Journal of Luminescence 192 (2017) 595–598

Contents lists available at ScienceDirect

Journal of Luminescence

journal homepage: www.elsevier.com/locate/jlumin

Phase-shifted response of plasmonic nanostructures: Implications to luminescence upconversion

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ARTICLE INFO

Keywords:
Surface plasmons
Quantum plasmonics
Luminescence
Fluorescence
Luminescence upconversion

ABSTRACT

We analyze the dynamics of a quantum dipole emitter (QDE) illuminated by a resonant electromagnetic field and placed close to a metal nanostructure, whose response to the incident field is phase shifted by $3\pi/2$ ($-\pi/2$). It is found that, due to the phase shift in a field scattered by the nanostructure (and acting on the QDE along with the incident field), QDE dynamics is characterized by a fast QDE transition to the excited state followed by relaxation to a stable superposition (of the excited and ground states) with a close to 1 probability of the QDE to be found in the excited state. We further argue that this effect can advantageously be used for luminescence upconversion enhancement when being realized for a lower excited state in the energy transfer upconversion process since, by largely eliminating the radiative relaxation channel, the probability of excitation transfer will be increased.

1. Introduction

Frequency conversion of infrared radiation into visible light, i.e., frequency upconversion, in the process of luminescence (rather than being based on nonlinear susceptibility) has recently started to receive renewed attention due to a considerable progress in the development of upconversion nanomaterials and various configurations ensuring luminescence upconversion (LUC) enhancement. Typically, LUC features low conversion efficiency due to small absorption cross-section for infrared light and a slow rate of energy transfer, impeding thereby various LUC applications, for example when using diffuse sunlight or in imaging tissue samples. One can exploit unique properties of surface plasmons (SPs), in which electromagnetic fields are coupled to collective oscillations of free electrons in metals, to boost up the LUC efficiency by strongly enhancing local electromagnetic fields at the site of an upconverting emitter placed near plasmonic nanostructures [1]. Recently, various scenarios for the realization of SP-based LUC enhancement have been overviewed concentrating on the energy-transfer upconversion mechanism, in which the LUC occurs through the population of and subsequent energy transfer between real intermediate states [2].

The origin of SP-based LUC enhancement can fundamentally be attributed to the following two major effects: (*i*) an increased excitation rate of an radiation absorbing ion due to the SP-mediated local field enhancement, and (*ii*) an increased emission rate when a plasmonic nanostructure acts as an optical nanoantenna influencing the emitter's radiative decay rate [1,2]. In many systems, both factors play important roles in enhancing the LUC intensity, being extremely sensitive to the relative spectral position of excitation and emission spectra of the fluorophores with respect to the SP resonance frequency of the metal nanostructure. At the same time, a number of experiments reveal features that are difficult to explain by considering only these two effects. Thus a nonmonotonic dependence of the LUC enhancement on the excitation power density was observed with LUC nanocrystals being coupled to gold island films [3]. Presence of the apparent maximum in the LUC enhancement factor dependence cannot be explained by saturation of the LUC emission with respect to the excitation power. It was also observed that the LUC enhancement factor obtained when changing the separation of LUC nanocrystals and metal nanoparticles is sharply peaking up at a certain separation [4,5]. Contrary to what might be expected, the substantial LUC enhancement is observed even in the cases, where the presence of metal nanoparticles slightly reduces or without reduction in the LUC decay time [4,6,7]. Overall, even though the fact that the LUC emission can be enhanced by plasmonic nanostructures is well established, there can be yet unknown factors at play contributing to the LUC enhancement [2,3,6].

