Nonradiative recombination channel of dark excitons in colloidal CdSe nanoplatelets

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Abstract. Nonradiative recombination channel of spin-forbidden dark excitons in colloidal 4 ML thick CdSe nanoplatelets synthesized in argon and ambient atmosphere is revealed by theoretical analysis of time-resolved photoluminescence. The nonradiative recombination lifetime $\tau_{nr} \approx 11$ ns is found to be independent on nanoplatelets synthesis atmosphere. It is shown that the presence of the nonradiative recombination channel affects spin polarization of dark excitons and results in the time dependence of the circular polarization degree of photoluminescence in the external magnetic field.

1. Introduction

Recombination dynamics of excitons in ensembles of colloidal semiconductor quantum dots usually demonstrates multiexponential behavior [1]. The reason is dispersion of exciton lifetimes within an ensemble, trapping and de-trapping processes of photoexcited electrons and holes, nonradiative energy transfer between closely spaced quantum dots. As it was demonstrated recently, all these factors hold for colloidal quasi-two-dimensional CdSe nanoplatelets as well. It was shown that photoexcited excitons decay nonradiatively due to trapping of hole or electron to unpassivated surface states [2, 3]. Wherein in [3] trapping of carriers was shown to be reversible. The increase of trapping states number in nanoplatelets with larger lateral sizes was found in [4]. Influence of nonradiative Auger recombination was studied in [5-7]. Besides, it was shown that nanoplatelets tend to assemble in stacks – an analog of epitaxial superlattices. As the distance between nanoplatelets in stacks is of about 5 nm, an effective resonant energy transfer between neighboring nanoplatelets is realized [8-10].

The present paper is devoted to theoretical study of exciton recombination dynamics in ensembles of colloidal bare-core 4 ML ($\approx 1.2$ nm) thick CdSe nanoplatelets synthesized in argon (hereinafter referred as Sample 1) or ambient atmosphere (hereinafter referred as Sample 2), which were previously studied experimentally in [11]. For this purpose, characteristic lifetimes of photoluminescence (PL) decay, determined from three exponential fitting, are analyzed in terms of temperature and magnetic field dependences of dark exciton lifetime. For both studied samples the presence of nanoplatelets sub-ensemble with nonradiative recombination lifetime of dark excitons 11 ns is found. It is also shown that the presence of the nonradiative recombination channel affects polarization properties of dark excitons PL in the external magnetic field. It results in different degrees of circular polarization of PL in sub-ensembles with and without the nonradiative channel as well as in time dependence of the total degree of circular polarization of PL.
2. Model

2.1. Fitting of photoluminescence intensity decay
Experimental temperature dependences of PL decay in Samples 1,2 from [11,12] are fitted by sum of three exponential functions:

\[ I(t) = I_1(t) + I_2(t) + I_3(t) = A_1 e^{-t/\tau_1} + A_2 e^{-t/\tau_2} + A_3 e^{-t/\tau_3} \] (1)

here \( \tau_{1-3} \) and \( A_{1-3} \) are characteristic times and amplitudes of each decay component.

To study magnetic field dependence of PL decay and time dependence of degree of circular polarization of PL in external magnetic field \( (P_c) \) we perform three exponential fitting of polarized intensities difference \( \delta I(t) = I^+(t) - I^-(t) \) and sum \( I(t) = I^+(t) + I^-(t) \) with the same decay times. Here \( I^\pm(t) \) are PL intensities of \( \sigma^\pm \) circularly polarized light. Decay of intensities sum coincides with decay of total PL intensity and fitted by equation (1). The time dependence of intensities difference is fitted in a similar way:

\[ \delta I(t) = I^+(t) - I^-(t) = \delta I_1(t) + \delta I_2(t) + \delta I_3(t) = \delta A_1 e^{-t/\tau_1} + \delta A_2 e^{-t/\tau_2} + \delta A_3 e^{-t/\tau_3} \] (2)

here lifetimes \( \tau_{1-3} \) are the same as in equation (1). Note, that amplitudes \( \delta A_{1-3} \) can be negative.

