



Static cooperative luminescence quenching in nanoparticles

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ABSTRACT

In nanoparticles (NPs) static quenching of luminescence may be slower than in bulk media due to the space restrictions on acceptor location. Many-body cooperative quenching (manifesting itself as, e.g., down-conversion) occurs when the donor energy is transferred to two-, three-, or more particles (a cooperative acceptor) at once. Random distribution of acceptor particles in diluted media accounts for the non-exponential form of the kinetics. When the analytical expression for the kinetics form is known, it can be fitted to the experiment in order to find various micro- and macro-quenching parameters of the luminescent material. In this paper, we present an analytical law for cooperative quenching kinetics in NPs at longer time. Its clear and compact form reflects the fact that, on average, donors located on the surface of NPs are the last to decay having acceptors on one side only. We compared the resulting formula with the Monte-Carlo computer simulation, and they show good agreement.

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1. Introduction

In the literature, nanostructures of various forms are considered promising for a wide range of applications in physics, biology, and medicine. These include polymer coils in solutions [1], photonic crystals [2], porous glasses [3,4], and nanoparticles [5]. As the popularity of nanomaterials grows, the theoretical study of their properties becomes vital. We are particularly interested in luminescence quenching kinetics, as its form may be used to define all types of micro- and macro-parameters associated with the media and energy transfer, such as the minimal donor–acceptor distance R_0 , type S and microefficiency C_{DA} of multipole donor–acceptor interaction; see Refs. [6–8]. If energy acceptors are located only within NPs, then the probability of irradiative energy transfer (luminescence quenching) may decrease, and the luminescence quantum yield may increase, in comparison with bulk media, simply because for some (surface) donors there are less acceptors around. In Ref. [9] authors have shown (both theoretically and by computer simulation) that luminescence quenching in NPs can be slower than in bulk, the more so the smaller the NPs. Very recently, this was confirmed experimentally [10]. Apart from the regular case of luminescence quenching when a donor transfers energy to a single acceptor particle, in this work we are interested in a cooperative energy transfer when the donor energy

gap is equal to twice (or, generally, n times) the energy gap of the acceptor particle. For rare-earth (RE) ions, this cooperative energy transfer ($\text{Nd} \rightarrow 2\text{Ce}$, $\text{Tm} \rightarrow 2\text{Ce}$, $\text{Tb} \rightarrow 2\text{Yb}$, and $\text{Er} \rightarrow 3\text{Ce}$) was experimentally shown to be the dominant quenching process [11–13]. Usage of quantum cutting for solar batteries (conversion of one visible photon into two or three photons with a few times longer wavelength) is one modern example of perspective application of cooperative energy transfer [14]. The down-conversion is a much more efficient process than the up-conversion (see Refs. [15,16] for pioneering experiments). Roughly speaking, the probability of up-conversion is proportional to the number of possible excited donors, while the probability of down-conversion is proportional to the number of possible pairs of acceptor particles, which is one or two orders of magnitude greater. In this paper we study only the case of cooperative energy transfer from donors to many-particle acceptors but not the opposite.

We started our study of cooperative energy transfer by considering the quenching in bulk media when the donor energy approximately doubles the acceptor energy [17]. In work [18], we generalized the analytical solution for the long-time-stage kinetics of donor excitation energy transfer in an ensemble of acceptors, each consisting of randomly distributed two, three, or n particles ($n+1$ body interaction): $I_n(t) = \exp[-(Wt)^{1/(nS/d - n + 1)}]$. We used a continuum approximation and showed that the expression works well for a small acceptor particle concentration. The time power in the exponent has interesting dependence on the interaction multipolarity S and the space dimension d . The average quenching rate $W \sim c^{nS/d}$ depends on the acceptor particle concentration c to the power nS/d , which is similar to the classical Forster case ($c^{S/d}$),

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but has a factor n —the number of particles comprising a cooperative acceptor. In this paper, we address the question of how the kinetics of static cooperative luminescence quenching changes by moving from bulk material to NPs.

1.1. Mathematical model

Recently, we investigated the problem of static quenching in NPs for the case of energy transfer from a donor to one-particle acceptors [9,19]. A donor located near the surface of an NP cannot be surrounded by acceptors from all sides (we assume that acceptors are located only within NPs), so it has a smaller probability to decay than a donor in the bulk media with the same acceptor concentration. The expression for luminescence quenching contains two terms: the first one is similar to the formula for quenching in bulk material, and the second one describes the quenching of surface donors (roughly, with a twice smaller rate).

We consider the effect of restricted geometry factor, exclusively. We do not take into account surface distortions, NPs size difference, presence of outer quenchers (like OH ions), spectral shifts in nanostructured media in relation to bulk, etc. To understand the complex kinetics, it is reasonable to start by studying the influence of each factor separately. In this, computer simulation is indispensable. While the extra, unwanted, factors are hard to eliminate in real experiment, computer simulation of quenching can be as pure numerical experiment as we wish.

In this work, we present the expression for static quenching kinetics in spherical NPs in the case of cooperative energy transfer from a donor to n -particle acceptors. We assume the acceptor ions with the small concentration $c_A \ll 1$ to be uniformly distributed in the volume of NPs. In addition, the donor excitation density is taken to be small, so that we can neglect the donor-to-donor excitation migration and the donors do not compete for the acceptor ions. In the computer simulation we have put exactly one excited donor in one NP, at a random position. The number of acceptor ions in one NP has a Gaussian distribution around the mean, which equals the number of available positions (lattice sites) multiplied by concentration (we define the concentration c_A as the probability of a certain position to be occupied by an acceptor particle).