Among LUC nanoparticles, $NaYF_4$ crystals doped with lanthanide ions Yb^{3+} and Er^{3+} remain one of the most efficient LUC materials. These nanocrystals provide an opportunity to study LUC in the green and red spectral regions (centered at 540 and 650 nm, respectively)

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http://dx.doi.org/10.1016/j.jlumin.2017.07.047
Received 19 January 2017; Received in revised form 11 June 2017; Accepted 26 July 2017
Available online 27 July 2017

when being illuminated with 980-nm-wavelength light. Yb^{3+} ions absorb most of the excitation light due to a larger absorption cross section and much higher density than Er^{3+} ions [8,9]. The absorbed energy is then transferred to Er^{3+} ions (in two consecutive steps) and emitted eventually in the visible region of the spectrum. Consequently, by prolonging the lifetime of the Yb^{3+} ion excited state one would increase the probability of energy transfer to the Er^{3+} ion and thereby enhance LUC.

Here, we establish the conditions under which the metal nanostructure enables the formation of a stable excited state of a two-level system. In our analysis, we pay particular attention to the fact that a metal nanostructure not only enhances local electromagnetic fields but also responds with a phase shift with respect to the driving field. It is shown that, in the case of the $3\pi/2$ phase shift, the dynamics of a quantum dipole emitter (QDE) placed nearby the metal nanostructure is characterized by a fast QDE transition to the excited state followed by relaxation to a stable superposition (of the excited and ground states) with a close to 1 probability of the QDE to be found in the excited state. We further argue that this effect can advantageously be used for LUC enhancement since, by largely eliminating the radiative relaxation channel, the probability of excitation transfer will be increased.

Our present analysis is based on the previous work where we established, using a quantum coherent state representation of a localized SP (LSP) supported by a metal nanoparticle, that the LSP excitation resonantly coupled to the QDE (excited by a short laser pulse) changes dramatically the QDE relaxation dynamics [10]. The main physical consequence of these changes is that the exponential decay of the QDE excited state changes to step-like behavior with the radiation emission reaching its maximum with a significant delay in time. It should be noted that the well-known effect of fluorescence enhancement due to reduction in the lifetime of the QDE excited state [11] is preserved also in this description [10,12]. The key feature of the resonant LSP-QDE coupling is that the particle polarizability becomes purely imaginary, so its response exhibits the $\pi/2$ phase shift. In this case, the QDE relaxation process can be considered as the self-stimulated QDE transition from the excited into ground state because it is stimulated by the LSP field (excited by the QDE dipole) acting back on the QDE [12]. The ensuing lifetime reduction together with the Purcell effect [13] results in considerable amplification of the fluorescence [10]. Here we analyze the QDE-nanostructure configuration illuminated with the cw (continuous wave) resonant optical field and characterized by the $3\pi/2$ phase shift in the nanostructure response. We show that, due to the latter feature, the lifetime of a lower excited state (in the energy transfer LUC process) can be prolonged, increasing thereby the probability of the excitation transfer and contributing to the LUC enhancement. In fact, significantly prolonged (due to the presence of gold nanoparticles) lifetimes of Yb^{3+} ions have been experimentally observed along with the considerable LUC enhancement [14]. In principle, the exact composition of a plasmonic nanostructure is not important as long as it is characterized by the $3\pi/2$ (or $-\pi/2$) phase shift in its response to the external electromagnetic field. We chose here a conical metal tip (CMT) that can provide both field enhancement and the $-\pi/2$ phase shift in a wide range of tip parameters [15]. Importantly, tip-enhanced LUC (by a factor of $\sim$ 10) has been measured with a gold-coated tip approaching a single Yb^{3+}-Er^{3+}-co-doped $NaYF_4$ nanoparticle [7].

2. Theory

The system under consideration is schematically presented in Fig. 1 and consists of a two-level QDE [3,4] and a CMT. It is assumed that the external pump laser illuminates the CMT-QDE configuration at the frequency ω_0 of the QDE transition (Fig. 1). In the presence of the pump field, the QDE wave function can be represented as the coherent superposition state:

