and thus low external quantum efficiency [12], which remains an obstacle, especially for applications in solar cells – the main focus of this investigation.

Several pathways for enhancing the upconversion process have been proposed during the past decade, some of which focus on increasing the absorption by co-doping with a sensitizer [13] while others utilize photonic enhancement through wave-guiding effects and Bragg stacks [14, 15] or through surface-plasmon resonances [16, 17]. Common for all photonic enhancements of lanthanide-based upconversion is that they affect the upconversion process in two ways: First, they can influence the relaxation rates both positively, through enhanced coupling to the radiation field, and negatively, through quenching via ohmic heating in the surrounding material [16, 17]. Second, they can cause an increase in the electric field at the location of the lanthanide ions and hence also increase the absorption, which in turn will improve the upconversion efficiency [16, 17].

This work considers an upconverting material consisting of erbium ions (Er^{3+}) doped into a TiO₂ thin film (TiO₂:Er). The Er³⁺ ions are able to absorb light at wavelengths in the vicinity of 1500 nm [10] and in turn emit upconverted electromagnetic (EM) radiation at 980 nm due to the process sketched in Fig. 1a. Carefully designed periodic gold nanostructures are placed on the surface of the TiO₂:Er film, as sketched in Fig. 1b, in order to couple incident 1500 nm EM radiation into the film and thereby concentrate it. These nanostructures lead to an increased

Email address: brianj@phys.au.dk (Brian Julsgaard)

¹Contributted equally to this work



Figure 1: In a), the excitation process is sketched in two erbium ions. Initial ground-state absorption excites two erbium ions to the intermediate state ${}^{4}I_{13/2}$ indicated with green vertical arrows. In ${}^{4}I_{13/2}$, the two ions can interact with each other via an energy-transferupconversion process illustrated with red curved arrows, which leaves one ion in the ground state and the other in the doubly-excited state: ${}^{4}I_{9/2}$. From here, a two-step relaxation process indicated with curly blue arrows is most likely to occur. First, the ion will predominantly relax to the ${}^{4}I_{11/2}$ by a nonradiative relaxation due to the small energy difference between the ${}^{4}I_{9/2}$ and ${}^{4}I_{11/2}$ levels. Second, the ion will relax to the ground state either nonradiative (loss channel) or radiative by emitting a photon of higher energy than was initially absorbed. In b), the model setup is shown. The gold nanostructure (indicated in black) is placed in a 50 nm-high design domain on top of a 320 nm-thick film of erbium-doped TiO₂ (green) on top of a 0.5 mm SiO₂ substrate (gray). In c), the upconversion-luminescence is exemplified by two spectra showing the measured upconversion luminescence with (red) and without (blue) the gold nanostructure present on the film surface.

emission of upconverted radiation, which is directly measurable, as exemplified in Fig. 1c. Since the wavelength of the upconverted light falls within the absorption range of crystalline silicon solar cells, the upconversion process has the potential to improve the efficiency of such solar cells, and the ability to enhance the upconversion process constitutes an important step toward this goal.

There are two main results of this work: First, it is demonstrated that a well-chosen film geometry, which supports wave-guided modes of 1500 nm EM radiation, in combination with light concentration, facilitated by the well-chosen gold nanostructures, leads to an unprecedented enhancement of the upconversion-luminescence (UCL) yield. Second, it is demonstrated how the numerical calculation of electric fields within the upconverting film in combination with a recently developed analytical model for the upconversion process can account rather accurately for the observed UCL enhancement for varying intensities, incidence angles, and polarization orientations. As a result, the relation between the measured enhancements and the concentration factor of the incident radiation becomes apparent, which enables a justified prediction of the steps required before such upconverting materials can reach efficiencies relevant for improving the performance of solar cells.

