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Modeling the influence of silver nanoparticles on the f–f luminescence of the EuEDTA complex in the polyvinylpirrolidone polymer



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1. Introduction

The influence of metallic nanoparticles, mainly silver and gold, on the luminescence processes of lanthanide compounds has been considerably investigated, both by experimental and theoretical means, once it may be of high interest to the field of plasmonics [1–13]. Collective correlated electron excitation modes in materials are well known, mainly in metals, and it is also known that even isolated molecules show this property [14]. From Mie theory to Drude's model, applied to metals, the electromagnetic classical view has been very successful in describing collective charges light absorption processes. From microwave to hard X-ray absorption by the water molecule (in liquid phase), the measured spectrum shows at 21 eV a peak assigned to a collective plasmon absorption of the water molecule electrons [14]. Other well-known processes, like interband and exciton transitions, and photo-ionization may eventually accompany these collective (plasmon) absorptions.

Mie resonances (plasmon resonances) require the presence of a radiation field and a material source in which the absorbing, emitting or scattering species feel the enormous gradient field nearby the resonance source. Historically the subject has initiated with the Surface Enhancement Raman Scattering (SERS) in which Raman scattering cross sections may be enhanced by factors as large as 10⁶ [15]. In composite bulk materials with nanoparticles (NPs) [2] not only plasmon absorption, but also scattering by the

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ABSTRACT

A theoretical analysis on experimental results previously obtained on the influence of silver nanoparticles in a polyvinylpirrolidone (PVP) polymer film containing a trivalent europium complex with EDTA ligand is made. Depending on the excitation source (at 393 nm with a xenon lamp or at 532 nm with a focused diode laser) the characteristic Eu³⁺ luminescence is observed to be enhanced by factors between 5 and 50. The theoretical analysis presumes a migration process of the EuEDTA complex units towards the silver nanoparticles, during the synthesis of the composite samples, and subsequently the treatment of the competition between local high field gradient effects and Eu³⁺ ion to the silver nanoparticles energy transfer successfully accounts for the observed luminescence enhancement factors. © 2015 Elsevier B.V. All rights reserved.

> NPs are important to describe their effects on the luminescence of nearby molecular species, depending on the NPs nature, concentration and filling factor. Moreover, and decisive, non-radiative energy transfer from the absorbing or emitting molecular species (in our case a trivalent europium complex) nearby the NPsmay be quite operative, and a balance between these effects has to be considered, which may eventually lead actually to luminescence quenching [16-19].

> In an idealized model system of metallic NPs distribution in a host medium, a theoretical approach to these effects has been developed based on the NP's polarizability and the fact that the NP's plasmon lifetime is extremely short. Therefore, non-radiative energy transfer from the NP to the absorbing/emitting species is not operative [5].

> In the present work, we have used the theoretical predictions for the local high field gradient effects discussed in Refs. [2–5] to rationalize the unusual luminescence enhancement effects observed by Reisfeld et al. [20] in a EuEDTA coordination compound contained in a composite medium constituted by the polyvinylpyrrolidone (PVP) polymer and silver NPs (Ag-NPs). Indeed, this is the most evident opportunity to apply our theory and the present approach might be a useful tool to predict a way to get 4f–4f luminescence enhancement through plasmon resonances from metallic nanoparticles, which is certainly of potential interest in the photonic field. The preparation, characterization, measurements and theoretical analyses of several similar composite systems are already in progress in our group in a joint project with our colleagues from the University of São Paulo. Differently from the SERS effect, in the case of linear one-photon absorption



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and emission processes, even if non-radiative energy transfer to the NPs is negligible, luminescence enhancement factors orders of magnitude smaller than 10^6 are expected. For lanthanide compounds (trivalent europium, Eu³⁺, is commonly used) in the presence of Ag-NPs, 4f-4f luminescence enhancement factors around 5, or less, may be considered typical values. However, depending on the excitation conditions, in the work by Reisfeld et al. [20] a trivalent europium luminescence enhancement by a factor of 50 is observed. The viscosity of the PVP polymer is very low. Thus, it is plausible that in the synthesis of the composite medium the EuEDTA complex units undergo a migration process towards the Ag-NPs. Here we will present and discuss the successful theoretical results that are obtained when this migration process is assumed.

2. Theoretical

We begin by considering the energy level diagram shown in Fig. 1 and follow the theoretical approaches developed in Refs. [2–5]. In the absence of metallic NPs the integrated emission intensity (power) from level 2 to level 1 reads:

$$I_{12} = \hbar \omega_{12} W_{12} N \eta_2 \tag{1}$$

where $\hbar\omega_{12}$ is the peak transition energy, W_{12} is the spontaneous transition rate from level 2 to level 1, *N* is the total number of emitting ions and η_2 is the normalized population of level 2. This level diagram is particularly applicable to the case of the Eu³⁺ ion.

