Magnetic circular polarization of photoluminescence of an inhomogeneous ensemble of colloidal nanocrystals

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Abstract. In this paper, we theoretically analyze the recombination and spin dynamics of excitons in an inhomogeneous ensemble of colloidal nanocrystals, which consists of several subensembles with different lifetimes and degrees of circular polarization of exciton photoluminescence (DCP). Each subensemble is described within a three-level model of interacting exciton states, including two excited states and a ground state. Various ratios of parameters, leading to a nontrivial time-dependent DCP and a difference in the integral and equilibrium DCP characteristics, are considered. It is shown that the presence of subensembles with different polarizations and lifetimes results in nonmonotonic dependence and a change in the sign of the DCP in magnetic field and as a function of time can occur. The theoretical model was implemented to describe the time dependences of the DCP in ensembles of colloidal CdSe nanoplatelets synthesized in the air and argon atmosphere.

1. Introduction
Spin properties of quantum dots, including colloidal ones, have been attracting researchers attention since the beginning of the century \cite{1, 2}. The spin relaxation time of charge carriers and exciton complexes is one of the important parameters under study. A typical method for determining the spin relaxation time of exciton complexes is the analysis of circularly polarized time-resolved photoluminescence (PL) in an external magnetic field with time resolution. Depending on the type of quantum dots, the observed rise times and establishment of asymptotic polarization vary from tenths to tens of nanoseconds \cite{2-5}. Previously, these times were interpreted as the spin relaxation times of excitons or trions. Such an interpretation is justified in the case of monoexponential PL decay (see Fig.1, dashed lines). However, as we show in this paper, inhomogeneity of the lifetimes and the degrees of polarization of excitonic complexes results in similar to the spin relaxation time dependence of the degree of circular polarization (DCP) (see Fig.1, solid lines). The possibility of such a scenario complicates analysis of exciton spin dynamics and determination of the spin relaxation time in the system directly from the time dependence of the DCP.

In the present work, we consider a model, representing an example of nanocrystals ensemble with inhomogeneous PL properties. This scenario is realized when the ensemble is formed by subensembles of nanocrystals with different, for instance, exciton lifetimes and DCPs. We consider various cases of model parameters and the resulting behavior of experimental data from...
Figure 1. Time dependences of DCP (a) and PL intensity (b) in the case of the homogeneous ensemble with $\tau = 1$ ns, $\tau_s = 5$ ns and $P_{as} = -0.5$ (dashed lines); in the case of inhomogeneous ensemble with $\tau_A = 3.3$ ns, $\tau_B = 1$ ns and $P_A = -0.77, P_B = -0.1$ (solid lines). DCP time dependence for homogenous ensemble is calculated according to equation (3) and for inhomogeneous one according to equation (5) in assumption of fast spin relaxation ($\tau_s \ll 1$ ns) in both subensembles.

The whole ensemble. It is shown that even in the simplest inhomogeneous ensemble with two independent groups nonmonotonic time and magnetic field dependences of DCP and its sign reversal can be observed.

The theoretical model, its description and the modeling results for some cases with fixed parameter sets are described in the next section. In section 3, the theoretical model is applied to the ensembles of colloidal CdSe nanoplates grown under various conditions for a description of the experimental data. In conclusion a potential generalization of the considered model and, as a consequence, the diversity of the possible behavior of DCP and PL intensity are discussed.

2. Theoretical model and results

The scheme of two arbitrary non-interacting subensembles $A$ and $B$ is shown in Figure 2. Each subensemble $(A, B)$ is described by a three-level model consisting of two excited states with populations $N_{1A,2A}$ and $N_{1B,2B}$, respectively. Energy splitting between excited levels is $\Delta E_{A,B}$. Relaxation processes between excited levels as well as recombination to ground level are illustrated by arrows on the scheme. In general, the order of all sub-levels in the ensemble can be arbitrary.

The number of nanocrystals in the subensemble counts populations of the excited levels and the ground one $N_{1A,B} + N_{2A,B} + N_{0A,B} = N_{A,B}$, where $N_{A,B}$ characterize the relative number of subensemble nanocrystals in the ensemble:

$$N_{A,B} = \frac{n_{A,B}}{n_A + n_B},$$

where $n_{A,B}$ is the total number of nanocrystals in the corresponding subensemble. We assume that the total number of nanocrystals in the subensembles is a constant $n_A, n_B = const$. It is the level populations that determine the characteristics observed in the experiment: the PL intensity and its DCP. Both pulsed and continuous wave excitation can be considered. In the case of pulsed excitation, the behavior of excited populations in time is found by solving a system of balance equations. For continuous wave excitation, we are interested in stationary solutions of the same system of equations. Further, we consider the case of equal relative number of nanocrystals in subensembles $N_A = N_B$ and the same exciton generation rate.
Figure 2. A scheme of two independent subensembles $A, B$ including four excited levels. $N_{1A}, N_{2A}, N_{1B}, N_{2B}$ are the populations of corresponding excited levels, $N_{0A}, N_{0B}$ are the populations of ground state in corresponding subensembles, $\Delta E_{A,B}$ are the energy splittings in subensembles. Schematic representation of the photoluminescence is shown on the right.