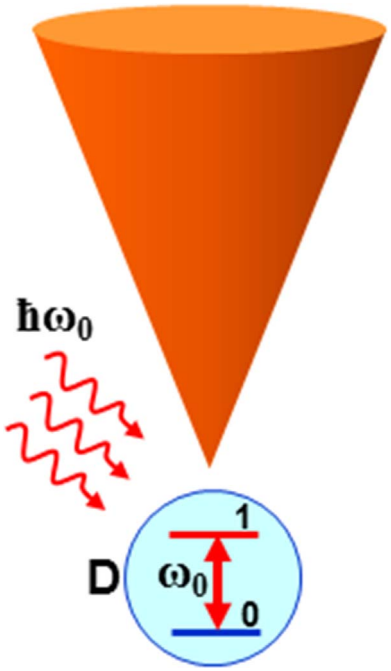

Fig. 1. Schematic of a considered system with a QDE denoted as **D** and placed near a generic CMT, indicating the QDE energetic levels D1 and D0.

$$\Psi(t) = a_1(t)\phi_1 \exp\left(-\frac{i}{\hbar}E_1 t\right) + a_0(t)\phi_0 \exp\left(-\frac{i}{\hbar}E_0 t\right), \tag{1}$$

where ϕ_1 and ϕ_0 are the wave functions of the QDE in states D1 and D0, characterized by the energies E_1 and E_0, respectively, while $a_1(t)$ and $a_0(t)$ are the corresponding (time-dependent) probability amplitudes describing the transition D1 → D0. The QDE dipole moment is thereby given by

$$\overrightarrow{D}(t) = a_1 a_0^* \overrightarrow{d_{10}} \exp(-i\omega_0 t) + a_0 a_1^* \overrightarrow{d_{10}^*} \exp(i\omega_0 t), \tag{2}$$

with the asterisk denoting the complex conjugate, and $\overrightarrow{d_{10}} = \int \phi_1 e\vec{r}\phi_0^* dV$ and $\hbar\omega_0 = E_1 - E_0$ being the dipole moment and energy of the transition D1 → D0, respectively.

In the considered configuration, the QDE and CMT are subjected not only to the incoming laser field but also to the fields produced and scattered by the QDE and CMT, respectively. The CMT provides thereby feedback to the QDE by scattering back the field generated by the QDE dipole moment [Eq. (2)]. We assume that the QDE is located at the CMT axis at the distance $r << \lambda$ from the CMT extremity (λ is the wavelength corresponding to the frequency ω_0), and that its transition dipole moment is directed along the CMT axis. Then the feedback field acting on the QDE is also polarized along the CMT axis and can be written in the form:

$$\overrightarrow{E}_{fb} = \frac{A(r)\overrightarrow{d_{10}} a_1 a_0^*}{4\pi\varepsilon_0 r^3} \exp(-i\omega_0 t) + c.\,c.\,, \tag{3}$$

where $A(r)$ is a parameter describing the CMT enhanced response to the incoming field. We consider the situation when this parameter is negative imaginary (i.e., the response phase is $-\pi/2$ phase-shifted [15]): $A = -iA_0\ ,\quad A_0 > 0$. This feedback field acts on the QDE together with the resonant external field, which is also enhanced by the CMT:

$$\overrightarrow{E_{ex}} = \overrightarrow{E_0}[1 + A(r)]e^{-i\omega_{10}t} + c.\,c.\,, \tag{4}$$

where $\overrightarrow{E_0}$ is the amplitude of the incoming laser field, which is also polarized along the CMT axis.

Using the time-dependent Schrödinger equation for a two-level system in the total driving field $\overrightarrow{E_{fb}} + \overrightarrow{E_{ex}}$ [Eqs. (3) and (4)] and carrying out standard manipulations, one obtains the following system of

two coupled equations for the probability amplitudes:

$$\frac{da_0}{dt} = \mu a_1^* a_1 a_0 + \beta a_1, \tag{5a}$$

$$\frac{da_1}{dt} = -\mu a_0^* a_0 a_1 - \beta^* a_0, \tag{5b}$$

where μ characterizes the CMT feedback on the QDE, i.e., the QDE-CMT coupling:

$$\mu = \frac{A_0 \left|\vec{d}_{10}\right|^2}{4\pi\hbar\varepsilon_0 r^3}, \tag{6}$$