2. Theory

The upconversion process has a nonlinear dependence on the excitation intensity, which saturates as the intensity is increased. For two-photon upconversion, the upconversionintensity dependence will saturate from a quadratic dependence in the low-excitation limit toward a linear dependence in the high-excitation limit [18]. In a recent paper [19], we have shown that for a bare upconverting film the intensity dependence of the UCL yield, $Y_{\rm UCL}$, is given by

$$Y_{\text{UCL}} = A \left\{ 1 + \ln \left[\frac{\sqrt{1 + 2I/I_{\text{sat}}} + 1}{2} \right] + \frac{I}{2I_{\text{sat}}} - \sqrt{1 + 2I/I_{\text{sat}}} \right\}$$

$$\equiv Af \left(I/I_{\text{sat}} \right)$$
(1)

where A is an amplitude factor, accounting for material parameters and detection efficiency, and I_{sat} is the excitation intensity where the upconversion process starts to saturate. A good upconverter has a low saturation intensity, exemplified by the fact that an increased absorption cross section decreases the saturation intensity, whereas an increased nonradiative relaxation will increase the saturation intensity [19]. When gold nanostructures are added to the film surface, causing the enhanced UCL, as exemplified in Fig. 1c, the model becomes more involved. However, the UCL enhancement is straightforward to determine experimentally by measuring two spectra with laser excitation on and off the gold nanostructures, as exemplified in Fig. 1c, and subsequently calculating the ratio of the areas under these curves. In other words, the enhancement is a very convenient tool for characterizing the impact of photonic nanostructures, and it is, therefore, worthwhile to seek a theoretical understanding of this enhancement. By combining the above-mentioned analytical model with simulated electric-field distributions inside the film, the theoretical UCL enhancement, $L_{\rm UCL}$, defined as the ratio of $Y_{\rm UCL}$ with and without gold nanostructures present on the film surface, can be calculated as

$$L_{\rm UCL} = \frac{\int_{\mathcal{V}_{\rm UC}} f\left(\frac{|\tilde{\mathbf{E}}|^2}{|\tilde{\mathbf{E}}_{\rm s}|^2} \frac{I}{I_{\rm sat}}\right) \mathrm{d}V}{\int_{\mathcal{V}_{\rm UC}} f\left(\frac{|\tilde{\mathbf{E}}_{\rm b}|^2}{|\tilde{\mathbf{E}}_{\rm s}|^2} \frac{I}{I_{\rm sat}}\right) \mathrm{d}V},\tag{2}$$

where f is the saturation function defined in Eq. (1), and the integration is taken over the volume, \mathcal{V}_{UC} , of the upconverting film below one unit cell of the gold nanostructures, see Fig. 1b. All electric fields in this expression are simulated according to the relevant experimental conditions (i.e., angle of incidence and polarization), and $\dot{\mathbf{E}}$ and $\dot{\mathbf{E}}_{b}$ correspond to the fields in the presence and absence of gold nanostructures, respectively. Due to the linearity of the absorption process, the squared electric field inside the upconverting film is proportional to the intensity, I, of the incoming laser beam and hence only needs to be simulated once. The correct scaling is calibrated by reference to the laser-beam intensity, $I_{\rm sat}$, which drives the upconverter material into saturation, and the corresponding simulated electric field, $\tilde{\mathbf{E}}_{s}$, for the experimental conditions of this calibration measurement. The line over $|\tilde{\mathbf{E}}_{s}|^{2}$ in Eq. (2) denotes volume-averaging over \mathcal{V}_{UC} . Variations in the relaxations rates, e.g., quenching, are neglected since these effects will only be significant for the small population of erbium ions in close vicinity of the gold nanostructure, in agreement with Ref. [20]. A detailed derivation of Eq. (2) is available in Sec. 4.1 of the supporting information, and later in this manuscript, we shall explain how the enhancement relates to the more general description of light concentration and improvement of photovoltaics.

