Enhanced upconversion quantum yield near spherical gold nanoparticles – a comprehensive simulation based analysis

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Abstract: Photon upconversion is promising for many applications. However, the potential of lanthanide doped upconverter materials is typically limited by low absorption coefficients and low upconversion quantum yields (UCQY) under practical irradiance of the excitation. Modifying the photonic environment can strongly enhance the spontaneous emission and therefore also the upconversion luminescence. Additionally, the non-linear nature of the upconversion processes can be exploited by an increased local optical field introduced by photonic or plasmonic structures. In combination, both processes may lead to a strong enhancement of the UCQY at simultaneously lower incident irradiances. Here, we use a comprehensive 3D computation-based approach to investigate how absorption, upconversion luminescence, and UCQY of an upconverter are altered in the vicinity of spherical gold nanoparticles (GNPs). We use Mie theory and electrodynamic theory to compute the properties of GNPs. The parameters obtained in these calculations were used as input parameters in a rate equation model of the upconverter β-NaYF₄: 20% Er³⁺. We consider different diameters of the GNP and determine the behavior of the system as a function of the incident irradiance. Whether the UCQY is increased or actually decreased depends heavily on the position of the upconverter in respect to the GNP. Whereas the upconversion luminescence enhancement reaches a maximum around a distance of 35 nm to the surface of the GNP, we observe strong quenching of the UCQY for distances <40 nm and a UCQY maximum around 125 to 150 nm, in the case of a 300 nm diameter GNP. Hence, the upconverter material needs to be placed at different positions, depending on whether absorption, upconversion luminescence, or UCQY should be maximized. At the optimum position, we determine a maximum UCQY enhancement of 117% for a 300 nm diameter GNP at a low incident irradiance of 0.01 W/cm². As the irradiance increases, the maximum UCQY enhancement decreases to 20% at 1 W/cm². However, this UCQY enhancement translates into a significant improvement of the UCQY from 12.0% to 14.4% absolute.

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1. Introduction

Photon upconversion refers to the non-linear process of converting two or more photons into one photon that carries more energy than each of the previously absorbed ones. Upconversion materials are discussed in the literature for a variety of applications ranging from biological markers [1], to medical therapy [2,3], and spectral conversion [4–7] in photovoltaics. Because of their stability and the ability to convert near infrared photons, frequently lanthanide doped upconverting materials are used [7]. A quite fundamental challenge of lanthanide doped upconverting materials is how to overcome their low absorption coefficient. Another major challenge is how to increase the upconversion quantum yield (UCQY) especially under low incident irradiance. The UCQY is one of the most significant parameters for photon upconversion as it determines the brightness of the upconverter together with the upconverter’s absorptance of incident photons [7]. One possible way to overcome the above limitations lies in photonic manipulation of the involved physical processes. Plasmonic or photonic structures can be designed to perturb the local optical field to exploit the non-

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The linearity of the upconversion processes and to simultaneously enhance desired radiative transitions as well as suppress unwanted radiative transitions.

On the theoretical side, the interaction of electric dipole emitters in the vicinity of metal surfaces has been investigated in detail [8–10] and the influence of noble metal nanoparticles on electric dipole emitters has been studied with simplified rate equations for three level systems [11,12]. Going further, we introduced in Refs [13,14], a more comprehensive computational study on the plasmon enhanced upconversion luminescence, where we combined a rate equation model of the upconverter $\beta$-NaYF$_4$ doped with 20% Er$^{3+}$ under 1523 nm illumination with optical simulations of a spherical gold nanoparticle (GNP) with a diameter of 200 nm. A maximum local enhancement of the upconversion luminescence, i.e. the emission rate of upconverted photons, of $4.3 \times$ was computed for an irradiance of 0.1 W/cm$^2$. Using a similar approach, Herter et al. computed upconversion luminescence enhancements of $3.3 \times$ as well as an UCQY enhanced by a factor of $1.8 \times$ for a dielectric photonic structure using an incident irradiance of 0.02 W/cm$^2$ [15].