First of all, we consider one homogeneous ensemble providing the description of a subensemble separately. We introduce the DCP as follows:

$$P_c = \frac{I_1 - I_2}{I_1 + I_2},$$

(2)

where $I_{1,2} = \Gamma_{1,2}^{\text{rad}} N_{1,2}$ are the photoluminescence intensities from corresponding levels, where $\Gamma_{1,2}^{\text{rad}}$ are the radiative recombination rates from the levels.

This characteristic attains its asymptotic value $P_c^{\text{as}}$ at long times. The integral value $P_c^{\text{int}}$ is obtained by replacing the intensities with their time integrals after pulsed excitation and is equivalent to the stationary value under continuous wave excitation.

For clarity, in this paper, we consider the simplest case when the recombination rates of the excited states including both radiative and non-radiative channels coincide $\Gamma_{1,2} = \Gamma = \Gamma^{\text{rad}} + \Gamma^{\text{nr}}$. The intensity decay is described by the monoexponential dependence $I = \exp(-t/\tau)$, where $\tau = 1/\Gamma$. This case corresponds to the dashed line in Figure 1(b). The DCP time dependence in the case of monoexponential PL decay is shown by the dashed curve in Figure 1(a), and can be expressed as:

$$P_c(t) = P_c^{\text{as}}(1 - e^{-\frac{t}{\tau_s}}),$$

(3)

where $\tau_s$ is the relaxation time between excited levels. The asymptotic value $P_c^{\text{as}}$ and integral value $P_c^{\text{int}}$ are determined as follows:

$$P_c^{\text{as}} = -\tanh\left(\frac{\Delta E}{2k_B T}\right), \quad P_c^{\text{int}} = \frac{P_c^{\text{as}}}{1 + \frac{\tau_s}{\tau}}$$

(4)

where $k_B$ is the Boltzmann constant, $T$ is the temperature. The splitting $\Delta E$ can be either existing without external factors, or a Zeeman splitting induced by magnetic field $B$ directed along the anisotropy axis of the nanocrystal. The latter at a fixed magnetic field is determined by the exciton $g$-factor $\Delta E = g_{ex} \mu_B B$, where $\mu_B$ is the Bohr magneton.

For an inhomogeneous ensemble, the full DCP is expressed by DCP in the subensembles $P_{A,B}$ with the corresponding weights:
\[
P_c = P_A \frac{I_A}{I_A + I_B} + P_B \frac{I_B}{I_A + I_B},
\]

where \( I_{A,B} = \Gamma_{A,B}^{rad}(N_{1A,B} + N_{2A,B}) \). Notice that Equation (5) is relevant for both time-dependent \( P_c(t) \) and time-integrated \( P_c^{\text{int}} \) values. In the first case we need to calculate \( P_c \) using time dependences of \( P_{A,B} \) and intensities \( I_{A,B} \) of separated subensembles. In the second case we should replace all variables with their integral values.

The simplest case of inhomogeneity is the difference of lifetimes in the subensembles A and B only. For the sake of clarity, we assume in the modeling that only radiative recombination of charge carriers in both subensembles is possible. For ensemble consisting of two subensembles, this results in the emergency of bieponential PL decay of the whole ensemble. The illustration is shown in Figure 1(b) by solid curve, where \( \tau_A = 3.3\text{ns} \) and \( \tau_B = 1\text{ns} \). However, in this case \( P_c = P_A = P_B \) is not affected by inhomogeneity. Generally, the lifetime difference can be also related to nonradiative recombination rates. When the number of subensembles significantly increases, or there exist additional recombination channels of excitons related with trapping and de-trapping processes of charge carriers, PL decay becomes essentially multiexponential. Decay of PL intensity in this case usually analyzed using Kohlrausch function [6].

The second case of inhomogeneity is related to subensembles with the same lifetimes but different degrees of polarization. For example, this can occur in the case of different energy splittings in separate groups of nanocrystals having different orientation of the quantization axis relative to the direction of the external magnetic field and therefore, by inequality of the effective \( g \)-factors. The asymptotic value \( P_c^{\text{as}} \) and integral value \( P_c^{\text{int}} \) in this case equal to sum of \( P_{A,B} \) from each subensemble weighted by corresponding relative intensity. An example of such inhomogeneity was studied in [7]. Time dependence of \( P_c \) in these both cases reflects the spin relaxation between excited levels.

