Kinetics of Cascade Photoluminescence of Exciton Complexes in CdSe/CdS/CdZnS Quantum Dots

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We demonstrate that in the study of time-resolved photoluminescence the signatures of biexcitons in QDs can be manifest themselves even when the system is excited by long laser pulses with their duration of the order of several tens of picoseconds. To describe the results of our measurements we propose an elegant theoretical model. It is based on the introduction of auxiliary sources in the rate equations. The parameters of the sources are determined by fitting the analytical solution of these equations that describes the full emission of the system to the experimental results obtained. Having found the parameters of the auxiliary sources we can determine the temporal dependences of the radiation from excitons and biexcitons separately. We find the spectral positions of the exciton and biexciton emission bands, their widths, and the biexciton binding energy.

Keywords — quantum dots; photoluminescence; exciton; biexciton; binding energy; rate equations

I. Introduction

Multiexciton states in semiconductor quantum dots (QDs) with two or more excited electron-hole (e-h) pairs play an important applied role in such devices as lasers, photodetectors, solar cells, light-emitting diodes, and photon-pair sources [1–6]. Owing to the enhanced interaction of charge carriers under conditions of quantum confinement, higher excitons in QDs are scattered mainly through a nonradiative Auger process, and effective photoluminescence (PL) can be realized only by single excitons [1,7]. In the simplest two-exciton case, the biexciton in the ordinary CdSe QD can emit a photon during its subnanosecond Auger lifetime [8], which is much shorter than the radiation lifetime of tens of nanoseconds for the remaining single exciton. This transient presence of biexcitons is not pronounced in time-integrated (cw) PL spectra and necessitates the use of ultrafast spectroscopic techniques and high-sensitivity experiments to detect their fundamental optoelectronic properties, such as PL lifetimes, spectral positions, and binding energies [9–15].

The relaxation kinetics of two, three, and four e-h pairs in CdSe QDs were studied in [1] using a femtosecond transient absorption spectroscopy. It was shown that the relaxation cascades are mediated by Auger processes. The studies of ultrafast PL of colloidal CdSe/ZnS QDs were carried out in [10]. A new transient emission band red shifted by about 10–30 meV relative to the band-gap luminescence was extracted. The authors attributed it to the neutral biexciton with very short measured lifetimes (⌴ 100 ps for QD radius of 3.5 nm) in agreement with transient absorption studies of the two e-h pairs in [1]. The bands associated with the radiative decay of the single exciton, biexciton, and triexciton in the transient spectra of time-resolved PL were clearly observed in [11] for CdSe QDs in hexane. The detailed study of the multiexcitonic effects in CdSe QD based on the energetics, the lifetimes, and the pump-power dependence of various emission bands was presented in [12,13]. All measurements in [10-13] were performed at room temperature. We also draw attention to the papers [14-17] on this issue. As shown in [10,11,13], the positions of the exciton and biexciton bands do not depend on the pump power indicating that each of them is due to the emission from QDs in the well-defined one- and two-particle states.

To explain the time evolution of the system, the following scenario was expected. Initially, the sample is excited by an ultrashort laser pulse, so that in a selected QD some quantity of e-h pairs with the energy much higher than the QD energy gap is generated. For example, in [11] a pulse of 300 fs at 400 nm was used. After that, the system is left to itself (without any external influence). At the next stage the electrons and holes relax to the lowest states on a picosecond time scale [18-22] due to the fast intraband Auger-like and phonon emission processes. Then, at the third stage, a relatively slow process of recombination of e-h pairs occurs within a time interval from several tens picoseconds to ten nanoseconds. This final stage of the time evolution of the system can be described by a simple set of coupled rate equations [11] and reflects in the time-resolved kinetics of PL studied in [10-13].

After rapid intraband relaxation, a quasi-equilibrium state is established in the sample. In different QDs from one (exciton) to several (multiexciton) e-h pairs can be excited depending on the excitation intensity. Their number in the selected QD is described by the Poisson statistics [18]. The Poisson distribution is valid if the probability of generating the e-h pair in a QD is independent of the number of e-h pairs already existing in it [23]. Therefore, it is applicable for the case of ultrashort pulse excitation well above the PL band-edge and makes it possible to supplement the set of rate equations by the initial conditions [11].