Especially metal nanostructures have attracted a lot of interest to enhance the absorption and the spontaneous emission properties of lanthanide-doped materials [16–22]. Experimental investigations reach from hybrid systems of core-shell structures with a gold shell around $\beta$-NaYF$_4$: Er$^{3+}$, Yb$^{3+}$ nanocrystals [23] or inverse structures with a gold core and an ambient upconverting shell [24] to nanostructured metal arrays and metal nanoparticles [18,19,25–27]. Large enhancement factors of the upconversion luminescence of up to $220 \times$ are reported for Er$^{3+}$-doped Al$_2$O$_3$ films on a Ag island array [26]. For hybrid systems as well as nanostructured arrays it has been shown that the luminescence enhancement factors strongly depend on the irradiance [19,23]. For lower irradiances larger upconversion luminescence enhancement factors were determined. On the other hand, strong quenching is expected when the upconverter and the metal are too close. For example, Dulkeith et al. reported strong quenching of the luminescence of a dye molecule in the vicinity of a spherical GNP [28]. Despite all the experimental and theoretical efforts, however, the dynamic of the upconversion processes interacting with plasmonic fields need further elucidation [29]. For example, the question of whether or not metal nanostructures can enhance the efficiency of the upconversion process – more precisely the UCQY defined as the ratio of the number of the emitted high energy photons to the number of absorbed low energy photons – has not been addressed in the literature yet. Often, the reported luminescence enhancements might be attributed solely to a larger portion of absorbed photons and the upconversion process itself could actually be quenched although the sample appears brighter. However, in applications where it is in principle possible to achieve complete absorption by the use of sufficient upconversion material, such as in photovoltaics, the UCQY is the limiting factor for overall device performance.

In this paper, we address this issue and clarify the relations between absorption, upconversion luminescence, and UCQY enhancement. Therefore, we combine a rate equation model to describe the upconversion with optical simulations of spherical GNPs, as described in previous literature [13,14,30]. We determine the enhancement factors for luminescence and absorption in a three-dimensional space around spherical GNPs with different diameters and as a function of the irradiance of the excitation. We calculate the change of the internal UCQY in the presence of the GNP and further evaluate the potential for spherical GNPs to enhance absorption, upconversion luminescence, and/or UCQY.

2. Methods

In the simulations, we model the different transition processes in and between Er$^{3+}$ ions in the vicinity of a spherical GNP. Therefore, we calculated the locally perturbed optical field around GNPs using Mie theory. Next, we used electrodynamic theory (e.g. finite element method using COMSOL software) to determine the modified radiative rates as well as additional non-radiative ones of dipole emitter. The additional non-radiative rates arise due to energy transfer from the dipole emitter to the gold nanoparticle. The modified radiative and additional non-radiative rates were calculated for all relevant transition wavelengths used in...
The upconversion rate equation model, and as a function of the radial distance between the dipole emitter and the GNP. Due to the spherical symmetry one has to consider only radial distances and two polarizations, parallel (PPOL) and perpendicular (SPOL) to the surface of the GNP. Finally, the locally perturbed optical field, the modified radiative rates, and the additional non-radiative rates were implemented into the upconversion rate equation model and the model was solved at every point around the GNP to determine the changes in absorption, upconversion luminescence, and UCQY.

Here, we use the rate equation model established in [30] which describes the upconversion dynamics in hexagonal sodium yttrium tetrafluoride ($\beta$-NaYF$_4$) doped with 20% Er$^{3+}$, which is known to be one of the most efficient upconverter materials for NIR to NIR and NIR to VIS upconversion [7,31–33]. Figure 1 displays the energy levels and transitions considered in this model. Additionally, we take into account two effects of the metal nanoparticle, the perturbed optical local field and the radiative coupling, which are schematically depicted in Fig. 2. We have assumed a refractive index of 1.5 for the surrounding medium in all simulations, which corresponds to the refractive index of the upconverter material. In the following, we shortly outline the model framework. More details can be found in Refs [13,14,30,34].

2.1 Locally altered optical field

Under illumination with a plane wave, oscillations of the conduction electrons are induced in the metal nanoparticle [35]. These oscillations lead to the generation of the near-field. The local optical field around a metal nanoparticle is the result of the near-field generated by the electron oscillation in the nanoparticle and the incident radiation field [36,37]. A locally enhanced optical field can be used to enhance non-linear effects, such as upconversion. The local enhancement factor of the total optical field $\gamma_E(r)$ is determined by the ratio of the square of the optical field at a certain position described by the vector $r$ to the square of the optical field without the metal nanoparticle. The GNP-induced change in the energy density of the optical field $\gamma_E(r)$ can be translated to a change of the spectral energy flux density, i.e. the spectral irradiance $I_{\omega,\text{plasmon}}(\omega,r)$, acting on the upconverter material at the position $r$ as
where \( I_\omega(\omega) \) is the irradiance without the particle. The modified local spectral irradiance \( I_{\text{plasmon}}(\omega, r) \) affects all stimulated processes, which are ground state absorption (GSA), excited state absorption (ESA), and stimulated emission (STE). The latter can be neglected in most cases especially for low incident irradiances. An example of the enhancement factor \( \gamma_E(r) \) in the x-z-plane for a spherical GNP with a diameter of 200 nm under illumination with a plane wave polarized along the x-axis and a wavelength of 1523 nm is depicted in Fig. 2(a). The calculations were performed using Mie theory [13,34].