Within this consideration time dependence of \( P_c \) is described by:

\[ P_c(t) = \frac{\delta I(t)}{I(t)} = \frac{\delta A_1 I_1(t)}{A_1 I(t)} + \frac{\delta A_2 I_2(t)}{A_2 I(t)} + \frac{\delta A_3 I_3(t)}{A_3 I(t)} = P_{c,1} \frac{I_1(t)}{I(t)} + P_{c,2} \frac{I_2(t)}{I(t)} + P_{c,3} \frac{I_3(t)}{I(t)} \] (3)

In the fitting of experimental data fast spin relaxation \( \tau_s \ll \tau_c \), i.e. time independent amplitudes \( \delta A_i \) are assumed. For this reason \( P_{c,i} \) should be considered as equilibrium degrees of circular polarization of excitons corresponding to each decay component. For arbitrary relation between \( \tau_s \) and \( \tau_c \) time dependence of \( \delta A_i \) should also be considered.

2.2. Temperature-driven population of bright exciton state
As it was demonstrated previously in [12,13], low-temperature PL of CdSe nanplatelets is determined by recombination of dark spin-forbidden excitons. The nearest bright spin-allowed exciton state is placed few meV above. Considering Boltzmann populations of bright and dark excitons and purely radiative recombination of excitons, one can find temperature dependence of long PL decay component for such a system [14]:

\[ \tau_{L}^{-1}(T) = \frac{\Gamma_A}{2} + \frac{\Gamma_F}{2} + \frac{\gamma_0}{2} \coth \left( \frac{\Delta E_{AF}}{2 k_B T} \right) - \frac{1}{2} \left( \Gamma_A - \Gamma_F + \gamma_0 \right)^2 + \gamma_0^2 \sinh^{-2} \left( \frac{\Delta E_{AF}}{2 k_B T} \right) \] (4)

where \( k_B \) is Boltzmann constant, \( \Gamma_{A,F} \) are recombination rates of bright and dark excitons, \( \gamma_0 \) is zero temperature relaxation rate of bright exciton, \( \Delta E_{AF} \) is energy splitting between bright and dark exciton states. For modelling of temperature dependence of long PL decay component, we use \( \gamma_0 \) and \( \Gamma_A \) determined in [12].

2.3. Mixing of bright and dark exciton states in transverse magnetic field
It is well established fact that transverse magnetic field results in admixture of bright exciton state to the dark exciton state [15]. As a result, the dark exciton lifetime (time of the long PL decay component) shortens in a following way [11]:


\[ \tau_2^{-1}(B) = \Gamma_e + \frac{(g_e \mu_B B \sin \theta)^2}{4 \Delta E_{AF}^2} \Gamma_A \]  

where \( \mu_B \) is Bohr magneton, \( \theta \) is an angle between nanoplatelet quantization axis and direction of magnetic field \( B \). In further analysis electron g-factor \( g_e = 1.7 \) determined in [16] is used.

3. Revealing a nonradiative recombination channel

Considering three decay components, we achieve a successful fit of the experimental time dependences of PL decay over the entire time range. The short decay component with \( \tau_1 = 0.3 \) ns is found to be temperature and magnetic field independent. It corresponds to recombination and relaxation from the bright exciton to the dark exciton state. However, analysis of polarization properties for this component is hampered by time resolution of experimental setup, which exceeds bright exciton lifetime [11]. Further we focus on the analysis of intermediate (\( \tau_2 \)) and long (\( \tau_3 \)) decay components.

