Kinetics of luminescence decay of nanocrystals: physical models and approximation by a sum of three exponential functions

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The measurement of the kinetics of luminescence decay of nanocrystals (NCs) — quantum dots (QDs), nanowires, nanoplates and quantum rings — is an important tool for studying the photodynamics of their excited states, that allows identifying the type and number of traps for charge carriers (electrons, holes) or acceptors of excitation energy (molecules, other QDs) located on the surface or near the NCs, as well as to estimate the energy of traps and to determine the mechanism of transfer of the energy of electronic excitation from the NCs to acceptors. Usually, the kinetics of luminescence decay is approximated by a sum of two or three exponential functions. In this case, the fitting parameters are the amplitudes and decay times of the exponential components. This paper analyzes the experimental conditions under which such an approximation has a clear physical meaning (long-range nonradiative energy transfer, contact quenching of luminescence, reversible trapping of charge carriers), and establishes a relationship between the fitting parameters.

Keywords: nanocrystals, kinetics of luminescence decay, approximation by a sum of three exponential functions.

Introduction

The kinetics of luminescence decay of nanocrystals (NCs) — quantum dots (QDs), nanowires, nanoplates and quantum rings — contains important information about the structure of the electronic levels of the NCs and about the interaction mechanisms of (i) NCs with acceptors of the energy of electronic excitation and (ii) of charge carriers (electrons, holes) in NCs with traps. The analysis of the kinetics of luminescence decay makes it possible to identify the type and number of charge carrier traps or excitation energy acceptors (molecules, QDs) located on or near the surface of the NCs, as well as to estimate the energy of the traps and to determine the mechanism of electronic excitation energy transfer from NCs to acceptors [1–9].

The normalized kinetics of luminescence decay of an ensemble of QDs $I(t)$ ($I(0) = 1$) is usually not exponential, and it is often approximated by a sum of exponential functions, for example three components:

$$I(t) = A_1 e^{-t/\tau_1} + A_2 e^{-t/\tau_2} + A_3 e^{-t/\tau_3}, \qquad (1)$$

where the fitting parameters are the decay times τ_1, τ_2, τ_3 ($\tau_1 > \tau_2 > \tau_3$) and the amplitudes A_1, A_2 and A_3. Taking into account the normalization condition ($A_1 + A_2 + A_3 = 1$) in equation (1) there are five independent fitting parameters (three decay times and two amplitudes).

We note that the above representation (1) of the function $I(t)$ in the form of a series is actually its discrete Laplace transform. It is clear that such an approximation of $I(t)$ is the more accurate the more terms there are in the series. In this connection, the question arises about the physical meaning of the fitting parameters (decay times and amplitudes).

The approximation of the kinetics of the luminescence decay of a QD ensemble by a sum (1) is justified, for example, in the case of low temperatures. Indeed, according to the generally accepted QD model [10–13], the electronic structure of the QDs can be characterized by three levels: the ground state and two closely spaced excited state levels (the upper bright state and the lower dark state). The transition from the dark state to the ground state is forbidden, so that the radiative lifetime of the dark state is much longer than the radiative lifetime of the bright state (corresponding to the transition from the bright state to the ground state). The QD is excited into the bright state. As a result of the electron-vibrational interaction, there is a rapid redistribution of excitation between the bright and dark states. At low temperatures, when the energy difference between the QD bright and dark states is much greater than $k_B T$ (k_B — Boltzmann constant, T — temperature), the kinetics of luminescence decay of the QD ensemble is described by a sum of two exponential components [14–16]. The component with a short decay time corresponds to QD luminescence due to a decrease in the population of the bright state as a result of the electron transition to the ground and dark states, and the component with a long decay time is due to the return of the excitation from the dark state to the bright state and subsequent radiative transition to the ground state (delayed luminescence [17]).

At room temperatures (when $k_B T$ is much greater than the energy difference between the bright and dark states), the populations of the bright and dark states are in equilibrium as a result of the electron-vibrational interaction. The kinetics of the QD luminescence decay becomes single-exponential, with the decay time equal to twice the lifetime of the bright state [3,10,13,16].

However, experimental studies show that the kinetics of the luminescence decay of a QD ensemble often remains non-exponential even at high temperatures. In this case, the approximation of $I(t)$ by a sum of exponential components (1) acquires physical meaning only if a specific physical model of the interaction of QDs with energy acceptors or traps is assumed. In this paper, which has a scientific and methodological nature, several such models are discussed.

Long-range energy transfer

Let us assume non-radiative energy transfer (Förster resonance energy transfer — FRET) from QDs to acceptors. In the absence of FRET, according to the theory, the kinetics of QD luminescence decay is exponential with time τ. We consider the critical radius of energy transfer R_0 (Förster radius) to be small, and therefore it is sufficient to take into account FRET only to acceptors located in the first (at a distance R_1) and second (at a distance R_2) QD coordination spheres ($R_1 < R_2$) [18].