The population of the QD states can change very rapidly, and a high time resolution is needed to study its dynamics. Therefore, in the experiments [10-13] ultrashort laser pulses and high-resolution measuring equipment were used. In this paper we report that the time-resolved photoluminescence (PL) from biexciton states in QD may be observed by more modest measuring means and with laser pulse whose duration is comparable with the lifetime of biexcitons. We find spectral positions of the exciton and biexciton emission bands, their widths, and the biexciton binding energy.

The use of long pulses significantly changes the physical picture. The intraband and interband Auger-like and relaxation processes continue to occur during the entire duration of the pulse. Therefore, the system emits photons in a substantially nonequilibrium state. Under these conditions, the Poisson distribution can no longer be accepted as the initial condition for the equations describing the kinetics of the system. Instead, in order to describe the results of our measurements we are forced to introduce auxiliary sources into these equations. The parameters of the sources are determined by fitting the solution of the equations that describe the full emission of the system to the experimental results obtained. Having found the parameters of the auxiliary sources we can determine the temporal dependence of the radiation from excitons and biexcitons separately.

II. Experiment

We used highly luminescent CdSe/CdS/CdZnS colloidal QDs prepared by a standard chemical synthesis method [24] that were dispersed in low concentration into toluen in a 1 mm length quartz cuvette. The two-shell structure of QDs provides an effective retention of wave functions of electrons and holes inside QDs, as well as high photochemical stability. The inner shell located between the core and the outer shell allows one to reduce the mechanical stresses inside the QD, since CdS has a lattice parameter intermediate between CdSe and CdZnS. This, allows obtaining a significant quantum yield of these QDs (up to 85%).

A sample with the maximum luminescence of 628 nm was studied by transmission electron microscopy, optical absorption spectroscopy, and luminescence spectroscopy using the calibration given in [25]. It was determined that the diameter of the CdSe nucleus of QD is 5.4 nm with the size dispersion of 8%. The thickness of the CdS/CdZnS shell is 2.6 nm. The QDs PL was excited by a single 30 ps pulse of the second harmonic (539 nm) of a mode-locked $YAlO_3$: Nd^{3+} laser at room temperature. The spectral decomposition of the PL signal collected from the front face of the cuvette was performed using a polychromator. The PL kinetics was recorded by a streak camera. The PL spectrum is located along the streak camera entrance slit. The image of time-resolved PL spectrum of QDs obtained on the streak camera screen was registered by a digital camera. The spectral resolution was about 5 meV and 9 meV for the time-integrated mode and the time-resolved mode, respectively, and an overall time resolution of about 40 ps was obtained. The time-resolved kinetics of PL is presented in Fig. 1.

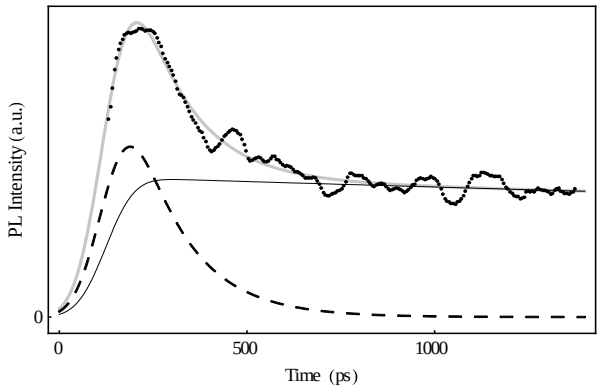

Fig. 1. The observed temporal dependence of the PL intensity is represented by dots. The thick gray line corresponds to the analytical solution of the coupled rate equations explained in the text. The thin lines describe the PL kinetics from excitons (solid line) and biexcitons (dashed line) separately. The exciting pulse with duration of 38 ps is centered at 154 ps.

The analysis of the time evolution of the main (low-energy) PL bands showed that the fitting curve for PL intensity decay can be decomposed into a sum of two exponents with different decays times. This means that only two types of emitters are excited in the system (biexcitons and single excitons) whose spectral bands strongly overlap. Their kinetics is governed by a stepwise two-cascade process and single-exponential decays [26-29]. The measured decay time of the exciton is 10 ns. Because of the highly effective interband Auger processes, the nonradiative decay of biexcitons is very fast and occurs within 135 ps.

Fig. 2 shows a transient PL spectrum extracted at the time 208 ps using a 50 ps integration window.