Fig. 1b shows the considered model setup for the simulation of the electric fields. A (x,y)-periodic unit cell consisting of a 320 nm-thick TiO₂:Er film with 50 nm-tall gold nanostructures placed on top, in the design domain. The goal is to obtain nanostructure designs, which enable efficient coupling of the incident light to guided modes in the TiO₂:Er film, and thereby, enhance the light intensity inside the film. The first step in designing such structures is to calculate the electric field accurately. Assuming nonmagnetic, linear, and isotropic materials, the Maxwell equations can be recast into the time-harmonic vector-wave equation [21]

$$\nabla \times (\nabla \times \boldsymbol{E}) - \omega^2 \mu_0 \epsilon(\boldsymbol{r}) \boldsymbol{E} = 0, \qquad (3)$$

where ω is the angular frequency, μ_0 is the free space permeability, and $\epsilon(\mathbf{r})$ is the position-dependent (complex) electric permittivity, with $\mathbf{r} = (x, y, z)$ denoting the spatial position. Eq. (3) is solved numerically using the finite element method [22]. Once the electric field can be calculated, the next step is to optimize the nanostructure design

to enhance the UCL yield, which is numerically evaluated through an appropriate merit function (to be introduced). The approach taken here, known as topology optimization, is to define a material distribution in the design domain and maximize the merit function by optimizing this distribution. This is achieved by changing $\epsilon(\mathbf{r})$ in Eq. (3), through a spatially dependent nonphysical field $\rho \in [0, 1]$ and expressing the permittivity as $\epsilon(\eta(\rho), \kappa(\rho))$ [23], where η and κ are the refractive index and extinction coefficient, respectively. The design domain is divided into equally sized voxels (cubes), and a single ρ -value is assigned to each voxel with a value of $\rho = 0$ corresponding to air and $\rho = 1$ to gold. Since ρ is initially allowed to be continuous, gradient-based optimization algorithms can be used to solve the optimization problem efficiently. Any nonphysical material mixes (where $\rho \neq 0$ and $\rho \neq 1$) are gradually removed over the course of the optimization using standard penalization tools [24, 25, 26], eventually forcing ρ toward either 0 or 1. This introduction outlines the general idea behind topology optimization. For an in-depth presentation of topology optimization applied to nano and microscale electromagnetism, the reader is referred to Ref. [27].

We choose to optimize the upconversion performance in the middle of the excitation regime, between the linear and quadratic intensity dependence, that is, for a cubic dependence on the electric field. The optimization problem is therefore formulated with the merit function [28, 29, 30, 31]

$$\Phi_{i,j} = \frac{\int_{\mathcal{V}_{\mathrm{UC}}} |\tilde{\boldsymbol{E}}^i(\boldsymbol{\rho}, \lambda_j)|^3 \, \mathrm{d}V}{\int_{\mathcal{V}_{\mathrm{UC}}} |\tilde{\boldsymbol{E}}^i_{\mathrm{b}}(\boldsymbol{0}, \lambda_j)|^3 \, \mathrm{d}V},\tag{4}$$

where *i* and *j* parameterize the polarization and wavelength of the incoming field, respectively. In order to promote a design with a reasonable robustness against slight experimental fabrication errors, the optimization problem is formulated as a *min-max* problem such that $i \in s$, p and $\lambda_j \in \{1490 \text{ nm}, 1500 \text{ nm}, 1510 \text{ nm}\}$ are considered simultaneously. By minimizing the worst performance in the set of all realizations, $\{-\Phi_{i,j}\}$, the sensitivity toward variation in polarization and wavelength, or equivalently size variations in the realized nanostructure array, is decreased.

