CHARACTERIZATION AND SIMULATION OF UPCONVERSION PROCESSES

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I INTRODUCTION

About 20% of the solar energy is not utilized in silicon solar cells because the photons with energies below the band-gap of silicon are transmitted through the device. Upconversion (UC) of these low energy photons is a promising approach to enhance the efficiency of solar cells. Hexagonal sodium yttrium fluoride (β-$NaYF_4$) doped with trivalent erbium (Er^{3+}), especially with a doping ratio of one erbium ion to four ytterbium ions (β-$NaEr_{0.2}Y_{0.8}F_4$), is known for its very high quantum yield for UC of near infrared (NIR) photons at wavelength around 1523nm. An UC quantum yield of 4.3% at an irradiance of 1370Wm^{-2} was measured by photoluminescence measurements [1]. Due to the non-linearity of the UC processes the UC quantum yield increases with increasing irradiance.

For a better understanding of the UC we developed a rate equation model. With experimentally determined parameters of β-$NaEr_{0.2}Y_{0.8}F_4$ we found a very good agreement between the simulations and the corresponding experiments. In addition, we connected the rate equation model with a simulation of noble metal nanoparticles. The influence of a metal nanoparticle on the upconverter was determined and spatially resolved in three dimensions.

II UPCONVERSION MODEL

The UC model considers ground state absorption (GSA), excited state absorption (ESA), stimulated emission (STE), spontaneous emission (SPE), energy transfer (ET) and multiphonon relaxation (MPR). In the model, the occupation vector $\vec{N}$ and its rate of change $\dot{\vec{N}}$ are described by the following differential equation:

$$\dot{\vec{N}} = (GSA + ESA + STE + SPE + MPR)\vec{N} + ET(\vec{N}, R)$$

In Figure 1 the various processes are shown. Cooperative processes are not considered because they contribute only marginal. A detailed description of the rate equations can be found in [2].

The determination of the simulation parameters constitutes the main challenge. The absorption coefficient α is one of the most important parameters. The Judd-Ofelt theory connects the dynamics of the rare earth ions, or rather the Einstein coefficients, directly with the absorption coefficient [3, 4]. We used the revised Kubelka-Munk theory to determine α of our samples [5, 6]. Since the upconverter β-$NaEr_{0.2}Y_{0.8}F_4$ is a microcrystalline powder strong scattering occurs making the optical measurements challenging. The average optical path length does not correspond to the geometrical sample thickness and is not precisely known. For these reasons and fundamental problems of spectrophotometers with luminescent materials the accuracy of the α is rather low. However, we will see that the Einstein coefficients calculated from the determined α are good input parameters for our model.

The phonon energies of β-$NaYF_4$ are very similar to the LaF_3. Therefore, the parameters for multiphonon relaxation were taken and estimated from [7]. Other parameters were first estimated from literature [8] and subsequently refined within the model.

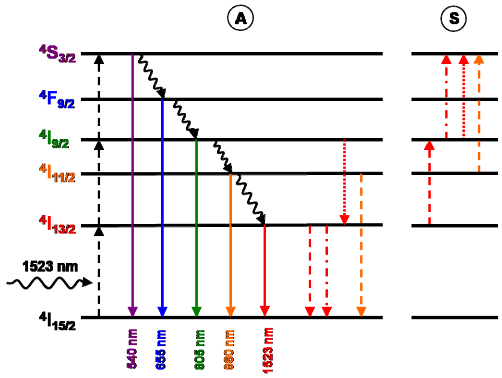


Figure 1: Energy levels of the trivalent erbium in the host crystal $NaYF_4$ with corresponding luminescence wavelengths from the excited states to the ground state (solid arrows). In the rate equation model we assume excitation with a wavelength of 1523 nm. Higher energy levels can be populated by ground state absorption followed by excited state absorption (black dashed arrows). Another possibility to populate higher energy levels is energy transfer (dashed and pointed arrows), where energy is transferred from one ion, the sensitizer (S), to a neighboring second ion, the activator (A). Additionally, we consider multiphonon relaxation to next lower energy levels (waved arrows).

