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Radiative recombination in photoexcited quantum dots up to room temperature: The role of fine-structure effects

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We demonstrate dominant radiative recombination in high-quality self-assembled quantum dots all the way up to room temperature. This allows a proof of the theoretically predicted characteristic doubling of the radiative recombination time with increasing temperature, entirely caused by fine-structure effects. Over the whole temperature range, the transient decay of the photoluminescence can be described by temperature-independent radiative decay rates of dark and bright excitons, respectively, taking into account a thermally activated interplay between dark and bright states and dark-exciton accumulation.

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Semiconductor quantum dots (QDs) have been a central topic in modern solid-state physics for more than two decades. The discrete energy-level structure and size-dependent light emission of QDs triggered a variety of innovative optoelectronic applications such as QD-based light emitters,[1,2] QD lasers,[3] single-photon sources,[4] and devices for quantum information technology.[5] For devices working under ambient conditions, zero-dimensional electronic properties have to be conserved until room temperature but QDs are actually mesoscopic systems: carrier interaction with phonons and the impact of excited energy states or surface/interface states in the QD and the host matrix will modify the emission, the quantum efficiency, and the carrier dynamics resulting in significant deviations from ideal zero dimensionality.

The analysis of the radiative recombination dynamics plays a key role in identifying true zero dimensionality.[6,7] A three-dimensional spatial confinement of excitons in QDs results in an increase in the radiative lifetime and, by neglecting any deviations from ideal zero dimensionality as well as any spin effects, one expects a temperature-independent radiative-exciton lifetime up to room temperature. However, the electron-hole exchange interaction in QDs lifts the degeneracy of the dipole forbidden $m=\pm 2$ exciton state ("dark state" with electron and heavy-hole spin parallel), being the lowest-lying excited state, and the dipole allowed $m=\pm 1$ "bright state" with antiparallel electron and hole spins. This has a fundamental consequence for the expected temperature dependence of the radiative lifetime in QDs: in case of negligible spin flip between bright-exciton (BE) and dark-exciton (DE) states, the decay rate will be dominated by the radiative lifetime $\boldsymbol{\tau_1}$ of the BE. In contrast, a rapid transfer between BE and DE states, i.e., triggered by acoustic-phonon scattering at elevated temperatures[8,9] will result in thermal equilibrium. Thus, at room temperature, both DE and BE levels will be populated nearly equally, and a common decay with the time constant $\boldsymbol{2\tau_1}$, i.e., twice the pure radiative lifetime of the BE, is theoretically predicted.[8,9]

Experimental evidence for this prediction, however, has not been given up to now. First of all, in all kinds of *epitaxially* grown QDs a general issue is the impact of nonradiative losses via defect states or by thermal emission into higher states or into the barrier.[10,11] This inhibits experimental access to the radiative recombination lifetime at elevated temperatures and, in particular, at room temperature. Moreover at low temperatures, a nonmonoexponential decay has been reported, e.g., for InP/GaInP QDs,[12] InGaAs/GaAs QDs (Ref. 13) or CdSe/ZnSe QDs (Refs. 14–16) and while the short component was, e.g., attributed to carrier transfer from the BE to the DE state,[17] the long component was claimed to be related to specific electronic states of the QDs (Ref. 14) or to a lateral carrier migration into the QDs.[15] Recently, also the contribution of the dark excitons to the transient luminescence signal involving a spin-flip process was considered in the low-temperature regime up to 140 K.[13,16] Apparently, in epitaxially grown QDs, the radiative recombination process all the way up to room temperature is still under discussion.