3. Materials and methods

3.1. Numerical calculations

The topology optimization was performed with a voxel size of $(5 \times 5 \times 5)$ nm and with a 2D ρ -field, extruded to a height of 50 nm to ensure the designs can be fabricated using electron-beam lithography (EBL). A unit-cell period of 780 nm was chosen to allow for efficient coupling to waveguide modes in the film [31]. Since the optimization problem is nonconvex, different geometries may emerge for different initial ρ 's. A set of calculations have been made with a random initial material distribution, resulting in a

(smaller) set of converged geometries. These geometries have been numerically characterized, and we have chosen one, which shows robustness toward a change in incidence angle, while still yielding high enhancements. In this procedure, we have on purpose excluded designs, e.g., a simple disk grating, which work better for a very particular wavelength and angle of incidence, since a specific narrowband solution is irrelevant with the perspective of developing devices, which utilize broad-bandwidth solar radiation. A movie showing the course of the topology-optimization process leading to the chosen design is found in the supplementary material, and the chosen design, denoted P780^{*}, can be seen in Fig. 2a.

Inspired by the simple square-ring structure of P780^{*}, we have optimized designs consisting of a square and a ring by tuning the square width, ring radius, and ring thickness using a derivative-free optimization algorithm (Nelder-Mead) to maximize the merit function in Eq. (4), as for P780^{*}. Unit-cell periods of 780 nm, 800 nm, and 1000 nm were chosen for the three designs and all other parameters kept the same as for the topology-optimized sample P780^{*}. The resulting geometries denoted P780, P800, and P1000 can be seen in Fig. 2b-d.

More details of the numerical calculations are available in Sec. 1 of the supporting information.

3.2. Sample fabrication

Starting with a 0.5 mm-SiO_2 substrate, the TiO₂:Er was deposited using a radio-frequency (RF) magnetronsputtering system. The targets were commercially produced from powders of TiO₂ and Er₂O₃ at an erbium concentration of 5.1 at.%. The sputtering process was conducted in an argon atmosphere with 2% oxygen at a pressure of 3 mmHg. The sputtering was done with a fixed RF power of 100 W and with the substrate temperature fixed at 350 °C. These conditions were found to minimize unwanted nonradiative relaxations in the thin films [32]. The deposition time was calibrated to achieve a film thickness of 320 nm.

The gold nanostructures were fabricated by EBL in combination with physical-vapor deposition on an (1.2×1.2) mm area of the thin films to allow upconversion measurements with and without gold nanostructures on the surface, and to minimize the fabrication time. The EBL process was corrected for proximity effects using the procedure described in Ref. [33] to obtain a better resolution. The fabricated gold nanostructure had sidewalls with an inclination angle of 75° at variance to vertical sides (90°) assumed in the topology optimization. For more information on the EBL, the reader is referred to Sec. 2.2 of the supporting information.

3.3. Optical diffraction measurements

After EBL fabrication, the mean unit-cell period of the nanostructures was measured using optical diffraction. The measurements were conducted by transmitting a heliumneon laser onto the nanostructure facing a screen where the created diffraction could be seen. The unit-cell period was then calculated from Bragg's law using: the wavelength of the laser, the distance to the wall, and the distance from the zeroth to the first-order diffraction peak on the wall.

This investigation showed an asymmetry in the horizontal and vertical directions (defined by the SEM image), which leads to ambiguities when measuring the optical properties at different polarization orientations and angles of incidence. We have chosen to present the results with the electric field of the excitation source, parallel to the vertical period of the nanostructures here, while the case with the electric field parallel to the horizontal period can be seen in Fig. S2 in the supporting information.

A thorough explanation of the measurements and results are placed in Sec. 3.1 of the supporting information.

3.4. Upconversion luminescence measurements

The UCL yield was measured by illuminating the samples with 1500 nm laser light and recording the luminescence with an integrated spectrometer and CCD camera. The UCL-enhancement measurements were conducted with the samples placed in an integrating sphere with a diameter of 150 mm to obtain identical collection efficiencies for all used geometries. The UCL yield is determined by integrating across the 980 nm peak shown in Fig. 1c. The enhancement is defined as the ratio of the UCL yield on and off the gold nanostructures.

The UCL enhancements were measured at varying angles of incidence between 0° and 25°, for both s and ppolarization, and for two excitation intensities, 323 ± 97 W cm⁻² and 5.8 ± 0.5 W cm⁻², obtained using two different laser-beam areas. The rather high uncertainty in the high-excitation intensity originates from the laser-beam area, see Sec. 3.3 of the supporting information. The enhancements with the horizontal period parallel to the electric field are shown in Fig. S2 of the supporting information.