In the presence of spherical Ag-NPs, which usually present plasmon energy in the range 400–450 nm depending on their characteristics (average size, specific volume (filling factor) and the surrounding medium) the integrated intensity now reads:

$$I_{12}^* = \hbar \omega_{12} 4\pi C^* W_{12}^* \int_a^{R_0} \eta_2^*(R) R^2 dR$$
⁽²⁾

where the asterix indicates the presence of Ag-NPs. C^* is the concentration of emitting ions, a is the average NP's radius and R_0 is a radial parameter that defines a sphere, concentric with the NP, inside where the emitting ions are confined, as depicted in Fig. 2. We assume that inside this sphere the emitting ions distribution is uniform. In addition, it is important to note that the number of emitting ions must be the same in the absence and in the presence



Fig. 1. Level diagram used for the rate equations. |m > (|p >) is the nanoparticle ground state (plasmon band). Level |2 > corresponds to the emitting ${}^{5}D_{0}$ level, and level |3 > stands for the ${}^{5}L_{6}$ (${}^{5}D_{1}$) level when the excitation is at 393 (532) nm. The dotted lines represent the local field gradient due to the plasmon excitation.



Fig. 2. The cubic Ag-NPs idealized uniform distribution, with *D* as the cell parameter. *a* is the NP radius and R_0 defines the radius of the region where the emitting ions are confined.

of NPs. Thus, the concentration C* is defined in such way that:

$$\frac{C^*}{C} = \frac{D^3}{\left(\frac{4\pi}{3}\right)(R_0^3 - a^3)}$$
(3)

where C is the concentration of emitting ions.

These assumptions constitute the way we simulate the migration of the Eu^{3+} complex units towards the Ag-NPs. In our original model no migration was postulated and R_0 was taken equal to half of the unit cell parameter (D/2) in an idealized cubic network of NPs. Both in the absence and in the presence of NPs, the normalized population of level 2 in Eqs. (1) and (2) is found by solving appropriate systems of rate equations as described in details in Ref. [5].

The dielectric constant, $\epsilon(\omega)$, of the composite medium is given by:

$$\varepsilon(\omega) = \varepsilon_0 + \frac{q\omega_p^2}{\omega_R^2 - \omega^2 - i\gamma\omega}$$
(4)

where ε_0 is the dielectric constant of the medium in the absence of NPs, ω_p is the characteristic metal plasma frequency, γ is the damping factor (the width at half height of the plasmon absorption band) and the Mie resonance frequency of the plasmon in the NPs is given by:

$$\omega_R = \left(\frac{1-q}{3\varepsilon_0}\right)^{1/2} \omega_p \tag{5}$$

In Eqs. (4) and (5) *q* is the specific volume of NPs, given by:

$$q = \frac{4\pi}{3} \frac{a^3}{D^3} \tag{6}$$

In this model the distance dependent field gradient produced in the surrounding medium by the NPs under the action of an electromagnetic field with angular frequency ω is described by the index of refraction, $n^* = Re [\varepsilon(\omega)]^{1/2}$, of the composite medium and the NP's polarizability, given by [5]:

$$\alpha = \frac{1}{3} \frac{\omega_p^2}{\omega_R^2 - \omega^2 - i\gamma\omega} a^3$$
(7)

In this way, both effects of absorption and scattering by the NPs are taken into account. The appropriate forms of the distance dependent rates $W^*_{30}(R)$ and $1/\tau^*_{3}(R)$ [5] are:

$$W_{30}^*(R) = \left(1 + \frac{2\alpha^2}{R^6}\right) W_{30}^* \tag{8}$$

and

$$\frac{1}{\tau_3^*(R)} = W_{23} + \left(1 + \frac{2\alpha^2}{R^6}\right) W_{03}^* \tag{9}$$

where the ratios between the distance independent rates W^* and W, both for absorption and emission, are functions of the dielectric constant and index of refraction [2,5]. It is considered that the non-radiative decay rate, W_{23} , does not depend on the presence of the Ag-NPs. The distance dependent form of Eqs. (8) and (9) expresses the effect of the dipolar component of the field gradient nearby the metallic NP. In the Mie resonance, or quasi-resonance ($\omega \approx \omega_R$), the large effect that may be caused by this field gradient on absorption and emission rates of the luminescent species (in the present case a Eu³⁺ complex) competes with non-radiative energy transfer from the excited luminescent species to the NPs. As mentioned before, the reverse energy transfer process is not operative due to the very short lifetime of the NP's plasmon. The energy transfer ratecan be expressed as [4]:

$$W_T(R) = \frac{4}{3}\pi^{3/2}\omega_R \frac{a^3}{R^6} \mu^2 \frac{\sqrt{\ln 2}}{\hbar\gamma} \exp\left(-\frac{\Delta^2}{\left(\hbar\gamma\right)^2}\ln 2\right) = \frac{k}{R^6}$$
(10)