In nanocrystals, where room-temperature quantum yields far above 50% can be reached, the situation is different. In high-quality QDs, radiative recombination dominates even at room temperature. Because of the fast spin flip from the BE to the DE state, however, a rapid thermalization between both exciton states is usually assumed even at low temperatures.[18] Thus, the decay observed at low temperatures is given by the bright-dark transfer time in the subnanosecond regime followed by long photoluminescence decays with time constants in the order of microsecond,[8,18,19] usually related to the decay of dark excitons. As a consequence, the pure bright-exciton lifetime $\boldsymbol{\tau_1}$ cannot be accessed directly by experiment and instead has to be extracted by fitting the temperature-dependent decay time.[8,18,20] Note that according to theory, at room temperature, where thermal equilibrium results in an almost equal population of dark states and the lowest bright states, the decay rate is given by $\boldsymbol{2\tau_1}$ instead of the pure bright-exciton lifetime $\boldsymbol{\tau_1}$.[8,9]

In this Rapid Communication, we present time-resolved optical spectroscopy on specially designed self-organized CdSe/ZnSSe/MgS QDs with exceptionally high quantum confinement that are found to be an ideal model system for tracking the radiative recombination dynamics in zero-dimensional semiconductors all the way up to room temperature. The whole range from quasi-isolated spin states at low temperatures (spin-flip time between BE and DE states $\gg$bright exciton lifetime[21–23]) to thermal equilibrium between BE and DE states at room temperature (spin-flip

time ≪ bright exciton lifetime) is covered without the need of considering nonradiative losses. This allows the demonstration of the theoretically predicted characteristic doubling of the radiative lifetime in zero-dimensional system with increasing temperature caused by fine-structure effects. A three-level model which explicitly includes dark-exciton accumulation gives a good description of the recombination dynamics over the whole temperature range.

Self-organized CdSe/ZnSe QDs with a density of $\approx 5 \times 10^{10}$ cm^{-2} were grown by migration-enhanced epitaxy and embedded into specially designed symmetric barriers consisting of 1.4-nm-thick $ZnS_{0.4}Se_{0.6}$ layers between MgS layers of 1.0 nm thickness, which provide a high confinement for both electrons and holes. This design allows us to preserve a very high quantum yield up to 300 K and to study single-QD emission even at room temperature.[24] Time-resolved photoluminescence (PL) measurements with an overall resolution of about 8 ps were performed in a temperature range of 7–300 K. The setup includes a frequency doubled Ti:Sa picosecond laser (λ_{exc}=400–490 nm), a monochromator with a spectral resolution better than 1 meV and a streak camera for detection. The average power density of the exciting laser was kept below 50 W/cm^2 to avoid many-particle effects and heating of the samples. For studies in the nanosecond time domain, a pulsed diode laser (λ_{exc} =405 nm) with a repetition rate of 1–80 MHz was used for excitation and a time-correlated single-photon counting system with a microchannel-plate multiplier for detection. The overall time resolution here was better than 100 ps.

The temporal decays of the spectrally integrated PL intensity of the QD ensembles at 7 K and at room temperature are depicted in Fig. 1(a). The 7 K decay curve shows two clearly distinguishable regimes given by a fast initial decay time with a time constant of $\tau_{7K,fast} \approx 0.65$ ns and a long component with a time constant $\tau_{7K,slow} \approx 50$ ns, respectively. At room temperature, we find a decay with a time constant of τ_{300K}=1.3 ns. It is remarkable that apparently the room-temperature lifetime is twice the fast component $\tau_{7K,fast}$ found at 7 K.

As illustrated in the inset of the Fig. 1(a), we model the recombination dynamics in the frame of a standard three-level system consisting of the ground state and DE and BE states with radiative lifetimes $\boldsymbol{\tau_2}$ and $\boldsymbol{\tau_1}$, respectively, separated by the energy ΔE.[8,18] The transfer between DE and BE states and vice versa, which involves a spin flip of either the electron or the hole, is described by $\boldsymbol{\tau_{21}}$ and $\boldsymbol{\tau_{12}}$, respectively. As this spin-flip process is mainly driven by acoustic phonons,[20] the relevant time constants can be described by

$$1/\boldsymbol{\tau_{12}}(T) = [N_B(\Delta E) + 1]/\boldsymbol{\tau_s}, \quad 1/\boldsymbol{\tau_{21}}(T) = N_B(\Delta E)/\boldsymbol{\tau_s} \quad (1)$$

with the Bose factor $N_B(\Delta E) = 1/[\exp(\Delta E/kT) - 1]$ and the spin-flip time $\boldsymbol{\tau_s}$ from BE to DE at T=0 K. This results in population dynamics of the BE and DE level, n_1 and n_2, respectively, given by the rate equations

$$dn_1/dt = -n_1(1/\boldsymbol{\tau_1} + 1/\boldsymbol{\tau_{12}}) + n_2/\boldsymbol{\tau_{21}} \text{ and}$$
$$dn_2/dt = -\boldsymbol{\tau_2}(1/\boldsymbol{\tau_2} + 1/\boldsymbol{\tau_{21}}) + \boldsymbol{\tau_1}/\boldsymbol{\tau_{12}}. \quad (2)$$