To allow comparison with Eq. (2), the saturation intensity of the sample was measured at a 50° angle of incidence and a p-polarized excitation, and by fitting UCL intensitydependence data to Eq. (1), we have determined the corresponding saturation intensity to $I_{\text{sat}} = 20 \pm 6 \,\mathrm{W \, cm^{-2}}$, see data and fit in Fig. S3 of the supporting information.

A thorough account of the UCL measurements, including the determination of the saturation intensity, is placed in Sec. 3.2 of the supporting information.

4. Results

In Fig. 2a, the topology-optimized design is shown in the upper row with the electric-field enhancement and distribution underneath, and a scanning-electron microscope (SEM) image of the EBL produced sample in the lowest row. The samples presented in Fig. 2b-d will be discussed later. The measured UCL enhancements with the vertical period parallel to the electric field are presented in Fig. 3



Figure 2: Optimized and fabricated designs a) P780^{*}, b) P780, c) P800, and d) P1000. In the top row, the unit cell designs are shown with white representing air and black representing gold, with the gray frame indicating the unit-cell boundary. In the middle row, the polarization-averaged energy-density enhancement in the film, $1/2 \sum_{s,p} |\mathbf{E}|^2 / |\mathbf{E}_b|^2$, at $\lambda = 1500 \text{ nm}$ is shown. In the bottom row, SEM pictures of the EBL fabricated gold nanostructures are shown with the scale-bars indicating 1 µm.

with the high and low-intensity cases in the upper and lower panels, respectively. The theoretically predicted upconversion enhancement, $L_{\rm UCL}$, shown as solid curves in Fig. 3, was calculated using Eq. (2). A reasonable qualitative agreement between the measurements and simulations is observed: the order of magnitude, as well as the trend of the variations with incidence angle and polarization, agree mostly. We emphasize that the calculated UCL enhancements are computed from only the simulated electric-field distribution and the experimentally determined saturation intensity. Moreover, we emphasize that the electric-field calculations are made from the ideal unit-cell design shown in the upper row of Fig. 2, which is not reproduced in the actual samples as seen in SEM images in the lower row of Fig. 2. The model is hence only expected to be able to describe the general trend of the UCL enhancement caused by the nanostructures.

A significant UCL enhancement has been found for a wide range of incidence angles, especially for p-polarized excitation, contrary to what is generally reported in the literature, where high UCL enhancements typically are coupled to a strong angular dependence [15, 34]. A broad angular acceptance is essential when considering the end goal of improving photovoltaics by concentrating solar radiation. Noteworthy is also the fact that the enhancements reported here are obtained in thick samples (320 nm) contrary to the case of previously reported high-UCL enhancements, which were recorded from upconverting film thicknesses below 25 nm [34, 35]. Due to the low absorption cross-section of erbium, thick upconverters are essential to achieve adequate external quantum efficiency. From the absorption cross section of erbium [36] and the general concentration level of erbium-doped upconverters the absorption length is on the order of 1 mm at 1500 nm, hence we will need even thicker films to achieve adequate external quantum efficiencies; however, the results reported here provides a starting step on the way to the realization of upconversion enhanced solar cells.



Figure 3: UCL enhancements for all four nanostructure designs at high excitation intensity $323 \,\mathrm{W \, cm^{-2}}$ (upper row), and low intensity $5.8 \,\mathrm{W \, cm^{-2}}$ (lower row). The measurements are plotted by circles, and the calculated values are represented with solid curves. Red is used for the p-polarized case and blue for the s-polarized case.

