

Stretched exponential (Kohlrausch) relaxation function in the analysis of colloidal quantum dot luminescence decay

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The study of the luminescence decay of colloidal semiconductor quantum dots is fundamentally important for their characterization and for a variety of applications (sensing, energy harvesting, lasing, theranostics, etc.), but the interpretation of the commonly obtained non-exponential decays [1] is far from trivial, hindering the understanding of the quantum dot system properties and progress in the potential applications. The assumption of multiple discrete exponential components with distinct lifetimes for resolving the decays is often arbitrary and may lead to ambiguity in their interpretation, since pre-exponential factors and decay times in non-exponential luminescence decays have clear physical meaning only in the simplest cases. [2] On the other hand, the non-exponential room temperature luminescence decay of colloidal quantum dots is often well described by a stretched exponential function. However, the physical meaning of the parameters of the function is not clear in the majority of cases reported in the literature. [3-5]

In this work, the room temperature stretched exponential luminescence decay of colloidal quantum dots is investigated theoretically in an attempt to identify the underlying physical mechanisms associated with the parameters of the function. The non-radiative transition processes in the colloidal quantum dots systems leading to a stretched exponential functional form of the decay are identified and shown to be linked with the stretching parameter β of the stretched exponential kinetics. It is shown that a stretched exponential functional form of the experimental luminescence decay is adequately described by $I(t) = \exp[-(t/\tau) - a(t/\tau)^\beta] = \exp(-t/\tau)I_{rel}(t)$, derived from realistic decay models of luminescence quenching. The use of this equation for fitting the experimental non-exponential luminescence decay of colloidal quantum dots at room temperature allows the separation into the exponential component of the decay, $\exp(-t/\tau)$ (with τ equal to twice the radiative lifetime of the bright state), and the non-exponential component, $I_{rel}(t)$, due to additional channels of energy relaxation. Recently, the room temperature luminescence decay of trioctylphosphine oxide-capped CdSe/ZnS quantum dots in solution was fitted using the equation above with $\beta = 0.5$. [6] This value of the stretching parameter was interpreted as the result of FRET with the quantum dots as energy donors and the role of energy acceptors played by high-frequency anharmonic vibrations of randomly distributed -CH groups of the capping molecules (Electronic-Vibrational Förster Resonance Energy Transfer). Here, it is shown that multiphonon relaxation cannot explain a stretched exponential functional form of the luminescence decay while such dynamics of relaxation can be understood in terms of long-range resonance energy transfer to acceptors (molecules, quantum dots, or anharmonic molecular vibrations) in the environment of the quantum dots acting as energy-donors or by contact quenching by acceptors (surface traps or molecules) distributed statistically on the surface of the dots. The fact that the parameter β takes different values depending on the mechanism of quantum dot luminescence quenching constitutes an invaluable tool for the experimenter, hence the novel approach presented in this work has important practical implications.

- 1) M. Jones *et al.*, *J. Mater. Chem.*, **2010**, 20, 3533.
- 2) M. N. Berberan-Santos *et al.*, *Chem. Phys.*, **2005**, 315, 171.
- 3) V. N. Soloviev *et al.*, *J. Am. Chem. Soc.*, **2001**, 123, 2354.
- 4) O. Schöps *et al.*, *J. Phys. Chem. B*, **2006**, 110, 2074.
- 5) S. Sadhu *et al.*, *J. Phys. Chem. C*, **2011**, 115, 16867.
- 6) E. N. Bodunov *et al.*, *Ann. Phys. (Berlin)*, **2016**, 528, 272.