In the above equation μ is the dipole matrix element of the transition in the luminescent species which is in resonance, or quasi-resonance, with the plasmon excitation and Δ is the energy difference that gives the energy mismatch condition between donor (Eu³⁺ ion) and acceptor (Ag-NP) separated by a distance *R* counting from the center of the NP. This equation presumes that the plasmon band width, γ , is much larger than the typical widths of lanthanide 4f energy levels.

According to the previous theoretical results obtained in Ref. [5] the ratio, c_R , between the intensities I_{12}^* (Eq. (2)) and I_{12} (Eq. (1)) is given by:

$$C_{R} = \frac{I_{12}^{*}}{I_{12}} = \frac{W_{23}W_{pm}\tau_{p}}{W_{30}} \left\{ \frac{M}{W_{23}} + \frac{1}{\sqrt{QW_{23}}} \frac{L - MQ/W_{23}}{R_{0}^{3} - a^{3}} \left[arctg\left(\sqrt{\frac{W_{23}}{Q}}R_{0}^{3}\right) - arctg\left(\sqrt{\frac{W_{23}}{Q}}a^{3}\right) \right] \right\}$$
(11)

This ratio then quantifies the effect of the NPs on the emission intensity of a luminescent species to which the level diagram in Fig. 1 applies. Depending on the balance between the high field gradient and non-radiative energy transfer contributions, this effect might be a luminescence enhancement or quenching. In Eq. (11), the quantities *M*, *L* and *Q* are defined by:

$$M = \frac{W_{30}^*}{W_{pm}\tau_p} \tag{12}$$

$$L = k + 2\alpha^2 M \tag{13}$$

and

$$Q = k + 2\alpha^2 W_{03}^* \tag{14}$$

where τ_p is the plasmon lifetime and the transition rates involved, W, are indicated in Fig. 1. The balance between the local field gradient effect and lanthanide ion to the Ag-NP energy transfer depends on the relative contributions of k and α , defined in Eqs. (7) and (10), to the intensity ratio c_R given in Eq. (11), provided no additional energy transfer channels, e.g. due to the presence of very small Ag aggregates (a few atoms), is operative [21].

3. Results and discussion

The experimental results obtained by Reisfeld et al. [20] are briefly described as follows. Two samples of PVP films containing

the same amount of a Eu³⁺ complex with a deprotonated EDTA ligand (EDTA=ethylenediaminetetraacetic acid) were prepared. The first coordination sphere contains 3 water molecules, which are, presumably replaced by carbonyl groups from the polymer. One of the samples is Ag-NPs free and the other contains quasispherical Ag-NPs with average radius of 17.5 nm and average distance, D, between them \approx 160 nm, as shown by SEM images. The Ag-NPs plasmon absorption band is peaked at 437 nm, and from its large width at half height one may conclude that the NP's size distribution is rather large. The Eu³⁺ luminescence from both samples was excited either with a xenon lamp at 393 nm or with a focused diode laser at 532 nm. For the excitation at 393 nm the sample containing Ag-NPs presented a luminescence enhancement, with respect to the Ag-NPs free sample, by a factor around 5, while for the excitation at 532 nm with the focused diode laser the enhancement factor observed was around 50. It is of relevance to mention that the method of synthesis of the Ag-NPs containing film sample precludes, in principle, the presence of few atoms aggregates, which could operate as additional channels of nonradiative energy transfer between them and the Eu^{3+} complex.

The model described in the previous section was then applied to this experimental case by postulating the following: (i) Once the density and viscosity of the PVP polymer are very low, during the preparation of the Ag-NPs containing sample at least a significant amount of the Eu³⁺ complex units migrate towards them and stabilize within spheres, concentric with the NPs, of radius R_0 . This migration process is known to occur in the preparation of gold and silver NPs functionalized with metal-complexes. Since the EuEDTA complex is negatively charged it could even replace citrate molecules as stabilizers on the NP's surface; (ii) By exciting at 393 nm, coinciding with the ⁵L₆ level of the Eu³⁺ ion, or at 532 nm, coinciding with the ⁵L₁ level of this ion, makes a large difference in the non-radiative decay rate W₂₃ (Fig. 1) responsible for populating the Eu³⁺⁵D₀ emitting level. This is due to the energy gap law for non-radiative decays in lanthanide compounds.