Now let us consider two subensembles that differ in both lifetimes (which are much longer than spin relaxation time \( \tau_s \) in each subensemble) and asymptotic degrees of polarization \( P_c^{\text{as}} \). Depending on the relation between \( g_A \) and \( g_B \), including their signs, nonmonotonic magnetic field dependence of \( P_c^{\text{int}} \) can occur. Some examples are shown in Figure 3 under assumption of zero-splitting in the absence of magnetic field: (a) \( g \)-factors are both positive, \( g_A = 1, g_B = 4.5 \) for the dashed curve and \( g_B = 0.15 \) for the solid one; (b) \( g_A \) is still unity, but \( g_B \) values have the same modules but opposite signs. We note that these results are also valid for the case when lifetimes in subensembles are the same.

At the same time, the asymptotic value \( P_c^{\text{as}} \) (chain curve in Figure 3) of the whole ensemble reflects the polarization of the long-living subensemble A and its behavior is determined by Equation (4) (Figure 3).

Solid line in Figure 1(a) reflects the time behavior of such inhomogeneity. Time dependent degree of polarization calculated at \( B = 5\text{T} \) (corresponds to vertical black dotted lines in Fig.3) is shown in Figure 4. Calculation is performed with the same set of \( g \)-factors as in Fig.3. Lifetimes of the subensembles are different and \( \tau_A = 10\text{ns}, \tau_B = 3.3\text{ns} \). One can see, that depending on the set of parameters either spin relaxation-like behavior (Figure 4, solid red curves) or nonmonotonic, including DCP sign reversal, behavior (Figure 4, dashed orange curves) can be expected.

3. Experimental example

In the paper [8] photoluminescence (PL) of excitons confined in bare core CdSe nanoplatelets synthesized in argon and ambient atmosphere was studied. Three exponential fitting of photoluminescence decay in both types of nanoplatelets reveals the presence of two subensembles (A and B) with different exciton lifetimes (see Figure 5a,c). After the initial stage of fast decay (\( t \approx 1\text{ns} \)) corresponding to the relaxation of bright excitons, recombination of dark
Figure 3. Magnetic field dependances of $P^{\text{int}}$ (dashed and solid curves) and $P^{\text{as}}$ (chain line) in various relations between $g_A$ and $g_B$: (a) $g_A = 1$, $g_B = 4.5$ (dashed), $g_B = 0.15$ (solid) (b) the same as in (a) but with opposite signs of $g_B$.

Figure 4. Time dependences of $P_c(t)$ with the same $g-$factors as in Figure 3 respectively in fixed magnetic field $B = 5$T and $\tau_A = 10$ns, $\tau_B = 3.3$ns. Dotted lines show $P^{\text{int}}_c$ and $P^{\text{as}}_c$ values from Figure 3 in $B = 5$T.

excitons in subensembles A and B determines long-term PL decay. The same fitting procedure applied to the difference between intensities of $\sigma^-$ and $\sigma^+$ polarized PL allows us to determine asymptotic values $P_A, P_B$ in both subensembles. Calculations according to equation (5) with $I_{A,B}(t)$, $P_{A,B}$ determined from fitting procedure give excellent agreement with experimental dependences of $P_c(t)$ for both types of nanoplatelets (see Figure 5b,d). In these particular cases, inhomogeneity of exciton lifetimes and DCPs is related to the presence of surface traps in a fraction of nanoplatelets in ensemble [8]. Thus, we demonstrate that long-term time dependences of $P_c(t)$ in CdSe nanoplatelets are fully described within our model and do not relate to exciton spin-relaxation, which occurs on sub-nanosecond timescale [8].

4. Conclusion

In conclusion, the proposed approach allows one to interpret the available experimental data and predict the possibility of experimental observation of nontypical time and magnetic field dependences of the photoluminescence characteristics. The analysis of the model including two subensembles showed that both the nontrivial behavior of DCP and its slow growth in time can be ascribed to heterogeneity, rather than relaxation processes in the system. It is important to
Figure 5. Time dependences of photoluminescence intensity (a,c) and degree of circular polarization (b,d) in bare core CdSe nanoplatelets synthesized in argon (a,b) and ambient (c,d) atmosphere [8]. Dashed lines show results of three exponential fitting. Dotted lines show contribution of A and B subensembles to total intensity ($I_A(t), I_B(t)$) and corresponding asymptotic degrees of circular polarization ($P_A, P_B$).

take into account such scenarios when studying ensembles of colloidal nanocrystals. The presence of a larger number of subensembles will also affect the characteristics considered. Under such conditions, their behavior can be even more complicated.

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