The three additional designs shown in Fig. 2b-d were parametrically optimized to investigate how the unit-cell period affects the UCL yield, as they exhibit, based on simple grating-coupling condition, an efficient, a moderate, and a weak waveguide coupling at normal incidence. The additional designs also further allow us to validate the UCL model under different illumination conditions. The obtained designs have been fabricated, and their upconversion properties measured similarly to P780^{*}. Looking at the field enhancements in the second row of Fig. 2, it is clear that the field distribution of P780 (and $P780^*$) resembles that of a waveguide mode with field enhancement spanning the entire film. In contrast, P1000 shows a field distribution with distinctly localized enhancements typically attributed to plasmonic resonances. In Fig. 3, large UCL enhancements are observed both experimentally and numerically at normal incidence for P780 (and P780^{*}), while the samples P800 and P1000 show significantly lower values at normal incidence and additionally have their peak efficiency at a nonzero angle of incidence. This observation can be attributed to the phase-matching criteria for coupling the incoming light to the waveguide mode is not exactly met at normal incidence, but instead, have a better match at some nonzero angle [31]. The UCL enhancements in Fig. 3 generally show a reasonable agreement between measured and calculated values in all cases, except in P800 at angles where the numerical data show strong resonances, which may not be present in the fabricated samples or is simply not captured due to the finite number of measuring angles. This generally good agreement between measurements and calculations is further backed by measured and calculated extinction cross sec-

measured at a similar angle of incidence and polarization but with the small laser-beam area taken from the upper panel of Fig. 3b, is included to present all relevant data. The measurements indicate that even stronger enhancements could be measured by decreasing the excitation intensity even more, which is, however, impractical due to the signal-to-noise ratio of the integrating-sphere setup used.

tions available in Fig. S5 of the supporting information.

UCL enhancement by decreasing the excitation intensity

(compare the upper and lower panels of Fig. 3), indicating

that the data are taken under the influence of saturation.

To demonstrate this, we investigate the best-performing

sample, P780, at the optimal conditions, i.e., 1° angle of

incidence and s-polarized excitation, at even lower excita-

tion intensities. The laser power, and hence the intensity,

is attenuated with neutral-density (ND) filters, thus main-

taining the same laser-beam area as was the case for the

results presented in the lower panels of Fig. 3. In this

case, we measured a maximum UCL enhancement factor of 913 ± 51 (see blue open-faced circles in Fig. 4) at an

excitation intensity of $1.7 \,\mathrm{W \, cm^{-2}}$. The blue data point

in Fig. 4 at high intensity and low UCL enhancements,

For all designs, we observe a drastic increase in the

Nevertheless, we have measured UCL enhancement factors between 30 and 913 for the same photonic structure at the same polarization and angle of incidence of the excitation source by merely varying the excitation intensity. This considerable span of enhancement factors demonstrates the arbitrariness in stating a UCL enhancement factor alone without explaining the proper experimental context. We wish to remove this arbitrariness,

once and for all, such that it is possible to make a sensible quantification of the ability of a photonic structure to enhance the UCL. To achieve this, we shall define below a light-concentration factor $C_{\rm ns}$ as the proper quantification of the photonic structure. In order to get there, we remind the reader that the UCL enhancement is defined by the ratio $Y_{\rm UCL}^{\rm on}/Y_{\rm UCL}^{\rm off}$, where we know from Eq. (1) that $Y_{\rm UCL}^{\rm off} \propto f(I/I_{\rm sat})$. It is thus tempting to investigate if we can find a similar relation for the UCL enhancement on the nanostructure. Therefore, we measure carefully the intensity dependence of the $Y_{\rm UCL}$ as exemplified in Fig. 1c, both on and off the gold nanostructures at the same polarization and incidence angle as in the enhancement measurements just described. These intensitydependence measurements are conducted without the use of an integrating sphere to improve the signal-to-noise ratio significantly, and the results are shown in Fig. 4 on (red circles) and off (red squares) the gold nanostructures. For both data sets, the solid black curves correspond to for both data sets, the solid black curves correspond to fits to Eq. (1). In other words, the experimental signals follow the model $Y_{\rm UCL}^{\rm off}(I) = A^{\rm off} f(I/I_{\rm sat}^{\rm off})$ and $Y_{\rm UCL}^{\rm on}(I) =$ $A^{\rm on} f(I/I_{\rm sat}^{\rm on})$, where the fitted saturation intensities are $I_{\rm sat}^{\rm on} = 0.59 \pm 0.05 \,\mathrm{W \, cm^{-2}}$ and $I_{\rm sat}^{\rm off} = 39 \pm 11 \,\mathrm{W \, cm^{-2}}$, re-spectively². The proportionality factors $A^{\rm off}$ and $A^{\rm on}$ depend on, among others, the experimental light collection efficiency, which is not the same on and off the nanostructures due to variations in the light-emission pattern.