and β characterizes the strength of the external resonant field acting (together with the CMT response) on the QDE:

$$\beta = -[i + A_0]\frac{\vec{d}_{10}\vec{E}_0^*}{\hbar}. \tag{7}$$

It is worth noting that μ and β are essentially the Rabi frequencies for the optical (acting on the QDE) fields given by Eqs. (3) and (4), respectively. Combining Eqs. (5a) and (5b) results in

$$a_1\frac{da_0}{dt} - a_0\frac{da_1}{dt} = \mu a_1 a_0 + \beta a_1^2 + \beta^* a_0^2, \tag{8}$$

along with $|a_0|^2 + |a_1|^2 = \text{const}$.

One of the most important assumptions made in our theoretical framework is related to the strength μ of the QDE-CMT coupling, which should ensure considerably faster QDE dynamics than that associated with the QDE relaxation rate γ_0 in free space: $\mu >> \gamma_0$. Their ratio can now be evaluated using Eq. (6) and the Weisskopf-Wigner result as follows:

$$\eta = \frac{\mu}{\gamma_0} = \frac{3A_0}{4}\left(\frac{\lambda}{2\pi r}\right)^3. \tag{9}$$

We now make use of relevant simulations [15] indicating that a gold CMT with the cone angle $\theta = 18^\circ$ and the tip radius of 2 nm would produce, when being illuminated at the wavelength of 1 μm, the field phase-shifted by -π/2 and enhanced by $A_0 \approx 3.3$ at the distance $r = 10$ nm from the CMT apex. Substituting these numbers into Eq. (9) results in the ratio $\eta \approx 10^4$, a value that justifies the aforementioned assumption.

The process described here can be affected by non-radiative decay of the excited state D1, i.e., quenching caused by the QDE coupling to high-order lossy LSP modes [16], that would shorten its lifetime. On the other hand, this quenching is strongly distance dependent with the distance being compared to the radius of a metal nanosphere [11,16], and its influence can be disregarded in the considered configuration with the QDE-CMT separation (10 nm) being much larger than the CMT radius (2 nm). It should also be noted that the wavelength range, in which the gold CMT response is expected to be properly phase-shifted (by -π/2), is sufficiently away from the gold absorption band [15].

3. Results and discussion

The most important parameter of the considered configuration is $\alpha = 2|\beta|/\mu$, which characterizes the balance between the QDE coupling to the external laser field (along with its reflection by the CMT) and the QDE-CMT coupling. The case with $\alpha = 1$ corresponds to the situation when the QDE field acting on the CMT is close in magnitude to the external laser field (assuming that $A_0 >> 1$). It can be shown that the normalized time τ of the considered dynamics is given by $\tau = \mu t = \eta\gamma_0 t$ and the probability of finding the QDE in the excited state D1:

$$|a_1(\tau)|^2 = \frac{\left[1 + \sqrt{1-\alpha^2}\coth(0.5\tau\sqrt{1-\alpha^2} - \sigma)\right]^2}{\alpha^2 + \left[1 + \sqrt{1-\alpha^2}\coth(0.5\tau\sqrt{1-\alpha^2} - \sigma)\right]^2}, \tag{10}$$

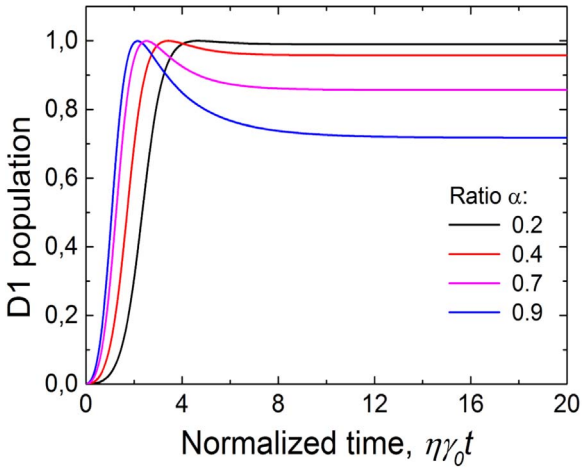

Fig. 2. Temporal evolution of the probability of finding the QDE in the excited state D1 for various levels of the QDE-CMT coupling with respect to the QDE coupling to the external resonant laser field for low pump fields ($\alpha < 1$).