Temperature dependences of lifetimes \( \tau_2 \) and \( \tau_3 \) determined from three exponential fitting for both samples are presented in figure 1 by open circles. Using equation (4) for temperature activation of the bright exciton we perform fitting of \( \tau_2(T) \) dependence (solid curves in figure 1) and determine the bright-dark exciton splitting \( \Delta E_{AF} = 4.6 \) meV – the same for both samples. In the paper [12] for the Sample 1 from biexponential fitting of temperature dependence of long PL decay component \( \Delta E_{AF} = 5 \) meV was determined, while \( \Delta E_{AF} = 4 \) meV was determined from fluorescence line narrowing method. The difference between \( \Delta E_{AF} \) determined within bi-ant three exponential fitting approaches is that biexponential fitting neglects intermediate decay component and gives an undervalued time of long decay component at low temperatures and thus overestimated \( \Delta E_{AF} \) determined from fitting.

![Figure 1](image-url)

**Figure 1.** Temperature dependences of lifetimes \( \tau_2 \) and \( \tau_3 \) for (a) Sample 1; (b) Sample 2. Open circles show lifetimes \( \tau_2 \) and \( \tau_3 \) obtained from three-exponential fitting of PL decay. Curves show results of theoretical modeling according to equation (4).

Temperature dependence of intermediate decay component is described within the same model in assumption of additional decay channel of dark excitons \( 1/\tau_2(T) = 1/\tau_3(T) + 1/\tau_{nr} \) with \( \tau_{nr} = 11 \) ns (dashed curves in figure 1). It is worth noting that lifetime \( \tau_{nr} \) is found to be the same for both studied samples, i.e. \( \tau_{nr} \) is independent from the nanoplatelets synthesis atmosphere. This result suggests for both samples under investigation the presence of two sub-ensembles of nanoplatelets, one of which contains an additional recombination channel of dark excitons.

Magnetic field dependences of lifetimes \( \tau_2 \) and \( \tau_3 \) determined from three exponential fitting are presented in figure 2 by open circles for both samples. Using equation (6) and refined \( \Delta E_{AF} \) value we performed modeling of \( \tau_2(B) \) and \( \tau_3(B) \) with the angle \( \theta \) being the only fitting parameter. It should be
noted that transmission electron microscopy studies of nanoplatelets orientation usually reveal two preferable orientations of drop-casted nanoplatelets – lying flat (corresponds to $\theta = 0^\circ$) or standing vertically in stacks (corresponds to $\theta = 90^\circ$). For the Sample 1 modelling of $\tau_3(B)$ dependence with $\theta = 90^\circ$ gives reasonable agreement with lifetimes extracted from three exponential fitting of PL decay (solid line in figure 2a). However, best fit for the Sample 1 is achieved with $\theta = 60^\circ$ and coincides with fit of $\tau_3(B)$ in assumption of random spatial orientation of nanoplatelets (dashed line in figure 2a). Best fit of $\tau_3(B)$ dependence for the Sample 2 is achieved with $\theta = 45^\circ$ (solid line in figure 2b). Assumption of random orientation in the case of Sample 2 overestimates shortening of lifetime $\tau_3(B)$ (dashed line in figure 2b). These results contradict simple scheme with bimodal spatial distribution with $\theta = 0^\circ$ and $\theta = 90^\circ$ of nanoplatelets on a substrate.

Let us now consider magnetic field dependence of intermediate decay lifetime $\tau_2 (B)$. Similar to the case of temperature dependence of lifetime $\tau_2$ we find for both studied samples $1/\tau_2 (B) = 1/\tau_2 (B)_r + 1/\tau_{nr}$ with $\tau_{nr} = 12$ ns for the Sample 1 and $\tau_{nr} = 11$ ns for the Sample 2. Thus, decay lifetimes $\tau_2$ again can be interpreted as lifetime of dark exciton in sub-ensemble of nanoplatelets with additional recombination channel.