Let us first focus on the results obtained at low temperatures,

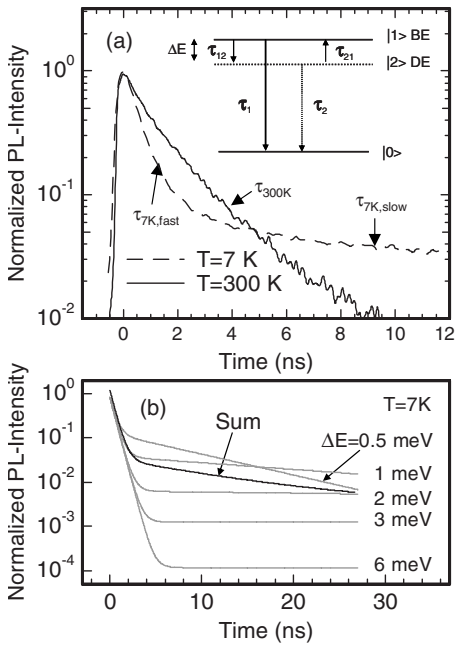

FIG. 1. (a) Transient decay of the photoluminescence from a CdSe/ZnSSe/MgS-QD ensemble for low (T=7 K) and high (T=300 K) temperatures. Inset: scheme of the three-level system used for modeling the recombination dynamics. (b) Calculated decays for different values of ΔE (gray) and the sum of the gray curves, exhibiting a nonexponential decay (black).

where $\boldsymbol{\tau_{21}} \gg \boldsymbol{\tau_{12}} > \boldsymbol{\tau_1}$. As the QDs are optically excited far above the ground state with unpolarized light, we assume an equal population of bright and dark states, n_1 and n_2, after the first laser pulse.[23] Because τ_2 is expected to be very large compared to the time scales under investigation, the decay in the beginning is controlled by the radiative recombination time of the BEs, i.e., $\tau_{7K,fast}$=650 ps $\approx \tau_1$. After depopulation of the BE state, the DEs can contribute to the emission only by flipping one of the carrier spins, i.e., by a transition to the BE state followed by radiative recombination. This means that the decay time now is given mainly by the transfer time τ_{21} from DE to BE under the precondition that $\boldsymbol{\tau_2} \gg \boldsymbol{\tau_{21}} \gg \boldsymbol{\tau_1}$. At room temperature, in contrast, both DE and BE states are nearly equally populated as the dark-bright splitting $\Delta E \ll$ thermal energy kT (see below). The transfer time τ_{21} becomes very short due to the large number of phonons available that make a spin flip possible. As discussed above, in that case a decay time of $2^*\tau_1$ should be observed.[8,9] Remarkably, our experimental data confirm this prediction very well. This indicates that τ_1 is indeed constant over the whole temperature range, as expected for an ideal three-dimensionally confined system, i.e., nonradiative losses apparently can be neglected even at elevated temperatures.[25]