Within the multipole FRET mechanism, the rates of energy transfer k_1 and k_2 to acceptors in the first and second QD coordination spheres, respectively, are equal to

$$k_1 = \frac{1}{\tau}\left(\frac{R_0}{R_1}\right)^s \qquad \text{and} \qquad k_2 = \frac{1}{\tau}\left(\frac{R_0}{R_2}\right)^s. \quad (2)$$

Here the parameter s is determined by the mechanism of interaction of QD and acceptors and is equal to 6, 8 or 10, respectively, for dipole-dipole, dipole-quadrupole or quadrupole-quadrupole interactions [19–21].

Under these assumptions, the kinetics of the luminescence decay of the QD ensemble will be described by a sum of three exponential components (1) with the parameters $\tau_1 > \tau_2 > \tau_3$ given by

$$1/\tau_1 = 1/\tau, \quad 1/\tau_2 = 1/\tau + k_2, \quad 1/\tau_3 = 1/\tau + k_1. \quad (3)$$

The amplitudes A_1, A_2 and A_3 have the meaning, respectively, of the QD fractions that do not have acceptors in the nearest coordination spheres ($\tau_1 = \tau$, the longest decay time), having an acceptor only in the second coordination sphere (τ_2) and only in the first coordination sphere (τ_3, the shortest decay time).

We note that in this model, according to formula (3), there is the following relationship between the times τ_1, τ_2 and τ_3 and the radii of the coordination spheres R_1 and R_2:

$$\frac{1/\tau_2 - 1/\tau_1}{1/\tau_3 - 1/\tau_1} = \frac{k_2}{k_1} = \left(\frac{R_1}{R_2}\right)^s. \quad (4)$$

This relationship (4) can be estimated by knowing the average size of the QDs and the structure of the QD environment.

Taking into account the normalization condition and equations (3) and (4) the number of fitting parameters in equation (1) decreases to four (A_1, A_2, τ_1, k_1).

If the critical radius R_0 is large (for example, $R_0 > R_2$) and it is necessary to take into account FRET to acceptors located at sufficiently large distances (larger than the size of the second coordination sphere), then a stretched exponential function should be used to approximate the kinetics of luminescence decay [3,4,6,7,9,22–24]

$$I(t) = \exp\left(-\frac{t}{\tau} - a(t/\tau)^\beta\right). \quad (5)$$

Here $\beta = d/s$, d is the dimension of the medium and the parameter a is determined by the concentration of acceptor molecules and the critical radius of energy transfer R_0 [3,4,20,25–28]. When approximating the experimental kinetics of luminescence decay by function (5), the number of fitting parameters is reduced (compared with (1)) to three (τ, β and a).

Contact irreversible trapping of charge carriers

Another model is contact irreversible trapping of charge carriers (electrons or holes) in NC by traps or FRET from NCs (acting as energy donors) to acceptors, occurring only at the closest possible distance between NC and the acceptor (i.e. they are in „contact"). Let the number of traps (or acceptors) per NC on average be small, and let it be sufficient to take into account a maximum of two traps (two acceptors). Let the rate of trapping of an electron (hole) by one trap or the rate of energy transfer to one acceptor be equal to k_1 and the same for all traps or acceptors (i.e. traps or acceptors are identical). Then the trapping rate of an electron (hole) by two traps or the rate of energy transfer to two acceptors will be equal to $2k_1$. Let us also assume that in the absence of energy transfer, the kinetics of NC luminescence decay is exponential with decay time τ. In this case, the kinetics of the luminescence decay of the NC ensemble can also be approximated by a sum of three exponential components (1) with the parameters $\tau_1 > \tau_2 > \tau_3$ given by

$$1/\tau_1 = 1/\tau, \qquad 1/\tau_2 = 1/\tau + k_1, \qquad 1/\tau_3 = 1/\tau + 2k_1. \quad (6)$$

The amplitudes A_1, A_2 and A_3 in this case have the meaning, respectively, of the fractions of NC that do not have traps or acceptors at the minimum distance ($\tau_1 = \tau$, the longest decay time) and having only one ($1/\tau_2 = 1/\tau + k_1$) or two traps (two acceptors) at this distance ($1/\tau_3 = 1/\tau + 2k_1$, τ_3 is the shortest decay time).

According to (6), the following relationship holds between the times τ_1, τ_2 and τ_3:

$$\frac{1/\tau_2 - 1/\tau_1}{1/\tau_3 - 1/\tau_1} = \frac{1}{2}. \qquad (7)$$

In this case, the number of fitting parameters is four (A_1, A_2, τ, k_1).

