Photoinduced carrier dynamics in colloidal CdSe/CdS nanoparticles

V G Nikiforov1,2, A V Leontyev1, A G Shmelev1, D K Zharkov1, V S Lobkov1 and V V Samartsev1

1Zavoisky Physical-Technical Institute, FRC Kazan Scientific Center of RAS, Sibirsky tract, 10/7, 420029, Kazan, Russia
2 Corresponding author: vgnik@mail.ru

Abstract. We have studied picosecond dynamics of photo-induced charge carriers in CdSe/CdS nanoparticles with sizes of 2.0 and 2.9 nm in toluene colloidal solutions using femtosecond up-conversion spectroscopy. The kinetics of nanoparticles luminescence excited by laser pulses of 50 fs duration at 350 nm were observed. The simulation of experimental data showed that electron thermalization occurs within 0.5 ps, while recombination processes have characteristic times of 5 and 20 ns, although these cannot be unequivocally identified using the simplest recombination model with direct transitions and single type of traps. However, a comparative analysis indicates a fundamental difference in the mechanisms responsible for the dynamics of charge carriers in the time interval up to 5 ps after laser excitation, which we associate with different structures of traps in 2.0 and 2.9 nm particles.

1. Introduction
Semiconductor quantum dots (QDs) with a core/shell structure are of particular interest both for fundamental physics and from the point of view of creating various optoelectronic devices (memory devices, emitters, solar panel elements, etc.) [1-5]. Among the numerous types of synthesized nanoscale heterostructures nanoparticles consisting of a CdSe core and a CdS shell are among the most studied QDs due to the fact that the luminescence wavelength of CdSe core can be adjusted across the visible range by varying its size. The CdS shell with a wider band gap than that of CdSe core prevents the transport of charge carriers to the surface, where they could be captured by defects and quenched.

It should be noted that the photoexcited charge carriers are distributed in accordance with the electronic structure of QDs. It is the dynamics of these carriers that determine the properties of QDs in photocatalytic and photovoltaic devices. Consequently, the factors influencing their dynamics and charge separation processes are decisive in terms of the design and optimization of these devices. In order to study the photophysical properties of QDs, optical spectroscopy methods including time-resolved luminescence detection based on up-conversion and femtosecond pump-probe experiments are extensively used. These kinds of experiments allow us to observe the processes of charge carriers cooling, electron-phonon interaction, charge capture by lattice defects, charge recombination, etc. [6-13].

Still, a number of questions regarding the mechanisms responsible for nonradiative processes in CdSe/CdS QDs remain open [14–16]. In particular, the participation of traps in nonradiative losses in QDs is a subject of ongoing theoretical and experimental research [15–18]. Various schemes of photophysical processes responsible for nonradiative losses in QDs are currently being discussed, but
there is still no detailed understanding of the structure of the most common traps, as well as the relative role of phonons, electron transfer processes and Auger effects in charge carrier recombination [14-16].

In this paper, we present the results of studying the dynamics of photoexcited charge carriers by detecting the luminescence of CdSe/CdS nanoparticles in a colloidal solution in the picosecond range using femtosecond up-conversion technique. We have found that the decay of the luminescence kinetics is two-exponential, and essentially depends on the size of the nanoparticles. It is shown that the simplest model, which only takes a single type of defects into account, allows simulating the experimental results with sufficient accuracy, however the following interpretation of the results may not agree with the conclusions of [19-21].

Figure 1. The luminescence kinetics of 2.0 and 2.9 nm CdSe/CdS QDs in a colloidal toluene solution detected at the wavelengths of 500 nm (top) and 570 nm (bottom). The solid line shows the experimental data, the dotted line indicates the simulation result.
2. Experimental
Details of the preparation of colloidal toluene solutions of CdSe/CdS QDs can be found in [22]. In this study we have used two solutions with QDs sizes of 2.0 and 2.9 nm, which were placed in 1 mm quartz cuvettes. In order to study the dynamics of photoinduced charges in QDs, an up-conversion technique was used allowing the detection of time-resolved luminescence signal in the picosecond range. The QDs luminescence was excited by the second harmonic of Ti:Sapphire laser emission (pulse duration of 50 fs, carrier wavelength of 770 nm, mean power of 450 mW) with a wavelength of 385 nm and mean power of 20 mW. The residual 350 mW radiation at 770 nm was passed through a delay line and used as a probe: the luminescence was collected by a parabolic mirror and focused onto a 0.5 mm thick BBO crystal along with a probe beam to generate a sum frequency emission. This signal was spectrally selected by a monochromator and then detected in photon counting mode.