2.2 Radiative coupling

The Einstein coefficients for spontaneous emission \( A_{if} \) of an emitter are affected by the modified local density of states of the optical field [8,9]. This can be expressed by an enhancement factor \( \gamma_{if,rad}(r) \) for every transition of the \( \text{Er}^{3+} \) from an initial energy level \( i \) to a final energy level \( f \).

Furthermore, non-radiative losses due to the transfer of energy from the lanthanide ions to the metal nanoparticle were considered [8,13,14,34]. These losses can be denoted as additional ohmic losses in the metal nanoparticle [35]. They are particularly strong in the UV as well as visible spectral region and for short distances to the surface of the metal [37]. The enhancement factors for these non-radiative losses \( \gamma_{if,nonrad}(r) \) can be introduced in the upconversion rate equation model by an additional non-radiative de-excitation pathway. A modified \( A_{if} \) can be used to describe this effective de-excitation of level \( i \) via a transition to \( f \) in the rate equation model:

\[
A_{if,plasmon}(r) = A_{if}(\gamma_{if,rad}(r) + \gamma_{if,nonrad}(r)).
\]

The dipole orientation is of great importance for the spontaneous emission rates because the enhancement factors \( \gamma_{if,rad}(r) \) and \( \gamma_{if,nonrad}(r) \) strongly depend on the orientation of the emitting dipole relative to the surface of the GNP, in general either parallel (PPOL) or perpendicular (SPOL). In our understanding, the contributions of PPOL and SPOL have to be geometrically averaged due to a complete loss of the initial polarization between excitation of the \( \text{Er}^{3+} \) and the emission of photons [14]. For spherical GNP geometries the enhancement factors can be averaged over the dipole orientations with relative weights of two times PPOL to one time.
SPOL, as discussed in Refs [13,14], and indicated in Fig. 2(b). The radiative and non-radiative enhancement factors ($\gamma_{\text{rad}}$ and $\gamma_{\text{nonrad}}$) were calculated with electrodynamic theory (e.g. finite element method using COMSOL software), in which the Er$^{3+}$ were treated as electric dipole emitters [10,34,38,39]. The partially magnetic character of the transitions is neglected here because the electromagnetic coupling of mixed electric-magnetic dipole transitions to metal nanostructures is still a very challenging problem, which is beyond the scope of the presented work. Some examples of $\gamma_{\text{rad}}(r)$ and $\gamma_{\text{nonrad}}(r)$ are shown in Fig. 3.

In regard to Förster energy transfer, which is crucial for energy transfer upconversion (ETU) - the most significant upconversion process for lanthanide-doped upconverter materials - there is an ongoing discussion in the literature whether or not the rate of Förster energy transfer is influenced by the local density of photon states [40–47]. Following the argumentation by Dood et al. [45] and the experimental findings by Rabouw et al. [46], no modification of the energy transfer rate due to a locally modified density of photon states due to the presence of the metal nanoparticle was implemented into the model used for the investigations presented in this paper. However, the energy transfer rate also depends on the occupation probability of the involved donor and acceptor energy levels [30], which is inherently included in our upconversion rate equation model. Consequently, we also consider a changed energy transfer rate due to an altered decay rate of the donor or acceptor state, as reported in literature [48].

![Graphs](image.png)

Fig. 3. Change factors of the spontaneous emission and additional non-radiative loss channels due to the presence of the GNP for PPOL and SPOL polarization of the electric dipole emitter as a function of the distance to the GNP with a diameter of 300 nm for (a) 1523 nm and (b) 980 nm dipole emitters. The radiative and non-radiative change factors averaged over the polarizations are shown in (c). An enlargement to better display the values close to 1 is shown in (d). The non-radiative losses are particularly strong at very short distances between the dipole emitter and the GNP. For distances larger than approximately 50 nm the non-radiative loss rates become lower than 10% of the intrinsic spontaneous emission rate.
2.3 Implementation