with $\sigma = \tanh^{-1}(\sqrt{1-\alpha^2})$ for the initial condition $|a_1(0)| = 0$. In the case of a relatively weak external field and significant QDE-CMT coupling, i.e., when $\alpha < 1$, the QDE dynamics is characterized by fast transition to a stable superposition with a relatively large probability of finding the QDE in the excited state D1 (Fig. 2). It is seen that this configuration is especially advantageous for weak pump fields ($\alpha << 1$), since the QDE superposition between the excited and the ground state reduces quickly to that dominated by the excited state. The main physical reason for such a behavior is related to the -π/2 phase shift in the CMT response, the phase shift that prevents the QDE transition from the excited state D1 back to the ground state D0 (Fig. 1).

The QDE transition from the excited to ground state would slow down also for other phase shifts close to -π/2. In general, the effect of slowing down this transition would be apparent, although to a lesser degree, once the imaginary part of the CMT response is negative. A nonzero real part of the CMT response would, on the other hand, result in the shift of the QDE resonance frequency [17]. Regarding the local field enhancement factor A_0 produced by the CMT response when the phase shift reaches -π/2, it is approximately two times smaller than its maximum value [15]. Note that, as seen from Eqs. (6) and (7), the crucial parameter $\alpha = 2|\beta|/\mu$ becomes independent on A_0 once it is large enough ($A_0 >> 1$). At the same time, the transition time constant, $\mu^{-1} = (\eta\gamma_0)^{-1}$, is inversely proportional to A_0 and proportional to the third power of the QDE-CMT separation [Eq. (6)], while the CMT response phase does not depend on the distance to the CMT within the electrostatic approximation [15]. From the viewpoint of speeding up the transition process, it is therefore advantageous to position the QDE sufficiently close to the CMT, but not too close that the quenching discussed above would become significant.

When increasing the power of the incident laser beam, one can realize the situation with the QDE coupling to the external field dominating over the QDE-CMP coupling, i.e., with $\alpha > 1$. In this case, the system enters the regime of Rabi oscillations with progressively smaller periods (Fig. 3). It is seen that the Rabi oscillations in this case differ considerably from harmonic oscillations, a feature that indicates the existence of high harmonics of the Rabi frequency. At any rate, the CMT facilitates fast transition from the ground state D0 to the excited state D1 and slows down the transition back to the ground state due to the -π/2 phase shift in the CMT response, influencing thereby strongly the QDE-CMT coupling process.

One of the important consequences of the considered QDE dynamics for LUC configurations is the possibility to substantially increase the QDE (excited state) lifetime, a feature that can advantageously be used for LUC enhancement when being realized for a lower excited state in

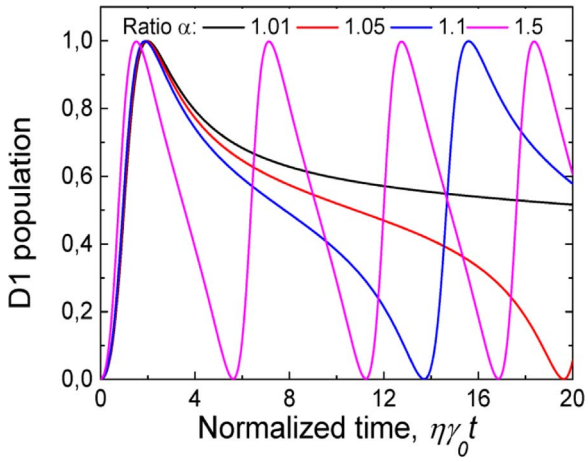

Fig. 3. Temporal evolution of the probability of finding the QDE in the excited state D1 for various levels of the QDE-CMT coupling with respect to the QDE coupling to the external resonant laser field for strong pump fields ($\alpha > 1$).