While we expect from Ref. [19] that Eq. (1) provides a good description for the intensity-dependence measurement off the nanostructures, it is quite surprising at first glance that a satisfactory fit can also be obtained on the nanostructures. One may be tempted to conclude that the approximation $f(x) \approx f(\overline{x})$ is valid even when the intensity distribution in the film is highly nonuniform under the influence of the nanostructures. However, in Sec. 4.2 of the supporting information, we argue that a better approximation is $f(x) \approx \zeta f(\overline{x}/\zeta)$, where ζ is a measure of the inhomogeneity of the intensity distribution inside the upconverting film and must be well-chosen in the range from 0.38 to 1. This fact explains why the UCL-intensity dependence on the gold nanostructure follow Eq. (1), and Sec. 4.2 of the supporting information also explains that the corresponding on-structure saturation intensity is given by

$$I_{\rm sat}^{\rm on} = I_{\rm sat}^{\rm off} \zeta \cdot \frac{\overline{|\boldsymbol{E}_{\rm b}|^2}}{|\boldsymbol{E}|^2} \equiv I_{\rm sat}^{\rm off} \zeta / C_{\rm ns},\tag{5}$$

where the concentration factor $C_{\rm ns} \equiv \overline{|\mathbf{E}|^2}/\overline{|\mathbf{E}_{\rm b}|^2}$ of the mean EM energy density was defined. Hence, if we can determine the value of ζ , it is possible in turn to calculate $C_{\rm ns}$ as a reliable, intensity-independent measure of the performance of the photonic structure. In order achieve this, we show in Sec. 4.2 of the supporting information that the

above-mentioned success of fitting the red data points in Fig. 4 to the f-function in Eq. (1) immediately leads to the conclusion that the theoretically predicted enhancement in Eq. (2) can be simplified to

$$\tilde{L}_{\rm UCL} = \zeta \frac{f\left(\frac{I}{I_{\rm sat}^{\rm on}}\right)}{f\left(\frac{I}{I_{\rm sat}^{\rm off}}\right)},\tag{6}$$

where $f\left(\frac{I}{I_{\text{sat}}^{\text{off}}}\right)$ and $f\left(\frac{I}{I_{\text{sat}}^{\text{off}}}\right)$ are exactly the functions known from the fitting in Fig. 4. It should be noted that using the same polarization and incidence angle for all data points in Fig. 4 is required for this relation to be valid. Hence, to establish the value of ζ , we only need to calibrate Eq. (6) to the experimental UCL enhancement measurements. The dotted blue curve in Fig. 4 is obtained exactly in this way by fitting Eq. (6) to the blue data points (excluding the outlier) while treating ζ as the only free parameter. With this, we have determined a reasonable ζ -value of 0.48, well within the allowed range. The outlier is measured at such high excitation intensities that deviations from Eq. (1) are expected to occur due to significant excitation to higherenergy states of Er^{3+} not included in the model. This was previously observed for a core-shell NaYF₄:Er sample with a saturation intensity similar to the $I_{\rm sat}^{\rm on}$ stated above [19]. With the ζ -value at hand, we can now determine $C_{\rm ns} = \zeta I_{\rm sat}^{\rm off} / I_{\rm sat}^{\rm on} = 32 \pm 10$. In comparison, the simulated concentration factor is moderately smaller at a value of 23, consistent with the fact that the experimental UCL enhancements are somewhat higher than the simulation for P780 at these experimental conditions, see Fig. 3b.

