Trapping-influenced photoluminescence intensity decay in semiconductor nanoplatelets

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Abstract. We present a diffusion-based simulation model for explanation of long time power-law decay of photoluminescence (PL) emission intensity in semiconductor nanoplatelets. In our model the shape of emission curves is an outcome of interplay of recombination, diffusion and trapping of excitons. At short times the excitons diffuse freely following the normal diffusion behaviour. The emission decay is purely exponential and is defined by recombination. At long times the transition into the subdiffusive motion happens and the emission occurs due to the release of excitons from surface traps. A power-law tail for intensity is a consequence of the release. The crossover from one limit to another is controlled by diffusion properties. The approach reproduces the properties of experimental curves measured for different nanoplatelet systems.

1. Introduction

Among novel semiconductor materials low-dimensional structures attract significant attention due to their peculiar optical properties [1, 2, 3]. The low-dimensional semiconductor nanocrystals such as quantum dots (QDs) and nanoplatelets (NPLs) receive considerable interest due to their high tunability. The outstanding features make NPLs promising candidates for making new generation of optical devices including flexible light emitters [4] and colloidal lasers [5]. Modern chemistry is capable of precise synthesis of a wide range of QDs and NPLs of various shapes and compositions [3, 6, 7]. The emission features of QDs and NPLs are mostly defined by the behaviour of excitons. In particular, the exciton diffusion and trapping can explain the PL power-law decay dynamics of CdSe and CdS NPLs [8, 9].

The high fraction of the surface in low-dimensional materials results in its crucial importance for response of the system to an external excitation. The PL spectrum and decay statistics are among examples of such response [10]. The PL signal is caused by the electron-hole recombination. Thus, reversible or irreversible trapping of excitons by surface trap states is
one of the main control factors of the decay statistics. The trapping can occur at dangling bonds which rearrange on the surface due to surface reconstruction and ligand adsorption [11].

NPL is a colloidal semiconductor nanocrystal which consists of a stuck of few atomic layers with areas of hundreds of $nm^2$ or more. With large surface to volume ratio these quasi-2D systems allow diffusion and trapping of excitons. For CdSe and CdS NPLs in Ref. [9] the power-law decay of PL intensity at long times was revealed in accordance with previous measurements of NPLs [12]. This decay was related with reversible trapping without radiation losses.

Most of the theoretical descriptions of PL intensity are built upon kinetic equations approach [9, 13]. The problem with purely kinetic techniques lies in the difficulty of exact interpretation of rates. This hinders a possible comparison with experiments. The exciton diffusion was also studied in free-standing and SiO$_2$ supported WS$_2$ monolayer semiconductors [14] and in 2D metal-halide perovskites [15]. In the latter case it was found to exhibit the transition from diffusive to a subdiffusive regime. This clearly points out to the existence of traps with a power-law distribution of trapping times [16]. Moreover, the subdiffusion due to trapping occurs for diffusion of copper adatoms on the graphene oxide support [17].

In our previous work [8] we have found that the power-law trapping of excitons indeed leads to power-law decay of PL intensity at long times. We supported the statement with theoretical arguments based on kinetic equations with a memory term as well as extensive simulations. Here we address the question of dependence of mean-squared displacement (MSD) of excitons on the density and trapping effects which occur at large densities of traps.

![Figure 1: 2D random walk model for exciton diffusion (see main text for description).](image1)

![Figure 2: Mean-squared displacement for exciton diffusion as a function of time on a double logarithmic scale in the absence of recombination.](image2)

2. Simulations. Mean-squared displacement of exciton diffusion. PL intensity.

In our simulations we study the motion of excitons with and without recombination. The former model (with the recombination) allows us to study the PL decay and compare the results with the experiment from Ref. [9]. We assume that the laser pulse produces excitons which then diffuse on the surface of a nanoplatelet. They can either be trapped or recombine with an emission of a photon. We assume that in the trapped state the recombination is not possible. We also neglect nonradiative recombination or exciton dissociation assuming high quantum yield. In the previous work [8] we have shown that 2D simulations produce qualitatively similar results to the 3D models with 3 to 5 atomic layers (which is a typical thickness in experiments [9]).
The diffusion is simulated as a discrete random walk on the 2D square lattice. We apply the periodic boundary conditions for the lattice $N \times N$. At every step, the simulated particle moves to one of the nearest neighbours (see Fig. 1) with equal probability $1/4$. The step duration is 1ps for all cases. The surface defects (traps) are positioned either regularly (periodically) or distributed randomly while the initial exciton position was sampled from a discrete uniform random distribution. The step duration was taken to be much smaller than the time scale of photoluminescence and trapping processes. The trapping occurs with certainty once the exciton hits the trap position. Importantly, in our model, the probability distribution of trapping times is non-exponential, having a power-law tail such that the average trapping time diverges. Such time distributions appear in the theory of transport in disordered media in the form of continuous time random walk model [16, 18]. This distribution of trapping times occurs, for example, in systems with an exponential distribution of depths of potential wells [19]. We sample the trapping times from the one-sided $\alpha$-stable distribution with the Lévy index $\mu$, $0 < \mu < 1$. Such distributions have long time asymptotics $\gamma(t) \sim \frac{t^{1+\mu}}{\Gamma(1+\mu)}$. The particle could be trapped again after it escaped a trap. Thus, a recurrent trapping is possible in our approach.