To proof that recombination channel in sub-ensemble with dark exciton lifetime $\tau_2$ is nonradiative, analysis of absolute time-integrated PL intensity in applied magnetic field in the Sample 1 was performed. The time-integrated PL intensity experiences 2.5-times increase at $B = 15$ T (see figure 3). By means of three exponential fitting of absolute PL decays it is established that increase of total time-integrated PL intensity is

![Figure 2](image.png)

**Figure 2.** Magnetic field dependences of lifetimes $\tau_2$ and $\tau_3$ for (a) Sample 1; (b) Sample 2. Open circles show lifetimes $\tau_2$ and $\tau_3$ obtained from three-exponential fitting of PL decay. Solid curves show results of modeling with fixed angle $\theta$, dashed curves show result of modeling for randomly oriented ensemble.

![Figure 3](image.png)

**Figure 3.** Magnetic field dependence of relative contributions of PL decay components with lifetimes $\tau_2$, $\tau_3$ to total time-integrated PL intensity in the Sample 1.
governed by rise of the PL intensity of intermediate decay component, while time-integrated PL intensity or long decay remains almost unchanged. Increase of radiative recombination rate of the dark excitons in applied magnetic field accompanied by increases of PL quantum yield suggests presence of a nonradiative recombination. It allows us to conclude that characteristic lifetime \( \tau_{nr} \) corresponds to a nonradiative recombination channel in sub-ensemble of nanoplatelets with lifetime \( \tau_2 \).

4. Time dependence of circularly polarized photoluminescence
Let us consider, how presence of two sub-ensembles with dark exciton lifetimes \( \tau_2 \) and \( \tau_3 \) manifests itself in time dependence of degree of circular polarization of PL in applied magnetic field. Note, that PL decay at \( t < 1 \) ns is strongly influenced by contribution of short decay component with lifetime \( \tau_1 = 0.3 \) ns. As it was already mentioned, analysis of polarization properties for this component is hampered by time resolution of experimental setup, which exceeds bright exciton lifetime. Thus, we are interested in analysis of \( P_c(t) \) behavior at \( t > 1 \) ns.

Figure 4. Time dependence of sum (a,d), difference (b,e) of polarized PL intensities and degree of circular polarization of PL (c,f). Panels (a-c) correspond to the Sample 1, panels (d-f) correspond to the Sample 2. Dashed lines correspond to the sub-ensemble with lifetime \( \tau_3 \), dash-dotted lines correspond to the sub-ensemble with lifetime \( \tau_2 \).
For the Sample 1 magnetic field dependence is monotonic and saturates at $t \approx 30$ ns. Using three exponential fitting of sum (figure 4a) and difference of PL intensities (figure 1b) we find that $P(t)$ behavior in the time interval 1 – 30 ns is caused by emission of dark excitons with lifetimes $\tau_2$ and $\tau_3$ with different $P_c$ (figure 4c). The same result is found in the case of the Sample 2, but $P_c$ signs in two sub-ensembles are found to be opposite. It results in $P_c(t)$ sign reversal at $t \approx 10$ ns (figure 4f).

Thus, for both studied samples $P_{c,2}$ in sub-ensemble with nonradiative channel differs from $P_{c,3}$ in sub-ensemble with purely radiative recombination of dark excitons. As it was shown in [11], total time-integrated $P_c$ in the samples under investigation is affected by interaction of dark excitons with unpaired surface spins. It can be assumed that presence of the nonradiative recombination channel influence this interaction and results in difference between $P_{c,2}$ and $P_{c,3}$ in each sample.

5. Conclusions
It is shown that in the case of colloidal CdSe nanoplatelets three exponential fitting of low-temperature PL decay accompanied by analysis of temperature and magnetic field dependences of the dark exciton lifetime allows to identify nonradiative recombination channel of dark excitons. The nonradiative recombination channel lifetime $\tau_{nr} \approx 11$ ns is found to be independent on nanoplatelets synthesis atmosphere. Different degrees of circular polarization of PL and different recombination lifetimes of dark excitons in sub-ensembles with and without nonradiative channel result in time dependence of total degree of circular polarization of PL.

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