The change factors $\gamma_L(r)$, $\gamma_{\text{rad}}(r)$, and $\gamma_{\text{nonrad}}(r)$ were implemented in the upconversion model and the rate equations were solved for every position $r$ in the simulation volume as discussed in Refs [13,14]. Here, we consider also different incident irradiances. The modified luminescence $L_{\text{if}}$ (i.e. emission rate of upconverted photons), the absorption $a_{\text{UC}}$ (i.e. photon absorption rate), and the UCQY from an initial energy level $i$ to a final energy level $f$ (UCQY$_{if}$) were determined at every position in the simulation volume. The modified luminescence $L_{\text{if}}$ was calculated by

$$L_{\text{if}}(r,I_0) = N_i(r,I_0) \gamma_{\text{if,rad}}(r) A_{if},$$

using the occupation of the initial energy level $N_i(r,I_0)$ at a certain position $r$ and a certain spectral irradiance $I_0$, the radiative enhancement factor $\gamma_{\text{if,rad}}(r)$, and the corresponding Einstein coefficient $A_{if}$. The local absorption was calculated by

$$a_{\text{UC}}(r,I_0) = \gamma_e(r) \frac{n}{c} I_0 (B_{if} N_i(r,I_0) + B_{if} N_i(r,I_0) + B_{if} N_i(r,I_0)),$$

using the refractive index $n$, the speed of light in vacuum $c$, the local field enhancement factor $\gamma_e(r)$, the spectral irradiance of the incident radiation $I_0$, the Einstein coefficient for stimulated processes $B_{if}$ from energy level $i$ to $f$, and the photon absorption rate in absence of the GNP $a_{\text{UC,0}}$ (see Refs [13,14,30] for details). Finally, the internal UCQY is derived by the ratio of the local emission rate of upconverted photons and photon absorption rate

$$\text{UCQY}_{if}(r,I_0) = \frac{L_{\text{if}}(r,I_0)}{a_{\text{UC}}(r,I_0)}.$$ 

The investigated model systems consist of spherical GNPs with diameters of 100, 140, 200 and 300 nm in the center of a cubic simulation volume with an edge length of 6 times the diameter of the respective spherical GNP but not exceeding 1200 nm, as depicted in Fig. 4(a). The volume was filled homogeneously with the upconverter assuming a refractive index of $\sim 2.3$. The incident irradiance was expected to be constant over the volume because the absorption coefficient of the upconverter is rather small ($\sim 5$ cm$^{-1}$) [30]. Thus virtually no attenuation of the irradiance is expected after a penetration length corresponding to the edge length of the simulation cube. The simulation volume was discretized in (5 nm)$^3$ large voxels with the corresponding position vector $r$. This means that on average 125 Er$^{3+}$ can be found in one voxel for the used Er$^{3+}$ doping of 20%. The incoming plane wave was polarized linearly along the x-axis and had a wavelength of 1523 nm. In the following, the discussion is focused on the model system for the 300 nm diameter spherical GNP because we determined the highest enhancement factors for this system. Similar results were found for the other diameters, which are included in the discussion later.

For every voxel with coordinates $r$ the upconversion rate equation model was solved with the corresponding enhancement factors $\gamma_L(r)$, $\gamma_{\text{rad}}(r)$, and $\gamma_{\text{nonrad}}(r)$ for different incident irradiances $I$. The local enhancement factors for the luminescence $\gamma_{\text{if,rad}}(r,I_0)$, the absorption $\gamma_{\text{Abs}}(r,I_0)$, and the internal UCQY $\gamma_{\text{if,UCQY}}(r,I_0)$ were determined by the ratio of the luminescence $L_{\text{if}}(r,I_0)$, the absorption $a_{\text{UC}}(r,I_0)$, and the internal upconversion quantum yield UCQY$_{if}(r,I_0)$ to the corresponding default values without the effect of the GNP.

3. Results

The local absorptance change factor $\gamma_{\text{Abs}}(r,I_0)$ in the x-z-plane for $y = 0$ nm, as schematically illustrated in Fig. 4(a), is shown in Fig. 4(d) for an irradiance of 0.1 W/cm$^2$ at 1523 nm. Accordingly the $\gamma_{\text{Abs}}(r,I_0)$ for the y-z-plane at $x = 0$ nm, as depicted in Fig. 4(b), and the x-y-plane with $z = 0$ nm, as depicted in Fig. 4(c), are shown in Figs. 4(e) and 4(f). The incident...
light propagates from negative z values to positive z values. Large $\gamma_{\text{Abs}}(r, I_\omega)$ in the direct vicinity of the GNP and along the x-axis are determined. The $\gamma_{\text{Abs}}(r, I_\omega)$ follows the local electric field enhancement $\gamma_{E}(r)$, as depicted in Fig. 2(a).