Considering τ_1 to be independent of temperature and being able to neglect nonradiative losses, only τ_{12} and τ_{12} are expected to vary with temperature according to Eq. (1). Therefore, the CdSe/ZnSSe/MgS QDs investigated here represent an excellent model system to analyze the dark-bright interplay from low temperatures, where $\boldsymbol{\tau_{21}}$, $\boldsymbol{\tau_{12}} \gg \boldsymbol{\tau_1}$, up to room temperature, where $\boldsymbol{\tau_{21}}$, $\boldsymbol{\tau_{12}} \ll \boldsymbol{\tau_1}$, without disturbing nonradiative effects. In Fig. 1(b), the decay after pulsed laser

excitation is modeled for $T=7$ K using $\tau_1=650$ ps (according to the lifetime observed for the fast component), $\tau_S=6$ ns, and different values for ΔE, while τ_2 was set in a first approximation to infinity. For large values of ΔE, the fast transient excitonic lifetime component related to τ_1 leads to a pronounced temporal decay of the overall intensity, followed by an extremely slow decay due to the very small number of phonons available that can trigger a transfer from the DE to the BE state. The smaller ΔE, the more efficient is the depopulation of the DE state via spin flip, which results in a pronounced shortening of the slow component. As can be seen experimentally [Figs. 1(a) and 3], the slow component at 7 K does not follow a single exponential law. Obviously, one has to take into account a variation in ΔE within the QD ensemble, resulting in a superposition of curves and thus in a deviation from the single exponential law.[8,18] From our data, we estimate a value of $\Delta E=(1.8\pm1)$ meV.

While at first glance the experimental results seem to agree quite well with our model calculations one has to be aware of a fundamental discrepancy between experiment and theory: due to their long lifetime, a significant amount of dark excitons generated by one laser pulse will be still present at the time of the subsequent pulse, leading to "memory effects"[26] that should depend on the laser repetition rate $1/\Delta t_{\text{laser}}$. Therefore, the initial assumption that $n_1=n_2$ at $t=0$ will be only valid, if all bright and dark excitons have vanished before the next laser pulse arrives. We define $n_{r,1}$ and $n_{r,2}$ as the remaining bright and dark excitons at time t_0 immediately before the next laser pulse, and $\alpha=(n_2/n_1-1)/(n_2/n_1+1)$ as an imbalance parameter that will become 0 for $n_1=n_2$ and approach 1, if $n_2\gg n_1$. Each laser pulse is assumed to generate n_0 excitons, i.e., $n_0/2$ DEs and $n_0/2$ BEs.

The rate equations are solved self-consistently, so that $n_{r,1}=n_1(t_0)$ and $n_{r,2}=n_2(t_0)$ are identical to $n_1(t_0+\Delta t_{\text{laser}})$ and $n_2(t_0+\Delta t_{\text{laser}})$, respectively, in order to account for the typical integration time over millions of subsequent pulses. Figure 2 depicts main results from the calculations (using $\tau_1=650$ ps, $\tau_S=6$ ns, and $\Delta E=1.8$ meV) the values for n_1, n_2, and α as function of time. The parameter α is deduced directly from the calculated populations. Immediately after the laser pulse it is strongly time dependent, at later times it remains nearly constant because the number of bright excitons is directly proportional to the number of DEs in the "reservoir" [see Fig. 2(a)]. For cryogenic temperatures, a significant amount of BEs is only present during the first few nanosecond after the pulse. Later, n_2 exceeds n_1 by about two orders of magnitude [see Fig. 2(b)], thus $\alpha\approx1$. At room temperature, in contrast, n_2 is comparable to n_1, and the decay rate is about $1/2\tau_1$ [see Fig. 2(a)] in agreement with former calculations.[8,9] The weaker influence of the DE accumulation with rising temperature becomes very clear in Fig. 2(d), where α is plotted as a function of temperature.

The influence of the DE reservoir at low temperature can be experimentally verified by varying the repetition rate $1/\Delta t_{\text{laser}}$ of the pulsed laser and by this the amount of accumulated DEs, when the subsequent laser pulse arrives. Figure 3 compares experimental findings, recorded for $\Delta t_{\text{laser}}=100$, 50, 25, and 12.5 ns, with calculations using again $\tau_1=650$ ps, $\tau_S=6$ ns, and $\Delta E=1.8$ meV. The theoretical data