If it is not possible to limit ourselves to taking into account only two traps (acceptors) per NC, then the function used to approximate the kinetics of the luminescence decay of the NC ensemble should be [1,2,4–7,29–31]

$$I(t) = \exp\left[-\frac{t}{\tau} - \bar{N}\left(1 - \exp\left(-K_1\frac{t}{\tau}\right)\right)\right]. \qquad (8)$$

In formula (8) $\bar{N}$ is the average number of identical traps (acceptors) per NC, $K_1 = k_1\tau$, and a Poisson distribution of traps over NC [32–34] is assumed. When approximating $I(t)$ by the function (8), the number of fitting parameters decreases to (τ, K_1, $\bar{N}$).

Contact reversible trapping of charge carriers by identical traps

The next model is contact reversible trapping of charge carriers in NCs (electrons or holes) by traps. Let the number of traps per NC on average be much less than one. Then, in the kinetics of the luminescence decay of the NC ensemble, it is sufficient to take into account only NCs that do not have traps and NCs that have one trap. Let the trapping rate of an electron (hole) by a trap be k_1, and the rate of return of the charge carrier from the trap to the NC be k_2. We assume that $k_2 \ll k_1$. Let us also assume that in the absence of trapping of charge carriers by traps, the kinetics of NC luminescence decay is exponential with decay time τ. In this approximation, the kinetics of luminescence decay $I(t)$ will be described by a sum of three exponential components (1) [7–9]

$$\begin{aligned} I(t) = A_1 & \left(\frac{k_2}{1/\tau + k_1 + k_2} e^{-t/\tau_1} \right. \\ & \left. + \frac{1/\tau + k_1}{1/\tau + k_1 + k_2} e^{-t/\tau_3} \right) + A_2 e^{-t/\tau_2} \end{aligned} \qquad (9)$$

with parameters $\tau_1 > \tau_2 > \tau_3$ given by

$$\frac{1}{\tau_1} = \frac{k_2}{1/\tau + k_1}\frac{1}{\tau}, \qquad \frac{1}{\tau_2} = \frac{1}{\tau}, \qquad \frac{1}{\tau_3} = \frac{1}{\tau} + k_1. \quad (10)$$

The term in (9) with amplitude A_2 is the contribution to luminescence from NCs without traps ($\tau_2 = \tau$). The two terms in (9) with a total amplitude of A_1 ($A_1 + A_2 = 1$) — luminescence of NCs having one trap. The first term in parentheses with the longest decay time τ_1 characterizes the delayed luminescence of NCs (due to the return of charge carriers from the trap to NC and subsequent luminescence of NC). Taking into account the normalization condition

$A_1 + A_2 = 1$ in equation (9) there are four fitting parameters (A_1, τ, k_1, k_2).

If it is not possible to limit ourselves to taking into account only one trap per NC, then to approximate $I(t)$, the following formula should be used [7–9]

$$I(t) = \sum_0^\infty e^{-\bar{N}}\frac{\bar{N}^N}{N!}\left(Ae^{-\alpha_1 t/\tau} + Be^{-\alpha_2 t/\tau}\right). \qquad (11)$$

When obtaining equation (11), a Poisson distribution of identical traps (i.e. traps having the same values of k_1, k_2) [32–34] per NC was assumed,

$$\alpha_1 = \frac{1}{2}(1 + NK_1 + K_2) + \sqrt{\frac{1}{4}(1 + NK_1 + K_2)^2 - K_2}, \qquad (12)$$

$$\alpha_2 = \frac{1}{2}(1 + NK_1 + K_2) - \sqrt{\frac{1}{4}(1 + NK_1 + K_2)^2 - K_2}, \qquad (13)$$

$$A = \frac{1 + NK_1 - \alpha_2}{\alpha_1 - \alpha_2}, \qquad B = 1 - A,$$

$$K_1 = k_1\tau, \qquad K_2 = k_2\tau. \qquad (14)$$

In equations (11)−(14) there are four fitting parameters (τ, K_1, K_2, $\bar{N}$). These equations were used to approximate the NC kinetics of luminescence decay in [7–9,23,30].

Thus, in the three experimental situations considered in this paper, the approximation of the kinetics of luminescence decay of the NC ensemble by a sum of three exponents (1) acquires a clear physical meaning.

Conclusion

Various experimental conditions (leading to long-range nonradiative energy transfer, contact quenching of luminescence, reversible trapping of charge carriers) have been analyzed, under which the non-exponential kinetics of luminescence decay of the NC ensemble (QDs, nanowires, nanoplates, quantum rings) at room temperature can be modeled by a sum of exponential functions. It has been shown what the quantitative relationship between the fitting parameters (the decay times of the exponential components and their amplitudes) should be. This allows us to reduce their number.

We note that the approximation of the kinetics of the NC luminescence decay by a sum of exponential functions is also useful for the analysis of sensitized luminescence of acceptors [35], to which energy is transferred from NCs.

Conflict of interest

The author declares that he has no conflict of interest.

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