Luminescent properties of nanocomposites based on the doped nanoparticles and isolated coated nanoparticles

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A B S T R A C T

Here we present a summary of the theoretical studies of the emission rates modifications of emitter placed inside or near the subwavelength nanoparticle that are embedded in a medium. The change in spontaneous emission rate as a function of the effective refractive index of the nanocomposite, as well as on the refractive indices of NPs and the substance filling the space between them is presented. Both naked and coated nanoparticles are considered.

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1. Introduction

Over the past decades, the dynamics of the localized excited states of an emitter situated inside or near a nanoparticle (NP) have found increased interest in the fundamental and applied physics. Specifically, the nanocrystals doped with transition ions (rare-earth or ions of the iron group) have recently been intensively studied due to their potential application in various fields [1–12]. The rare-earth (RE)-doped luminescent NPs possess enhanced physicochemical properties, so that they can be regarded as a new generation of biosensors. The functional NPs have stimulated growing interest in connection with their spectroscopic properties and biomedical applications in various fields such as biodetection, disease diagnostics, and therapeutics [9,10]. It is known that the radiative lifetimes of the excited atomic states in nanocrystalline dielectrics are different from those in the crystallographically equivalent bulk crystals of the same composition. As shown in Ref. [1], the radiative lifetimes of the RE excited states in nanocrystalline materials are appreciably longer than in the bulk, while the radiative rates depend heavily on the effective refraction index of a medium consisting of the NPs and a substance filling the space between them.

At present, a change in the intensities of optical transitions in atoms, molecules, and their ions in the near-field zone of nanoobjects has become a significant fundamental and practical interest. The RE ions are characterized by so-called hypersensitive

transitions, because of their high sensitivity to the field created by the neighboring particles. The hypersensitive nature of some electronic transitions of RE ions has long been known [13–15], rendering these ions particularly promising as sensitive reporters of the local properties of medium. This problem becomes presently more and more important, e.g., in biophysical and biochemical research works.

The luminescent properties of the nanocomposites based on the doped NPs and the luminescent properties of an emitter situated inside or near an isolated coated NP are considered in this work. More specifically, the goal is to examine the change of spontaneous emission rate of an emitter placed inside or near a subwavelength NP embedded in medium. The spontaneous emission is the key concept of the quantum theory of light. The modern theory of radiative transitions was developed on a basis of the quantum mechanics and quantum electrodynamics. It closely relates the probabilities of spontaneous and induced transitions to the probabilities of transitions accompanied by the radiation absorption [16]. For the thermal radiation, the relationship between these probabilities was established for the first time by Einstein in 1916. The spontaneous emission controls the laser pump-power threshold and the noise properties of photonic devices. Knowing the probabilities of spontaneous transitions, one can easily determine the probabilities of other transitions and, thus, the regularities in the absorption and emission cross sections and, hence, in the lasing threshold.

The work is organized as follows. Section 2 presents a summary of the theoretical studies on the luminescent properties of the

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nanocomposites based on the doped subwavelength NPs. Section 3 is devoted to the isolated coated NPs. Judds's method for calculating intensities of the hypersensitive RE transitions [14,15] in the presence of an inhomogeneous ligand field is extended to the near field of nanoobjects. Apart from the general formula for the rate of spontaneous transition, a simple analytical expression is obtained for the Judd–Ofelt intensity parameter Ω_2 for the RE ion in the field of core–shell spherical NP. The results are discussed in Section 4.

2. Luminescent properties of nanocomposites based on the doped subwavelength NPs

At present, there are two principal approaches in describing the luminescent properties of nanocomposites based on the doped subwavelength NPs. The first approach was originally proposed by Meltzer et al. [1]. It started with the well-known formula for the spontaneous electric-dipole (ED) radiative-decay rate of luminescent center located in a bulk crystal

$$A_{bulk}^{ed} = 1/\tau_{bulk}^{ed} = n_{cr} f_L (n_{cr}) A_0^{ed} \tag{1a}$$

where n_{cr} is the crystal refractive index, f_L is so-called local-field correction, and A_0^{ed} is the decay rate in the vacuum or in a medium with refractive index close to unity. The decay rate A_0^{ed} is given by the famous formula (see Ref. [16, Eq. (80), Ch. 10, p. 245])

$$A_0^{ed} = \left[4\pi^2 \omega |(i|\mathbf{d}|f)|^2 / 3\hbar \right] \rho_{vac} (\omega) = 4\omega^3 |(i|\mathbf{d}|f)|^2 / 3\hbar c^3. \tag{1b}$$

In this expression, ω is the transition frequency, $(i|\mathbf{d}|f)$ is the matrix element of electric dipole $\mathbf{d}$ between states $|i)$ and $|f)$ involved in the transition, $\rho_{vac} (\omega)$ is the density of photon states in vacuum, and $|(i|\mathbf{d}|f)|^2 = |(i|d_x|f)|^2 + |(i|d_y|f)|^2 + |(i|d_z|f)|^2$.