The luminescence enhancement factors $\gamma_{31,\text{Lum}}(r, I_\omega)$ for an incident irradiance of 0.1 W/cm$^2$ are shown in Figs. 4(g)-4(i) for the dominant upconversion luminescence transition
$^4I_{11/2} \rightarrow ^4I_{15/2}$ with a central emission wavelength of 980 nm. The 980 nm transition $^4I_{11/2} \rightarrow ^4I_{15/2}$ is by far the most important one, as more than 98% of the total UC luminescence originates from this transition [50]. The luminescence enhancement factors in the x-z-plane for the higher transitions $^4I_{9/2} \rightarrow ^4I_{15/2}$, $^4F_{9/2} \rightarrow ^4I_{15/2}$, and $(^2H_{11/2}, ^4S_{3/2}) \rightarrow ^4I_{15/2}$ with the corresponding transition wavelengths 805, 655, and 540 nm are depicted in Figs. 5(a)-5(c).

Similarly to $\gamma_{\text{Abs}}(r, I_\omega)$, large enhancements of $\gamma_{\text{if, Lum}}(r, I_\omega)$ were determined along the x-axis and in particular close to the nanoparticle. However, in the direct vicinity of the GNP the luminescence of the upconverter is strongly quenched by the non-radiative losses introduced by the GNP, which are described by $\gamma_{\text{if, nonrad}}(r)$. While these losses reduce the upconversion luminescence and produce heat in the GNP, they can be a desired effect in certain applications, for example in photo thermal therapy [24,51]. In order to increase the upconversion luminescence, a certain distance has to be ensured between the GNP and the active lanthanide ions of the upconverter to prevent losses due to energy transfer from the lanthanide ions to the metal nanoparticle. For distances shorter than 10 nm the upconversion luminescence is strongly quenched. However, for longer distances the upconversion luminescence can be strongly enhanced. For example, an upconversion luminescence enhancement up to a factor of $4.5 \times$ was computed for the $^4I_{11/2} \rightarrow ^4I_{15/2}$ transition at 980 nm at a distance of 35 nm from a 300 nm diameter GNP using an incident irradiance of 0.1 W/cm².

![Fig. 5. Enhancement factor of the upconversion luminescence $\gamma_{\text{Lum}}$ for a 300 nm diameter GNP and an irradiance of 0.1 W/cm² in the x-z-plane at y = 0 nm for the transitions to the ground state $^1I_{15/2}$ from (a) $^1I_{9/2}$ with 805 nm, (b) $^3F_{9/2}$ with 655 nm, and (c) $(^2H_{11/2}, ^4S_{3/2})$ at 540 nm. (d), (e), and (f) show the corresponding enhancement factors of the upconversion quantum yield $\gamma_{\text{UCQY}}$. Whereas the UCQY of the transitions $^3F_{9/2}$ and the $(^2H_{11/2}, ^4S_{3/2})$ to $^1I_{15/2}$ can be strongly enhanced at a larger distance of $>100$ nm to the GNP, a much weaker enhancement is determined for the $^1I_{9/2}$ transition. This can be mainly attributed to the strong multiphonon relaxation $^1I_{9/2} \rightarrow ^1I_{11/2}$, which remains the dominating de-excitation processes of the $^1I_{9/2}$ population.](image)

Here, we want to emphasize the difference between an enhanced upconversion luminescence / brightness and an enhanced UCQY. The luminescence enhancement may be solely a result of the enhanced absorption and may not be based on a more efficient upconversion process and therefore an enhanced UCQY. Whereas an upconversion
luminescence enhancement is more relevant for brighter nanoprobes in the life sciences, an UCQY enhancement is mandatory for spectral conversion to harvest the solar energy, for example. To address this issue we also determined the local change factors of the UCQY $\gamma_{31,UCQY}(r, I_{\omega})$. Figures 4(j)-4(l) show the $\gamma_{31,UCQY}(r, I_{\omega})$ which reflect the ratio of the absorption and luminescence enhancements in Figs. 4(d)-4(f) and Figs. 4(g)-4(i), respectively.

The hot spots (red regions) in Figs. 4(j)-4(l) clearly show that the internal UCQY of an upconverter can be enhanced significantly in the vicinity of a spherical GNP. However, the spacing between the GNP and the upconverter has to be much larger than the spacing required for an upconversion luminescence enhancement. To achieve a relevant enhancement, precise placing of the upconverter in respect to the metal nanoparticle is crucial, as well as the polarization of the incoming excitation wave. Figure 6 shows line scans along the x-axis at $y = z = 0$ nm, as indicated by the black dashed line in Figs. 4(d), 4(g), and 4(f). Along this line, the largest absorption rate enhancement is found close to the surface of the GNP. This enhancement follows the optical field enhancement. The 980 nm upconversion luminescence is suppressed at the surface but reaches a maximum enhancement factor of $4.5 \times$ at a distance of 35 nm from the GNP. At this distance, however, the UCQY is still reduced by a factor of $0.85 \times$. Further increasing the distance between the upconverter and the GNP enhances the UCQY by up to $1.45 \times$ at a distance of 125 nm, for an incident irradiance of 0.1 W/cm².