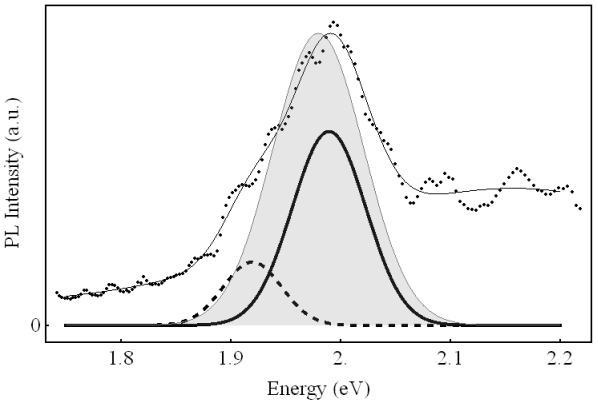

Fig. 2. Transient PL spectrum recorded at t=208 ps integrated within 50 ps gate (dots) and its fitting curve (thin solid line). The PL spectra for excitons (thick solid line) and biexcitons (thick dashed line). The normalized time-integrated PL spectrum is shown as a shaded area.

The asymmetric fitting curve can be decomposed into two main peaks centered at 1.92 eV and 1.98 eV. The spectral widths of these peaks are 38 meV and 47 meV, respectively. In the PL spectrum extracted at the time 800 ps there is only one peak at 1.98 eV whose position coincides with that one for

time-integrated PL. We associate this peak with the radiative decay of the single excitons. Accordingly, the rapidly vanishing peak at 1.92 eV appears as a result of the radiative decay of the biexcitons [19] whose lifetime is strongly limited by Auger processes. Consequently, the binding energy of the two excitons in the biexciton has a giant value ≈ 60 meV. The both spectral bands strongly overlap.

III. THEORETICAL DESCRIPTION

We assume that all microscopic processes occurring in the system can be divided into fast and slow ones. The rapid processes include an Auger-like process of scattering of the electron by the hole and subsequent intraband relaxation of the scattered hole with emission of phonons [18-21]. This sequence of processes leads to the fact that electron-hole pairs excited by a laser pulse near the $1P_e$-$1P_{3/2}$ state convert to excitons in the lowest state $1S_e$-$1S_{3/2}$. If the number of excitons in this state reaches the maximum value of two we can say that a biexciton is formed.

We can consider the annihilation of one of the electron-hole pairs in this state as a decay of the biexciton resulting in the creation of an exciton and a photon. The remaining pair can also annihilate; this means a radiative decay of the exciton. We assume that the both decay processes are slower than those indicated for the formation of excitons and biexcitons.

If the duration of the exciting laser pulses exceeds the time of formation of excitons and biexcitons in the ensemble of QDs, their slow temporal dynamics can be investigated by means of time-resolved luminescence. For its description we use simple rate equations

$$\frac{dn_{xx}}{dt} = -\frac{n_{xx}}{\tau_{xx}} + J_{xx}, \quad \frac{dn_x}{dt} = \frac{n_{xx}}{\tau_{xx}} - \frac{n_x}{\tau_x} + J_x, \quad \frac{dp_{xx}}{dt} = \frac{n_{xx}}{\tau_{xx}}, \quad \frac{dp_x}{dt} = \frac{n_x}{\tau_x}, \tag{1}$$

where n_{xx} and n_x are the numbers of biexcitons and excitons; p_{xx} and p_x are the numbers of photons with frequencies ω_{xx} and ω_x; τ_{xx} and τ_x are the decay times of biexcitons and created of them excitons; $\tau_R = \tau_x / 4$ is the radiative decay time of a biexciton [15-16]; the sources $J_{xx}(t)$ and $J_x(t)$ in the right-hand side of the equations (1) describe the formation of biexcitons and excitons, respectively. The radiation intensities I_{xx} and I_x at the frequencies ω_x and ω_{xx} are determined as $I_{xx} \propto n_{xx} / \tau_R$ and $I_x \propto n_x / \tau_x$.

The sources $J_x(t)$ and $J_{xx}(t)$ introduced into equations (1) do not have the nature of an incoming laser pulses, since excitation of the excitons and biexcitons into the state $1S_e$-$1S_{3/2}$ occurs indirectly via complex relaxation processes. Probably the only thing we can say about these sources is that they have a finite duration: they differ from zero within a finite period of time. For simplicity, we will assume that the both sources have a Gaussian shape $J_i(t) = J_i \exp\left[-\left(t - t_{0i}\right)^2 / T_i^2\right]$ ($i = xx, x$) and each of them is characterized by its position, width, and amplitude. We find all these parameters by comparing the solutions of equations (1) with the results of our measurements.