In the general case, f_L is defined as $f_L = (E^{loc}/E)^2$ [17], where E_{loc} and E are the microscopic and the average macroscopic values of the electric-field strength at the site of optical center, respectively. The quantity f_L is determined by a particular local-field model; in all existing models, f_L is a function of the refractive index n of the medium, i.e., $f_L = (E^{loc}/E)^2 = f_L(n)$ and $f_L(1) = 1$ (see Ref. [8] for a detailed review of the known models of the local field). It was suggested in Ref. [1] that the expression for the spontaneous electric-dipole transition rate of the optical center carried from the bulk crystal to a nanocrystal of the same composition and the same structure (A_{nano}) can be obtained by replacing in Eq. (1) refractive index of the crystal by the effective index n_{eff} of the nanocomposite; that is

$$A_{nano}^{ed} = n_{eff} f_L (n_{eff}) A_0^{ed}. \tag{2}$$

In Ref. [1], the effective refractive index n_{eff} is defined as

$$n_{eff} = x n_{NP} + (1 - x) n_{med}, \tag{3}$$

where x is the volume fraction (filling factor) of the NPs in a nanocomposite; n_{NP} and n_{med} are the refractive indices of the NP substance and the medium, respectively.

Hence, in the first approach, the ratio

$$A_{nano}^{ed}/A_{bulk}^{ed} = n_{eff} f_L (n_{eff})/n_{cr} f_L (n_{cr}). \tag{4}$$

This ratio depends on the choice of the particular local-field model, so that a certain ambiguity arises in the interpretation of experimental data, because the expressions for the correction factor f_L are different in different models.

The pioneer work [1] has stimulated the performance of the experiments aimed at revealing the influence of the local-field effects on the radiative transition rate in the optical nanocomposite materials (see recent review by Dolgaleva and Boyd [8]).

The second approach was proposed in our works [7,18–24]. The corresponding calculations are given for a nanocomposite containing subwavelength nanospheres [18]

$$A_{nano}^{ed}/A_{bulk}^{ed} = (n_{eff} / n_{cr}) \left[\frac{3}{2 + \varepsilon - x(\varepsilon - 1)} \right]^2 \tag{5}$$

where $\varepsilon = \varepsilon_{NP}/\varepsilon_{med}$; ε_{NP} and ε_{med} are the permittivities of the NP and medium, respectively; and n_{eff} is the effective refractive index of the nanocomposite. By employing the method used in deriving Eq. (5) (for detail see Refs. [18,21]) one obtains the following relationship for ε_{eff}:

$$\varepsilon_{eff} = n_{eff}^2 = \varepsilon_{med} \left[1 + \frac{3x\beta}{1 - x\beta} \right] \tag{6}$$

where $\beta = (\varepsilon - 1)/(\varepsilon + 2)$. Eq. (6) is nothing but the well-known Maxwell Garnet formula [25]. In deriving Eq. (5), the possible complications such as the size-dependent structural lattice rearrangements are neglected, although they may become important in certain cases. It is supposed that the atomic-scale local-field factor is the same in the bulk crystal and in the nanocrystal of the same composition and crystallographic structure. In contrast to the first approach, the ratio $A_{nano}^{ed}/A_{bulk}^{ed}$ does not depend on the local-field correction and, hence, on the chosen local-field model.

Let us consider the ratio $A_{nano}^{ed}/A_{bulk}^{ed}$ as a function of the filling factor x in the two limiting cases. For both approaches, $A_{nano}^{ed} \rightarrow A_{bulk}^{ed}$ as $x \rightarrow 1$. In the limit $x \rightarrow 0$ (isolated nanospheres), the first approach gives

$$A_{nano}^{ed}/A_{bulk}^{ed} = (n_{med}/n_{cr}) \frac{f_L (n_{med})}{f_L (n_{cr})} \tag{7}$$

and in the second approach

$$A_{nano}^{ed}/A_{bulk}^{ed} = \frac{n_{med}}{n_{cr}} \left[\frac{3}{2 + \varepsilon} \right]^2. \tag{8}$$

This expression agrees with the analytical result obtained by Chew in Ref. [26] without regard for the local-field effect. (H. Chew considered the ED radiation inside a sphere filled with a continuous dielectric substance.)

It is believed that two principal factors are responsible for a change in the spontaneous-transition rate upon carrying optical center from the vacuum to a medium. Firstly, the density of photon states changes in the nanocomposite. Secondly, the amplitude of the zero-point electric-field oscillations that are responsible for the spontaneous decay also changes. Since the Purcell's work [27], the first factor has been regarded as a source of the change in the spontaneous-transition rate. Although the Purcell effect was taken into account in Ref. [1], the result obtained for the change in the amplitude of zero-point oscillations was not quite correct.

3. The spontaneous emission rates of emitters outside and inside the core–shell nanoparticles

In Ref. [14], Judd analyzed the formerly proposed so-called inhomogeneous dielectric and dynamic coupling mechanisms of hypersensitivity to demonstrate their equivalence and offer clear physical interpretation of this phenomenon. Although the Judd's analysis was focused on the RE ions, the results obtained in Ref. [14] can as well be applied to the ions of other transition groups and to any small-sized optical center (OC).

It was shown in Ref. [14] that the influence of ligand field on the radiative transition amounts to the increase in the electric-dipole moment of OC by