5. Discussion

Let us use our new understanding to consider the applicability of existing upconverters for solar-cell improvements under realistic excitation conditions, i.e., one sun. The introduced concentration factor, $C_{\rm ns}$, becomes important for two reasons: First, the total-absorption rate of an upconverting film is enhanced exactly by $C_{\rm ns}$ when any kind of photonic enhancement is present, see Eq. (25) in Sec. 4.2 of the supporting information. Second, together with the ζ -parameter the concentration factor can be interpreted as a lowering of the saturation intensity by the factor $\zeta/C_{\rm ns}$, and as a result, the saturation intensity approaching the ideal excitation condition of $I \approx 10I_{\text{sat}}$, suggested in Ref. [19]. Nevertheless, the impressive $C_{\rm ns}$ -factor reported in this article is still not enough for a working solar-cell device with currently available erbium-based upconverters. To arrive at this conclusion, consider that the available radiation energy from the sun in the absorption band of trivalent erbium is about $3 \times 10^{-3} \,\mathrm{W \, cm^{-2}}$. This excitation intensity is roughly four orders of magnitude lower than the desired excitation regime for a TiO₂:Er upconverter. Even if we had chosen the more efficient upconverter system of NaYF₄:Er, with a significantly lower

 $^{^{2}}$ The difference in saturation intensities found off the nanostructure here and the value stated in Sec. 3.4 are due to different polarization and incidence angle of the excitation laser



Figure 4: The UCL enhancement for the P780 sample is plotted against excitation intensity in blue open-faced points. The red circles and squares are intensity-dependence curves measured on and off the gold nanostructure, respectively, for the P780 sample with corresponding fits shown by the black-solid curves. The blue dotted curve showing the theoretically expected enhancement is obtained by fitting the blue data points (excluding the outlier) to Eq. (6) with ζ as the only fitting parameter.

saturation intensity [19], we are still between one and two orders of magnitude short in concentration factor. This estimate is even assuming that we could achieve similar photonic concentration in the NaYF₄, which is highly unlikely due to the smaller refractive index limiting the waveguiding efficiencies [31]. Moreover, not much can be gained from a further photonic concentration since this must come at the expense of lowering the bandwidth of the photonic structure. A naive estimate on the bandwidth lowering is $1500 \text{ nm}/C_{\text{ns}} \approx 50 \text{ nm}$, which is already similar to the absorption bandwidth of Er^{3+} . Instead, new materials could be introduced to improve performance, such as fluorescent concentrators, concentrating the entire available EM radiation from the sun in the range from 1100 nm to 1450 nm into the absorption band of Er^{3+} as proposed in Ref. [37]. However, most desirable would be, also, to find new upconverting materials or hosts with larger absorption cross sections of the active material and ideally with high refractive index ensuring the capability of efficient waveguide coupling. After all, this will lower the saturation intensity as well as increase the total absorption rate, and thus significantly lower the demand for a high concentration of the EM radiation in large upconverting volumes.

6. Conclusion

In conclusion, we have designed and fabricated highly efficient photonic structures for enhancing the upconversion process in thin films of TiO_2 :Er. The dependence of the unit-cell period of the nanostructure is studied through parametrically optimized designs. An unprecedented UCL enhancement factor of 913 ± 51 has been measured at an excitation intensity of $1.7 \,\mathrm{W\,cm^{-2}}$. A theoretical model for the UCL enhancement is developed, which agrees reasonably with the measured UCL enhancements of the fabricated structures. The model further allows for an experimental determination of the concentration of the mean EM energy density in the upconverting film — an essential parameter when assessing the applicability of photonic enhanced upconverters for solar-cell applications.

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