Below we present a sketch of the derivation for the three-dimensional ($d=3$) case of cooperative quenching to two-particle acceptors ($n=2$). At the same time, we will use the symbols d and n in the notations below in order to exploit these same notations in a more general case.

1.2. Derivation of the long-time asymptotics

The probability of elementary act of energy transfer from a donor to a certain pair of acceptor particles, located at the distances r_i and r_j from the donor, is $W_{ij} = C_{DA}/(r_i^d r_j^d)$, where C_{DA} is the microparameter of cooperative energy transfer efficiency. Note that dimensionality of C_{DA} for cooperative energy transfer is different from that of energy transfer to one-particle acceptors.

We shall use the same approach as in Refs. [19,20]. In a crystal NP, let us number all the positions available for acceptor particles. Intensity of luminescence normalized by the maximum value I_0 at time $t=0$ (we assume instantaneous excitation) can be written in the form:

$$I(t) = \left\langle \prod_{i < j} [1 + p_i p_j (\exp(-W_{ij}t) - 1)] \right\rangle. \quad (1)$$

Here p_i is 1 if the position i is occupied by an acceptor particle, and 0 otherwise. We consider the distribution of acceptor particles

to be uniform

$$\langle p_i \rangle = c_A, \quad \langle p_i p_j \rangle = \begin{cases} \langle p_i^2 \rangle = \langle p_i \rangle = c_A, & i = j \\ \langle p_i \rangle \langle p_k \rangle = c_A^2, & i \neq j \end{cases}. \quad (2)$$

Averaging, denoted in the expressions above and below by angle brackets, of the product in Eq. (1) is the hardest problem of the theoretical treatment of the problem. In this work we use the same approximation as we did before in Refs. [17,18]

$$I(t) = \left\langle \prod_{i < j} [1 + p_i p_j (\exp(-W_{ij}t) - 1)] \right\rangle \left\langle \prod_{2 < j} [1 + p_2 p_j (\exp(-W_{2j}t) - 1)] \right\rangle \dots \quad (3)$$

This approximation is the roughest one in the present paper and can be justified only for small acceptor concentrations. The problem is that in Eq. (3) some of p_i s are treated as independent, while they are not, in fact, independent. As a result, $I(t)$ as described by Eq. (3) may go down faster than actual luminescence. We also need the condition of small acceptor concentration to exploit the continuum approximation in what follows.

A standard procedure to deal with the terms of Eq. (3) of the form $\langle \prod (1 + p_i p_j (\exp(-W_{ij}t) - 1)) \rangle$ is to transform them into $\langle \exp \sum \ln(1 + p_i p_j (\exp(-W_{ij}t) - 1)) \rangle$, as it is easier to work with sum rather than product. The expectation of the latter value will be $c_A \exp \sum \ln(1 + p_i (\exp(-W_{ij}t) - 1)) + (1 - c_A)$. Now we exploit the concerning approximation of the partial independence of p_i s and represent the product of similar expressions as $\exp \sum \ln(c_A \exp \sum \ln(1 + c_A (\exp(-W_{ij}t) - 1)) + (1 - c_A))$, where the first summation is over index i and the second summation is over index $j > i$.

In the continuum approximation we replace summation over lattice sites by integration over volume of a nanoparticle. Integration variables are the distances of the acceptor particles to the donor, on a condition that an acceptor particle is located within the NP. Therefore, for small donor-acceptor distances, we integrate over full 4π space angle, while for greater donor-acceptor distance (or, more importantly, for configurations where the donor is close to the NP surface) the quenching sphere will be located partially outside of the NP; hence a more complex term for space angle is used below.

Let all the NPs be of one size with the radius R . First, we shall write down an expression with respect to the donors located at the certain distance r_D from the center of an NP, and then we shall average the resulting expression over all r_D : $0 \leq r_D \leq R$. We present the luminescence intensity as

$$I(r_D, t) = \exp\{-f(r_D)\}, \quad (4)$$

where the function $f(r_D)$ is

$$f(r_D, t) = \frac{N_A}{V} \int_{R_0}^{R-r_D} 4\pi r_1^2 dr_1 \left(1 - \exp \left[\frac{N_A}{V} \left\{ \int_{r_1}^{R-r_D} -\frac{C_{DA}t}{r_1^d r_2^d} 4\pi r_2^2 dr_2 \right. \right. \right. \\ \left. \left. \left. + \int_{R-r_D}^{R+r_D} -\frac{C_{DA}t}{r_1^d r_2^d} 2\pi r_2^2 \Omega(r_2, r_D) dr_2 \right\} \right] \right) \\ + \frac{N_A}{V} \int_{R-r_D}^{R+r_D} 2\pi r_1^2 \Omega(r_1, r_D) dr_1 \left(1 - \exp \left[\frac{N_A}{V} \left\{ \int_{r_1}^{R+r_D} \right. \right. \right. \\ \left. \left. \left. -\frac{C_{DA}t}{r_1^d r_2^d} 2\pi r_2^2 \Omega(r_2, r_D) dr_2 \right\} \right] \right), \quad (5)$$

where $N_A = c_A N$ is the average number of acceptor particles in the unit space V , N is the number of positions available for acceptors in the unit space, and the space angle is

$$\Omega(r_i, r_D) = 1 + \frac{R^2 - r_D^2 - r_i^2}{2r_D r_i}. \quad (6)$$

The case of $r_D = R$ reflects the situation when the donors deposited on the surface of an NP decay with the help of the cooperative acceptors located in the whole volume of an NP. Then,

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