The highest determined change factors for the upconversion luminescence $\gamma_{31,Lum}$ and the UCQY $\gamma_{31,UCQY}$ for the dominant transition $^4I_{11/2} \rightarrow ^4I_{15/2}$ at 980 nm are shown in Figs. 7(a) and 7(b) as a function of the irradiance for spherical GNPs with diameters of 100, 140, 200, and 300 nm. The maximum enhancement factors increase for larger diameters of the spherical GNP. We found the highest luminescent and UCQY enhancement factors for the 300 nm GNP. This can be explained by the plasmon resonance, which shifts to longer wavelengths for larger particles, hence reaching further into the NIR wavelengths range and closer to the more relevant transitions of the Er³⁺. The first order plasmon resonance peak shifts from 608 nm for the 100 nm particle to 1235 nm for the 300 nm particle (see Fig. 8). Additionally, in larger particles a higher amount of oscillating electrons can also result in a higher light scattering efficiency and explain the increase of the maximum enhancement factors with GNP size.

Fig. 6. Change factors of absorption, upconversion luminescence, and UCQY as functions of distance between the upconverter and the surface of the GNP along the x-axis for $y = z = 0$ nm. For distances <10 nm, the upconversion luminescence and UCQY are strongly quenched. For larger distances the upconversion luminescence is enhanced, by up to a factor of $4.5 \times$ at a distance of 35 nm. At this distance the UCQY is still quenched but starts to be enhanced at distances >45 nm and peaks with a $\gamma_{31,UCQY}$ of $1.45 \times$ at around 125 nm.
Fig. 7. Highest locally determined values of the enhancement factors for (a) the upconversion luminescence and (b) the UCQY as a function of the diameter of the GNPs for the 980 nm transition $^{4}I_{11/2} \rightarrow ^{4}I_{15/2}$. Higher enhancement factors were computed for larger diameters of the spherical GNPs due to the plasmonic resonance shift to the NIR with increasing size.

Fig. 8. Scattering efficiency $Q_{\text{scat}}$ of spherical gold nanoparticles (GNPs) with different diameters. The resonance peaks shift further into the NIR for larger particles. Furthermore, the first order resonance peak broadens for larger particles. Additionally, higher order resonances at shorter wavelengths are more pronounced for larger gold particles.

The maximum $\gamma_{31,\text{Lum}}(r, \omega)$ as well as $\gamma_{31,\text{UCQY}}(r, \omega)$ strongly decrease with increasing incident irradiance, as shown in Figs. 7(a) and 7(b). While the 980 nm upconversion luminescence can be enhanced by a factor of $8.6 \times$ at 0.01 W/cm$^2$, it can only be increased by a factor of $2.2 \times$ at 1 W/cm$^2$. Accordingly, the $\gamma_{31,\text{UCQY}}(r, \omega)$ values range from $2.2 \times$ to $1.2 \times$ for incident irradiances ranging from 0.01 W/cm$^2$ to 1 W/cm$^2$, respectively. At lower incident irradiances, the UCQY values change more significantly with small variations in the local irradiance. This is a direct result of the steeper slope of the UCQY/irradiance dependence for lower irradiance values. For higher irradiances, saturation occurs and the slope of the UCQY flattens to a constant value. Consequently changes in the local irradiances do not result in strong changes in the UCQY. In other words, the non-linearity of the upconversion processes is more effectively exploited at lower irradiances. The results are also a strong indication of the local optical field enhancement being the major lever for the enhanced upconversion luminescence and UCQY.

Figures 9(a)-9(d) elucidate the potential of the GNPs to enhance the absolute value of the UCQY of $\beta$-NaYF$_4$: 20% Er$^{3+}$ when placed exactly at the hot spots, where the highest enhancement in the UCQY are found. These hot spots are located between $x = 255$ to 270 nm, $z = 105$ to 130 nm, and $y = 0$ nm with corresponding distances of 125 to 150 nm to the...
For increasing incident irradiance values, we observed the highest enhancement factors at larger distances between upconverter and the surface of the GNP. This shift towards larger distances for higher irradiances is related to the higher occupation density of excited states with increasing irradiance, which eventually results in higher energy transfer losses to the metal nanoparticles as well as a diminishing effect of the irradiance enhancement on the UCQY. For increasing irradiance the energy transfer losses are reduced by a larger distance between the lanthanide and the metal nanoparticle, while simultaneously smaller irradiance enhancement factors apply resulting in a lower gain in the UCQY due to the presence of the GNP.