For different irradiances, the occupation of the energy levels was simulated with a rate equation model. The simulated UC quantum yield was calculated by multiplying the occupations of the different energy levels with the corresponding Einstein coefficients. This quantity is expected to be proportional to the internal UC quantum yield. The sum over the simulated UC quantum yields of all considered energy levels above the energy of the band-gap of silicon is in very good agreement to the experiment, as shown in Figure 2.

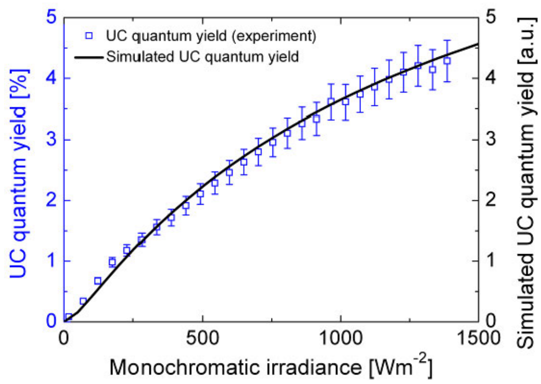


Figure 2: Comparison of the simulation (black line) with the UC quantum yield determined from calibrated photoluminescence measurements (blue squares)[1]. Due to the non-linearity of the UC the UC quantum yield increases with increasing irradiance.

Figure 3 shows the time dependent occupation probability of the considered energy levels without illumination. At the starting point at time t=0s only the highest energy level of our model ($^4S_{3/2}$) was populated. Over time, the other energy levels are populated and depopulated by SPE, MPZ and ET until the ground state is completely occupied. The inset in Figure 3 shows the dynamics in a logarithmic time scale.

To improve the model even further, time resolved photoluminescence measurements are needed to gain a higher accuracy of our model, a better understanding of the UC dynamics and for verification of the Einstein coefficients determined by the revised Kubelka-Munk theory.

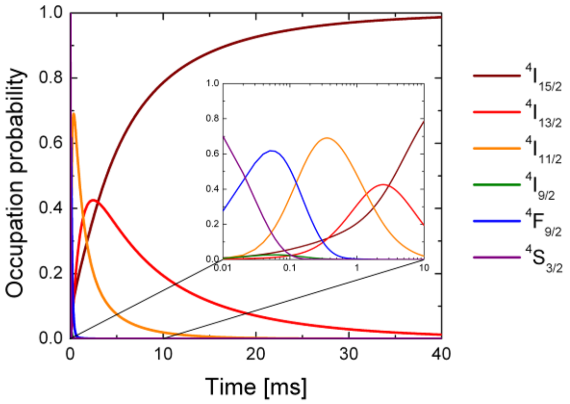
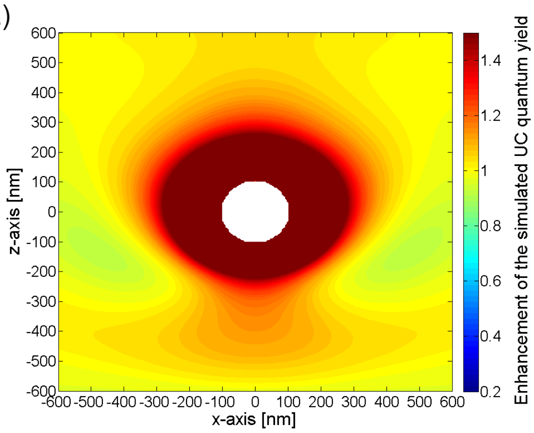


Figure 3: Simulation of population dynamics. At t=0s the $^4S_{3/2}$ levels is completely occupied while the other energy levels are empty. The time dependence was calculated without illumination.