the energy transfer LUC process since, by largely eliminating the radiative relaxation channel, the probability of excitation transfer will be increased. Here it should be emphasized that the phase shift in the metal nanoparticle response is strongly frequency dependent, especially in the vicinity of resonance. Therefore, the phase shift can be close to $-\pi/2$ at the resonant frequency of the D1 → D0 transition (which increases the excited state lifetime and thus the probability of excitation transfer), while being significantly different from that at the upconversion frequency. Generally speaking, if (by ingenious design) the $+\pi/2$ phase shift in the metal nanostructure response would simultaneously be realized at the upconversion frequency, the efficiency of the upconversion process will additionally be enhanced since, with this phase shift, the nanostructure accelerates the transition from the excited state to the ground state, increasing thereby the luminescence transition rate [10,12]. In principle, the resonantly enhanced CMT response at shorter wavelengths [15] can increase the contribution of sequential absorption by Er^{3+} ions, influencing the LUC dynamics, but our consideration is quite general and can be applied to different metal nanostructures with different absorption band profiles. Finally, we would like to remark that the influence of a metal nanoparticle on the energy transfer between two ions participating in the LUC is usually neglected due to a relatively small distance between these ions. The metal nanoparticle may however have an effect on the energy transfer process if the distances between the ions and nanoparticle are of the same order. Then, a special superposition state might be formed that effectively eliminates the response [18].

The analysis conducted in the work reveals a new feature in the CMT influence on the LUC process besides the local field enhancement – the influence of the CMT response phase that can slow down the QDE transition from the excited to ground state, increasing thereby the efficiency of non-radiative excitation transfer. This influence is especially pronounced for weak external (pump) fields when the QDE superposition reduces quickly to that dominated by the excited state (Fig. 2). It should be expected that the phase-shifted CMT response would also counteract other electromagnetic disturbances, such as electromagnetic vacuum fields, stimulating the QDE transition back to the ground state at the time scale of the QDE lifetime in vacuum. In the regime of strong pump fields, the asymmetry in population oscillations caused by the phase-shifted CMT response results in decreasing the excited state decay (Fig. 3), although to a lesser extent than in the case of weak pump fields. Finally, it should be emphasized that the optimum conditions for realizing the LUC enhancement due to the considered physical mechanism are achieved when the external (pump) field polarization and the QDE transition dipole moment are oriented along the CMT axis.

In the process of LUC with optically pumped Yb^{3+} ions transferring their energy to Er^{3+} ions, the former can be suggested for implementation of the considered here process. One can therefore suggest to directly observe the phenomenon discussed in this work by measuring the emission rate of optically pumped Yb^{3+} ions in the absence of Er^{3+} ions. It should be emphasized that the connection between significantly prolonged lifetimes of Yb^{3+} ions and considerable LUC enhancement has been experimentally established in the experiments studying LUC in the presence of gold nanoparticles [14], although without discussing the physical reasons that might be involved in the lifetime increase.

4. Conclusions

Our current and previous [10,12] studies of the QDE dynamics in the presence of plasmonic nanostructures reveal the importance of the phase delay in the nanostructure response to an external field. In the particular case of the resonant cw optical pump field and the $3\pi/2$ ($-\pi/2$) phase shift of the metal nanostructure placed nearby, the QDE dynamics is characterized by a fast QDE transition to the excited state where the QDE remain for a long time due to the properly phase-shifted feedback from the nanostructure. We further argue that this effect can advantageously be used for LUC enhancement since, by largely eliminating the radiative relaxation channel, the probability of excitation transfer will be increased. As a final remark, we would like to point out that, due to the similarity of physical processes involved, a similar effect would also contribute to enhancing the Raman scattering.

Acknowledgment

The authors gratefully acknowledge financial support for this work from the European Research Council, Grant No. 341054 (PLAQNAP) and from the University of Southern Denmark (project SDU 2020).