For a 300 nm diameter spherical GNP, the absolute UCQY of β-NaYF₄: 20% Er³⁺ can be enhanced by 20% from an absolute value of 12.0% without GNP to 14.4% with GNP at an irradiance of 1 W/cm². The UCQY of individual transitions can be enhanced from 11.2% to 13.1% for 980 nm emission ($^4I_{11/2} \rightarrow ^4I_{15/2}$), from 0.06% to 0.08% for 805 nm emission ($^4I_{9/2} \rightarrow ^4I_{15/2}$), and 0.56% to 0.83% for 540 nm emission ($^2H_{11/2}, ^4S_{3/2} \rightarrow ^4I_{15/2}$), which corresponds to relative enhancements of 17%, 33%, 58%, and 48%, respectively. At a lower irradiance of 0.1 W/cm² the absolute value of the UCQY integrated over all upconversion emissions considered in our model is enhanced from 4.6% to 7.9%, which corresponds to an increase of 72%. For an irradiance further decreasing to 0.01 W/cm², the UCQY can be enhanced by 117% from an absolute value of 0.66% without GNP to 1.44% with GNP.

All the results above were determined for the optimized case where upconverter particles are placed precisely at spots, for which the highest enhancement in the UCQY is achieved. In many experimental studies, however, the upconverter material is more randomly distributed with respect to the plasmonic structure. Therefore, we also calculated the average enhancement factors of the UCQY at certain distance ranges around the 300 nm diameter GNP and an irradiance of 0.1 W/cm² (see Table 1). Considering the complete simulation volume a γ₃₁,UCQY,avg of 0.95 was calculated, which means that the UCQY remains unchanged with respect to the GNP-free case. In the distance range between 0 nm to 50 nm, the UCQY is strongly quenched to less than 40% of the value without the GNP.

Table 1. Coordinates of the maximum enhancement factor of the UCQY for different GNP diameters and different irradiances of the incident excitation. The values of the enhancement factor are shown in Fig. 6. The coordinate y equals 0 nm in all cases and the values in parentheses are the distances between the surface of the GNP and the upconverter.

| GNP diameter [nm] | 0.01 W/cm² | 0.1 W/cm² | 1 W/cm² |
|-------------------|------------|----------|---------|
|                   | x-coord. [nm] | z-coord. [nm] | x-coord. [nm] | z-coord. [nm] | x-coord. [nm] | z-coord. [nm] |
| 100               | 95 (45)    | 0        | 100 (50) | 0        | 110 (60) | 5         |
| 140               | 125 (55)   | 5        | 130 (60) | 5        | 135 (65) | 10        |
| 200               | 185 (85)   | 30       | 210 (110)| 40       | 295 (195)| 95        |
| 300               | 255 (105)  | 105      | 255 (105)| 105      | 270 (120)| 130       |
Fig. 9. Upconversion quantum yield (UCQY) values calculated for different gold nanoparticle diameters as a function of the incident irradiance. UCQY values are shown for the transition from (a) $^4I_{11/2}$, (b) $^4F_{9/2}$, (c) $^4F_{9/2}$, and (d) $^4S_{3/2} + ^2H_{11/2}$ to the ground state $^4I_{15/2}$ with center emission wavelengths ($\lambda_{em}$) of 980, 805, 655, and 540 nm, respectively. The values were determined at the hot spots and therefore represent the upper limit of the UCQY enhancement in our analysis.

4. Discussion

In general, we think our findings can be transferred on a quantitative level to other upconverter systems, such as bi-doped systems of Yb$^{3+}$ with Er$^{3+}$ or Tm$^{3+}$. Using a bi-doped system, Schietinger et al. performed an experiment that is closest to our simulation approach [18]. They placed 30 nm large $\beta$-NaYF$_4$: Yb$^{3+}$,Er$^{3+}$ upconverter nanoparticles in the vicinity of spherical GNP with 50 nm diameter using an AFM tip. Although the upconverter material and the upconversion process are different from the one in our study, the upconversion luminescence enhancement of $4.7 \times$ for the 540 nm emission and $2.7 \times$ for the 655 nm that they determined are in the same order of magnitude as those presented in this paper. An enhancement of the UCQY, which is - as mentioned before - one of the most desired effects was not investigated by Schietinger et al.