First we perform the simulations for the case without recombination, i.e. the number of excitons stays constant. This allows us to plot meaningful MSD in Fig. 2. The different curves correspond to different trap densities. The lattice is $4096 \times 4096$ with randomly distributed traps. The red curves are for 1 defect per 225 sites, the green are for 1/100 density of defects, the purple are for 1/25 and the cyan curves are for 1 defect per 9 cites. The continuous curves stand for the exponent of trapping times $\mu = 0.8$, the dash-dotted are for $\mu = 0.6$ and $\mu = 0.5$ is pictured by dotted lines. The discreteness of the curves at short times is a lattice discretisation effect. The curves were obtained by ensemble averaging over 10000 trajectories for each curve. One can see that at short times the diffusion is Brownian, $\langle r^2(t) \rangle \sim t$ while at longer times it becomes subdiffusive $\langle r^2(t) \rangle \sim t^\mu$. For high densities of targets (1/9 and 1/25) in the transition region the MSD has a plateau at times between $0.1 - 1$ ns. This clearly points out to a caging effect. In order to see this in more detail we plot the fraction of unbound excitons in Fig. 3. In this plot in all cases $\mu = 0.8$. The curves from the upper one to the bottom one correspond to the following densities of traps 1/225, 1/100, 1/25, 1/9. For high densities of traps corresponding to plateaus in Fig. 2 there is a dip in the number of free excitons. This fall and the following recovery of the free exciton concentration can be explained by the shorter characteristic timescale

Figure 3: The fraction of free excitons for different trap densities for the case without exciton recombination (see the text for details).

Figure 4: Comparison of photoluminescence intensities between simulations (blue data) and experiments (black dots) as reported in Ref. [9].
of trapping in comparison of that of the escape. Once the trapping becomes slower as for the upper two curves in Fig. 3, the dip disappears.

For the study of PL intensity decay (see Fig. 4) we assume that an exciton in a free state can recombine with a probability $p = 10^{-3}$ at each step neglecting any interactions between the excitons. As in Ref. [9] we collect the recombination data in time bins and normalise the curve by the value of the first bin. This normalisation in practice could be different in experiments, hence one could compare the curves qualitatively rather than quantitatively. In Fig. 4 the shape is the same for our simulation model and the digitised experimental data from Ref. [9] for core-shell CdSe-CdS NPLs with CdS forming the outer layers. The simulations were performed on a $10 \times 10$ periodic lattice with a single defect per lattice (i.e. 1 defect per 100 sites positioned periodically), the exponent $\mu = 0.8$, number of simulated particles (runs) $N_{\text{sim}} = 10^7$ and the binning $t_{\text{bin}} = 0.025\text{ns}$. At long times the same power law $\sim t^{-1-\mu}$ is present. At shorter times possibly due to a different binning no caging effect was found in experiments while it was produced in the simulations. The caging explains a recovery in the PL intensity in Fig. 4 at the timescale of around 1 ns. The comparison with [8] also shows that the simulations match the theory based on the non-Markovian kinetic equations with a memory term. The simulations also work for pure core NPLs as well [8].

3. Conclusions
We have shown that the simulation approach based on 2D random walk reproduces the main power-law decay features of photoluminescence in semiconductor nanoplatelets. MSD plots demonstrate a clear transition from Brownian diffusion at short times to subdiffusion at long times. At high density of traps a plateau in MSD can be observed at intermediate time scales. This happens due to caging of excitons by the traps. The subsequent release leads to a temporary increase of number of free excitons and to some recovery in PL intensity. Our simulation approach can be applied for the further analysis of exciton kinetics in semiconductor nanoplatelets to include more subtle effects such as exciton-exciton interactions.

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