Inspection of Eq. (11) will show that the ratio c_R is not particularly sensitive to typical values of the rates W_{30} , W_{03} and $1/\tau_p$. Since the emission rate, W_{12} , is far from resonance with the plasmon excitation, the ratio c_R is practically independent on it. On the contrary, c_R is quite sensitive to the values of the radii a and R_0 , to the distance D, to the damping factor γ , to the energy mismatch condition expressed by Δ and to the decay rate W_{23} . The values of c_R for the two excitation sources were calculated, with a Mathcad[®]14 program, for a confinement radius $R_0 = 25$ nm and are displayed in Table 1. The typical values of the input data were [5]: $W_{30}^* \approx W_{30} \approx 10^{-3} \text{ s}^{-1}$, $W_{03}^* \approx W_{03} \approx 10^2 \text{ s}^{-1}$, $W_{pm} \approx 10^3 \text{ s}^{-1}$, $\tau_p \approx 10^{-14} \, \text{s}$ and the dipole matrix element (in units of the electron charge) $\mu/e \approx 10^{-11}$ cm. The damping factor, $\gamma = 6500$ cm⁻¹, was obtained from the plasmon absorption band in Ref. [20]. The value of the non-radiative decay rate, W_{23} , follows the energy gap law for lanthanide compounds. In coordination compounds W_{23} from the ${}^{5}D_{1}$ to the ${}^{5}D_{0}$ emitting level of the Eu $^{3+}$ ion is known to be typically of the order of 10^6 s^{-1} [22]. While the 5D_1 level is situated at $\approx 1700 \text{ cm}^{-1}$ above the emitting 5D_0 level, the 5L_6 is situated $\approx 8000 \text{ cm}^{-1}$ above it. Though exciting at the 5L_6 a cascade process will end up by populating the ⁵D₀, a corresponding effective non-radiative decay W_{23} is expected to be considerably

Table 1

The enhancement ratio, c_R , and the non-radiative transition rates associated to the different excitations.

Excitation (nm)	W ₂₃ (s ⁻¹)	C _R
393	10 ⁴	5.2 (3)
532	10 ⁶	50.0 (50)

reduced in comparison to the case of direct excitation in the ${}^{5}D_{1}$. An estimate of this effective non-radiative decay rate could be made from rise time values of the ${}^{5}D_{0}$ transient under UV excitation, which in inorganic materials is in the range of milliseconds [3]. In coordination compounds these measurements turn out to be difficult due to strong absorption by the ligands and subsequent intramolecular energy transfer to the Eu³⁺ ion, but the effective W_{23} should be certainly higher than in inorganic materials. Thus, for the 393 nm excitation case (${}^{5}L_{6}$) it is acceptable to take $W_{23} \approx 10^{4} \text{ s}^{-1}$.

With these input data a good agreement with the experimental results is obtained. An important question that may be raised concerning the reliability of the model here used lies on the sensitivity of the ratio c_R (Eq. (11)) on the non-radiative decay W_{23} , which is a crucial step for the population of the emitting Eu³⁺ level. It could be argued that since this decay rate, from a given excited level, is independent of the presence of the NPs, one should not expect the ratio c_R to strongly depend on it. The reason of this strong dependence is the fact that in the absence of NPs the lifetime of level 3 (τ_3) is largely dominated by W_{23} , while in the presence of NPs this rate strongly competes with the enhanced $W^*_{03}(R)$ decay and with the non-radiative ion-to-NP energy transfer $W_T(R)$. Thus, the effect from the enhancement in the absorption $W^*_{30}(R)$ rate becomes more manifested when W_{23} increases.

4. Concluding remarks

The theoretically calculated values of c_R (Table 1) are in good agreement with the reported values in Ref. [20]. The overall conclusion on the case here analyzed is that for both excitation wavelengths (393 nm and 532 nm) the balance between high local field gradients and ion-to-NPs energy transfer effects is favorable to the former one, and luminescence enhancement is observed in both cases in the presence of Ag-NPs, as compared to the samples without Ag-NPs. We have considered that the EuEDTA complex units migrate towards the NPs, during the synthesis of the composite material, and remain confined and uniformly distributed in spheres of radius R_0 concentric with spherical NPs of average radius a. However, for the excitation at 532 nm, very close to the Eu³⁺⁵D₁ manifold, one fact becomes by far more relevant: the non-radiative decay rate, W_{23} , populating the emitting ⁵D₀ level is much higher than its effective value (from a cascade process) when exciting at 393 nm in the ${}^{5}L_{6}$ manifold. This turns out to favor the high local field gradient enhancement effect on the EuEDTA luminesce under 532 nm excitation.

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