In our analysis, we have been able to find significant enhancements also for the UCQY at certain positions. However, the luminescence and especially the UCQY are reduced at many regions in the simulation volume. When averaged over the complete simulation volume, we observed a decreased UCQY in all considered cases. Consequently, the lanthanide positioning has to be controlled precisely with respect to the metal nanoparticle and the light polarization in order to ensure an enhanced UCQY of the system. This is a major experimental challenge and an obstacle for applications. The same might also be true for the frequently used random distributions of upconverter nanoparticles on different kinds of plasmonic array structures reported in the literature. Nevertheless, as high luminescence enhancement factors have been
reported for more complicated and symmetry breaking structures and for arrays of metal nanostructures as discussed in the introduction, it is possible that some of these structures are more beneficial also for the UCQY.

Furthermore, in our calculations we did not consider light attenuation due to absorption by the spherical GNPs, which will be another loss channel in the system that has to be taken into account when comparing to experimental results and for a high density of GNPs in a sample.

When not aiming for the highest possible enhancement factors, we can identify an interesting region where the upconversion luminescence as well as the UCQY is enhanced while simultaneously the upconverter can be placed with much more tolerance. Additionally, also the polarization dependence is mostly eliminated. In front of the GNP (negative z values) we have found a large volume where the upconversion luminescence as well as the UCQY are strongly enhanced. For the 300 nm diameter GNP this volume spans over the entire considered x-y-plane and along the z-axis from roughly $-450$ to $-300$ nm. The dotted lines in Figs. 4(j)-4(k) illustrate this region. Averaged over this complete volume the upconversion luminescence is enhanced by 56%, the absorption increases by 30%, and the UCQY is enhanced by 19% under 0.1 W/cm$^2$. This means that less upconverter material is needed and the internal UCQY of this smaller quantity of upconversion material is higher, which finally results in a larger external UCQY of the structure. All of these are desired effects and very promising for applications where the UCQY should be enhanced over a large area or volume, as is the case for harvesting of solar energy.

5. Conclusions

In our study, we have observed a maximum of the upconversion luminescence enhancement around a distance of 35 nm to the surface of a GNP with diameter 300 nm, whereas the UCQY was strongly quenched for distances $<40$ nm. However, we have also shown that the UCQY of the efficient upconverter material $\beta$-NaYF$_4$: 20% can be enhanced further by spherical GNPs in certain parts of the volume around the GNPs. Furthermore, we have observed a strong dependence of the highest possible UCQY enhancement factors on the irradiance of the excitation, where lower incident irradiances result in higher enhancement factors.

Compared to the case without the GNP, the high relative increase of the internal UCQY by 117% at 0.01 W/cm$^2$ drops to 20% at 1 W/cm$^2$ for a spherical GNP with a diameter of 300 nm. Consequently, the UCQY is enhanced from an absolute value of 12.0% to 14.4% at an irradiance of 1 W/cm$^2$. The corresponding coordinates for these UCQY enhancement factors as measured from the center of the 300 nm GNP are $x = 255$ nm, $z = 105$ nm, and $y = 0$ nm for 0.01 W/cm$^2$ and $x = 270$ nm, $z = 130$ nm, and $y = 0$ nm for 1 W/cm$^2$. Hence, for higher irradiances we found the maximum enhancement factors at larger distances between the GNP and the upconverter. Furthermore, we found that for the largest absorption enhancement the upconverter should be very close to the GNP, whereas highest luminescence enhancements can be achieved at larger distances. Highest UCQY enhancement requires an even larger distance to the GNP. To achieve highest UCQY enhancement the upconverter has to be placed more than 100 nm away from the GNP to avoid non-radiative losses caused by the presence of the GNP. When aiming for the highest enhancements the upconverter has to be placed very precisely with respect to the metal nanoparticle and the polarization of the incoming light. This implies the need of upconverter nanocrystals and very accurate control of the nanocrystal positioning. However, we have identified a large volume spanning the entire x-y-plane with a height of roughly 150 nm where the upconversion luminescence and the UCQY are both strongly enhanced. This volume is in front of the GNP from z coordinates $-300$ nm to $-450$ nm and hence 150 nm away from the surface of the GNP and we determined average enhancements at 0.1 W/cm$^2$ of 56%, 30%, and 19% for absorption, luminescence, and UCQY, respectively. For large area applications, such as harvesting the solar energy by photovoltaics, the upconverter could be placed in this region, where the upconverter nanomaterial can be placed without challenging alignment and the UCQY enhancement is independent of the polarization of the incident light.
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