III SIMULATION OF PLASMON ENHANCED UPCONVERSION

The upconversion model was coupled with simulations of plasmon resonances of spherical gold nanoparticles. The electric field scattered by the metal nanoparticle was calculated using Mie theory. The spatial simulation area was a cube with an edge length of six times the diameter of the nanoparticle. The enhancement of the electric field was calculated at every position. This modifies all stimulated processes (GSA, ESA, and STE) because this coupling changes the excitation rates. Additionally, the decay rates of all involved transitions probabilities are locally changed by the nanoparticle. All these impacts were calculated relatively and put in our UC model. We treated the UC like a dipole. Therefore, we had to consider two polarizations of the oscillating dipole: vertical (SPOL) and parallel (PPOL) to the surface of the spherical metal nanoparticle.

a)



b)

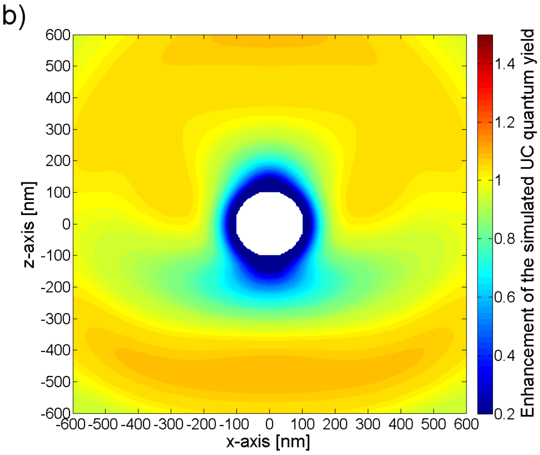


Figure 4: Exemplarily shown is the impact of a spherical gold nanoparticle with a diameter of 200nm on the simulated upconversion quantum yield for SPOL a) and PPOL b). For a clearer presentation the color scale was cut below 0.2 and above 1.5.

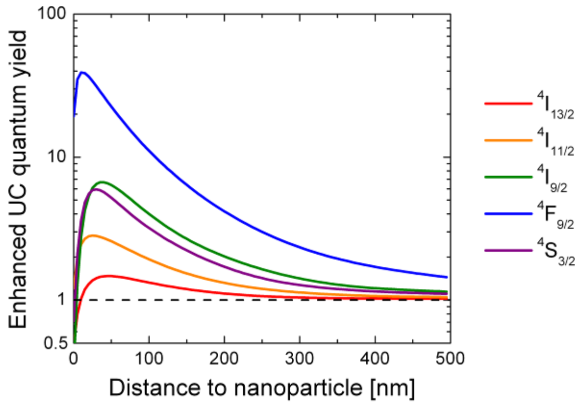


Figure 5: Average enhancement of the simulated UC quantum yield over spherical shells around the metal nanoparticle with defined distance and for the weighted average of SPOL and PPOL. The dashed line shows the case without metal nanoparticle. Overall an enhanced UC quantum yield of all involved energy levels can be determined.

For the energy level $^4I_{11/2}$ the enhancement of the simulated UC quantum yield is shown in Figure 4 for SPOL a) and PPOL b). The cubic simulation area was cut in the middle of the y-axis and the color scale was cut below 0.2 and above 1.5. With SPOL very high enhancements can be reached near the nanoparticle. For SPOL the simulated UC quantum yield is much lower close to the nanoparticle than without nanoparticle. In Figure 5 we calculated the weighted impact of SPOL and PPOL on the simulated UC quantum yield for defined distances to the surface of the nanoparticle. The average was calculated over spherical shells around the nanoparticle. It can be seen that even on average scale around the nanoparticle an increase of more than 40 times may be reached.

Over the total simulation area and the two polarizations the UC quantum yield may be enhanced by over 20% for the energy level $^4F_{9/2}$, but only 3% for the dominating transition from $^4I_{11/2}$ to the ground state. With optimized metal nanoparticles we expect much higher improvements of the upconversion quantum yield.

IV SUMMARY

We have shown that our rate equation model describes the UC dynamics of β-$NaEr_{0.2}Y_{0.8}F_4$ very well. With time resolved measurements the model will be improved and a better understanding of the UC processes generated.

We coupled the UC model with simulations of noble metal nanoparticles and considered changes in the transition probabilities as well as changes of the excitation rates. The effect of the plasmon resonance on the UC quantum yield varies strongly with the location and the polarization of the oscillating dipole. Depending on the location, the UC quantum yield can be highly enhanced by spherical gold nanoparticles. Even for homogenously dispersed upconverter an enhancement up to 20% was calculated.

V ACKNOWLEDGEMENT

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