3. Results and discussion
The recorded signal is shown in Fig. 1. It is a convolution of the temporal shapes of luminescence signals at 500 nm and 570 nm (for 2.0 and 2.9 nm QDs, respectively) and a probe pulse. Taking into account the laser pulse duration of 50 fs, we can conclude that the instrument function width (order of 100 fs) is significantly smaller than the times of both luminescence rise and decay.

\[ n_2(t) \propto \frac{k_{12}}{k_{12} - (k_{23} + k_{20})} \left( e^{-(k_{23} + k_{20})t} - e^{-k_{12}t} \right), \quad (1) \]

\[ n_3(t) \propto \frac{k_{12}k_{23}}{k_{23} - k_{12}} \left( \frac{e^{-k_{30}t} - e^{-k_{23}t}}{k_{30} - k_{23}} - \frac{e^{-k_{30}t} - e^{-k_{12}t}}{k_{30} - k_{12}} \right). \quad (2) \]

![Figure 2. Energy level structure in CdSe/CdS QDs.](image-url)
Assuming the recorded luminescence intensity is due to transitions (2-0) and (3-0), the expression for the luminescence kinetics will be:

\[ I(t) \propto n_2(t) + n_3(t), \quad (3) \]

which implies a two-exponential decay with decay times \( (k_{23} + k_{20})^{-1} \) and \( k_{30}^{-1} \). For the sake of simplicity of the experimental data description in expressions (1) and (2) in the picosecond range, the 50 fs laser pump pulse was assumed to have a \( \delta \) pulse shape, i.e. excitation was instant.

The simulation of experimental data is shown in Figure 1. The value of the rate constants in expressions (1) and (2) was determined while minimizing the sum of the standard deviations of the theoretical curve from the experimental data \( \sum_{i} (y_i \cdot I(t_i) - f_i)^2 \), where \( f_i \) is the value of the normalized signal at a delay \( t_i \), \( \gamma \) is the normalization constant. The analysis showed that the optimal parameters are the following sets of constants for 2.0 nm CdSe/CdS QDs: \( k_{12} = 4.5 \times 10^{12} \text{s}^{-1}, k_{23} = 8.3 \times 10^{12} \text{s}^{-1}, k_{30} = 9.1 \times 10^{10} \text{s}^{-1}, k_{30} = 5.5 \times 10^{10} \text{s}^{-1} \); and for 2.9 nm QDs: \( k_{12} = 2 \times 10^{12} \text{s}^{-1}, k_{23} = 6 \times 10^{11} \text{s}^{-1}, k_{20} = 7.2 \times 10^{11} \text{s}^{-1}, k_{30} = 2.7 \times 10^{10} \text{s}^{-1} \).

As it can be seen in Figure 1, the indicated sets of constants describe the experimental data well, which allows us to draw the following conclusions. The luminescence intensity rise occurs due to the process of electron thermalization, with the result that after 0.5 ps they are at the bottom of the conduction band. Then two processes take place: capturing of electrons by traps and recombination of electrons and holes. These processes correspond to the ‘fast’ decay of the luminescence kinetics up to 5 ps. The ‘slow’ decay after 5 ps is due to the processes of radiative and nonradiative relaxation of the excited traps states, indicated by level (3) in Figure 1, with a relaxation time of the order of 20 ps.

Despite the satisfactory fitting of the experimental data, we believe that the presented mathematical model lacks a number of important photophysical processes in nanoparticles. For example, it implies the presence of an effective process of radiative relaxation of trapped electrons. At the same time, it is believed that the energy levels of all traps are so close to the energy level of the bottom of the conduction band that they are difficult to separate spectrally. The presence of these specific defects acting as traps requires additional theoretical and experimental substantiation. On the other hand, it was shown in [19-21] that the luminescence kinetics from level (2) in CdS/CdSe nanoparticles do have components in the nanosecond range. This also does not agree with the results of the calculation based on the presented model.

Nevertheless, in our opinion, this model allows us to make a correct estimate of the time of electron thermalization in the conduction band. This fact indicates that the dynamics of photoinduced charge carriers is very different in 2.0 nm and 2.9 nm QDs. Firstly, the thermalization rate in 2.0 nm QDs is more than two times higher than that in 2.9 nm QDs. Secondly, for 2.0 nm QDs, the rate constant \( k_{30} = 9.1 \times 10^{12} \text{s}^{-1} \) responsible for the ‘fast’ decay of the luminescence kinetics up to 5 ps, is two times higher than the thermalization rate \( k_{12} = 4.5 \times 10^{12} \text{s}^{-1} \). Meanwhile, in the case of 2.9 nm QDs, the rate constant \( k_{20} = 7.2 \times 10^{11} \text{s}^{-1} \) is three times lower than the thermalization rate \( k_{12} = 2 \times 10^{12} \text{s}^{-1} \). These facts directly indicate different photophysical mechanisms that determine the dynamics of photoinduced charge carriers in QDs of different sizes up to 5 ps after the excitation. We believe that the main reason for this is the essentially different structures of defects and traps formed during the synthesis of 2.0 nm and 2.9 nm QDs, and in order to reveal those additional detailed studies are required.

4. Conclusion

The results of the studies of photophysical processes in the picosecond range in CdSe/CdS nanoparticles with sizes of 2.0 nm and 2.9 nm in colloidal toluene solutions are presented. A two-exponential nature of the decay of the luminescence kinetics was shown. It was demonstrated that the simplest model, which takes a single type of traps into account, allows satisfactory fitting of experimental data, however the interpretation of a certain parameters does not agree with the results of [19-21]. We believe that the presented mathematical model requires further elaboration, in particular to include, along with direct transitions (from the higher level to the next lower one), reverse
transitions due to thermal activation at room temperature. Nevertheless, the model made it possible to conclude that the mechanisms responsible for the dynamics of photoinduced charge carriers in QDs with sizes of 2.0 nm and 2.5 nm up to 5 ps after the excitation differ significantly, indicating, as we believe, a significant difference in the structures of traps, formed after the QDs synthesis.

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