The exact solution $n_i(t)$ of the set of linear equations (1) satisfying the initial conditions $n_i(-\infty) = 0$ can be presented in the form

$$n_{xx}(t) = \alpha\tau_R \frac{\tau_{xx} - \tau_x}{\tau_{xx} + \tau_R - \tau_x} e^{-(t - t_{0xx})/\tau_{xx}} \frac{1}{2}\operatorname{erfc}\left(\frac{t_{0xx} - t}{T_{xx}} + \frac{T_{xx}}{2\tau_{xx}}\right), \tag{2}$$

$$\begin{aligned} n_x(t) = -\alpha\tau_x \frac{\tau_R}{\tau_{xx} + \tau_R - \tau_x} \Bigg(& e^{-(t - t_{0xx})/\tau_{xx}} \frac{1}{2}\operatorname{erfc}\left(\frac{t_{0xx} - t}{T_{xx}} + \frac{T_{xx}}{2\tau_{xx}}\right) + e^{-(t - t_{0xx})/\tau_x} e^{(T_{xx}/2\tau_x)^2 - (T_{xx}/2\tau_{xx})^2} \\ & \left[\operatorname{erfc}\left(\frac{t_{0x} - t}{T_x} + \frac{T_x}{2\tau_x}\right) - \operatorname{erfc}\left(\frac{t_{0xx} - t}{T_{xx}} + \frac{T_{xx}}{2\tau_x}\right)\right]\Bigg) \\ & + \beta\tau_x e^{-(t - t_{0x})/\tau_x} \frac{1}{2}\operatorname{erfc}\left(\frac{t_{0x} - t}{T_x} + \frac{T_x}{2\tau_x}\right), \end{aligned} \tag{3}$$

where the constants α and β are related to the amplitudes of the sources J_i by the equations

$$\begin{aligned} J_{xx} &= \frac{1}{\sqrt{\pi}} \frac{\tau_R}{T_{xx}} e^{-(T_{xx}/2\tau_{xx})^2} \alpha \frac{\tau_{xx} - \tau_x}{\tau_{xx} + \tau_R - \tau_x}, \\ J_x &= \frac{1}{\sqrt{\pi}} \frac{\tau_x}{T_x} e^{-(T_x/2\tau_x)^2} \left(\beta + \alpha \frac{\tau_R}{\tau_{xx} + \tau_R - \tau_x} e^{(T_{xx}/2\tau_x)^2 - (T_{xx}/2\tau_{xx})^2} e^{-(t_{0x} - t_{0xx})/\tau_x}\right). \end{aligned} \tag{4}$$

Using (2) and (3) we obtain for the total intensity of emitted photons $I = I_x + I_{xx}$ the following expression

$$\begin{aligned} I \propto\ & \alpha e^{-(t - t_{0xx})/\tau_{xx}} \frac{1}{2}\operatorname{erfc}\left(\frac{t_{0xx} - t}{T_{xx}} + \frac{T_{xx}}{2\tau_{xx}}\right) \\ & + \beta e^{-(t - t_{0x})/\tau_x} \frac{1}{2}\operatorname{erfc}\left(\frac{t_{0x} - t}{T_x} + \frac{T_x}{2\tau_x}\right) \\ & + \alpha e^{-(t - t_{0xx})/\tau_x} \frac{\tau_R}{\tau_{xx} + \tau_R - \tau_x} e^{(T_{xx}/2\tau_x)^2 - (T_{xx}/2\tau_{xx})^2} \end{aligned} \tag{5}$$

$$\frac{1}{2}\left[\operatorname{erfc}\left(\frac{t_{0x}-t}{T_x}+\frac{T_x}{2\tau_x}\right)-\operatorname{erfc}\left(\frac{t_{0xx}-t}{T_{xx}}+\frac{T_{xx}}{2\tau_x}\right)\right]$$

that we use to fit the experimental results presented in Fig. 1. Substituting the fitting parameters into equations (2) and (3) we find the temporal dependence of the intensities I_x (thin solid curve) and I_{xx} (thin dashed curve). The ambiguity of the used approach does not affect the qualitative behavior of the investigated dependences and is not reflected in the order of values of the characteristic lifetimes τ_x and τ_{xx}.

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