References

[1] Di M. Wu, A. García-Etxarri, A. Salleo, J.A. Dionne, Plasmon-enhanced upconversion, J. Phys. Chem. Lett. 5 (2014) 4020–4031.
[2] W. Park, D. Lu, S. Ahn, Plasmon enhancement of luminescence upconversion, Chem. Soc. Rev. 44 (2015) 2940–2962.
[3] H. Zhang, D. Xu, Y. Huang, X. Duan, Highly spectral dependent enhancement of upconversion emission with sputtered gold island films, Chem. Commun. 47 (2011) 979–981.
[4] A.L. Feng, M.L. You, L. Tian, S. Singamaneni, M. Liu, Z. Duan, T.J. Lu, F. Xu, Distance-dependent plasmon-enhanced fluorescence of upconversion nanoparticles using polyelectrolyte multilayers as tunable spacers, Sci. Rep. 5 (2015) 7779.
[5] M. Saboktakin, X. Ye, U.K. Chettiar, N. Engheta, C.B. Murray, C.R. Kagan, Metal-enhanced upconversion luminescence tunable through metal nanoparticle – nanophosphor separation, ACS Nano 6 (2012) 8758–8766.
[6] W. Deng, L. Sudheendra, J. Zhao, J. Fu, D. Jin, I.M. Kennedy, E.M. Goldys, Upconversion in $NaYF_4$:Yb,Er nanoparticles amplified by metal nanostructures, Nanotechnology 22 (2011) 325604.
[7] G. Chen, C. Ding, E. Wu, B. Wu, P. Chen, X. Ci, Y. Liu, J. Qiu, H. Zeng, Tip-enhanced upconversion luminescence in $Yb^{3+}-Er^{3+}$ codoped $NaYF_4$ nanocrystals, J. Phys. Chem. C 119 (2015) 22604–22610.
[8] C. Strohhöfer, A. Polman, Relationship between gain and Yb^{3+} concentration in $Er^{3+}-Yb^{3+}$ doped waveguide amplifiers, J. Appl. Phys. 90 (2001) 4314–4320.
[9] J.F. Suyver, A. Aebischer, S. García-Revilla, P. Gerner, H.U. Güdel, Anomalous power dependence of sensitized upconversion luminescence, Phys. Rev. B 71 (2005) 125123.
[10] K.V. Nerkararyan, S.I. Bozhevolnyi, Relaxation dynamics of a quantum emitter resonantly coupled to a coherent state of a localized surface plasmon, Faraday Discuss. 178 (2015) 295–306.
[11] P. Anger, P. Bharadwaj, L. Novotny, Enhancement and quenching of single-molecule fluorescence, Phys. Rev. Lett. 96 (2006) 113002.
[12] K.V. Nerkararyan, S.I. Bozhevolnyi, Relaxation dynamics of a quantum emitter resonantly coupled to a metal nanoparticle, Opt. Lett. 36 (2014) 1617–1620.
[13] E.M. Purcell, Spontaneous emission probabilities at radio frequencies, Phys. Rev. 69 (1946) 681.
[14] N. Liu, W. Qin, G. Qin, T. Jiang, D. Zhao, Highly plasmon-enhanced upconversion emissions from Au@β-$NaYF_4$:Yb,Tm hybrid nanostructures, Chem. Commun. 47 (2011) 7671–7673.
[15] A. Pors, K.V. Nerkararyan, S.I. Bozhevolnyi, Scaling in light scattering by sharp conical metal tips, Opt. Lett. 39 (2014) 3308–3311.
[16] G. Sun, J.B. Khurgin, C.C. Yang, Impact of high-order surface plasmon modes of metal nanoparticles on enhancement of optical emission, Appl. Phys. Lett. 95 (2009) 171103.
[17] O.L. Malta, Emission yield enhancement for non-linear processes in the presence of small metallic particles, Phys. Lett. 144A (1986) 198–200.
[18] K.V. Nerkararyan, S.I. Bozhevolnyi, Entanglement of two qubits mediated by a localized surface plasmon, Phys. Rev. B 92 (2015) 045410.