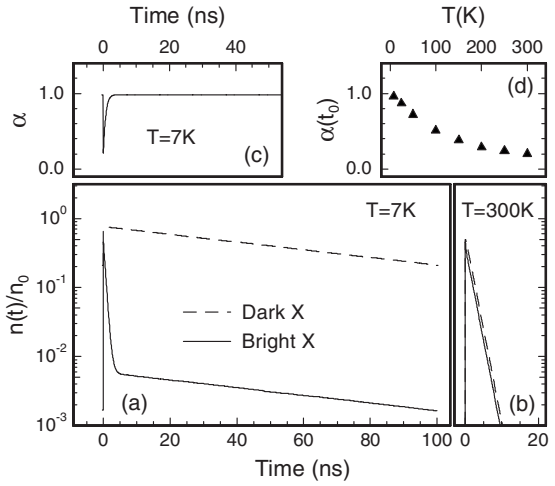

FIG. 2. Calculated population of the bright and the dark X states for (a) $T=7$ K and (b) $T=300$ K. (c) Imbalance parameter α at $T=7$ K in dependence of time. (d) Imbalance parameter α at the time t_0 [immediately before excitation, see (c)] for different temperatures.

exhibit an interesting dependence of the time-resolved signal on the repetition rate: both decay times τ_{fast} and τ_{slow} remain unchanged for different values of Δt_{laser}. This is not surprising, as both τ_1 and τ_S should be independent of the excitation rate. On the other hand, the transition between the fast and the slow decay shifts to earlier times, i.e., to higher intensities, with increasing repetition rate, a clear consequence of DE accumulation. The experiments confirm this prediction quite well. The small quantitative deviations are most probably related to the variation in ΔE, as discussed in Fig. 1(b), which is also evident by the nonmonoexponential decay in the regime of τ_{slow}.

We will now discuss the observed decay characteristics over the whole temperature regime up to 300 K taking into account the DE accumulation. To get a more detailed insight into the short-time regime, we used picosecond laser excitation with an excitation wavelength $\lambda=460$ nm, i.e., below the band gap of the ZnSSe barrier, and a streak camera with a time window of 2.2 ns for detection. In Fig. 4, the decay

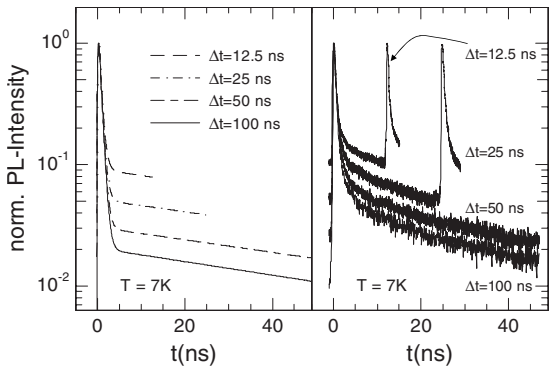

FIG. 3. Calculated (left) and experimentally obtained (right) decay curves at $T=7$ K for different values of the laser repetition rate Δt_{laser}. For the model, ΔE was set to 1.8 meV and the DE accumulation was taken into account.

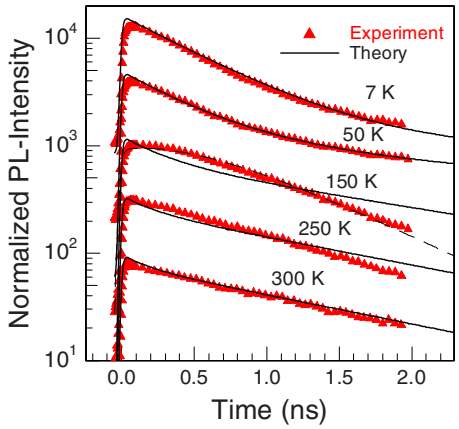

FIG. 4. (Color online) Experimental (triangles) and calculated (solid curves) decay curves under consideration of the DE accumulation for different temperatures (vertically shifted for clarity). Dashed curve: model calculation for $T=150$ K including a trionic decay channel.

curves for the whole temperature range between 8 K and room temperature are depicted, together with model calculations using the values introduced before. A very good agreement between model and experiment is found in particular in the low- and the high-temperature regimes. Most importantly, the data can be fitted without considering nonradiative losses. The transition between the radiative decay at low temperature, controlled by $\tau_1=650$ ps (i.e., τ_{12}, $\tau_{21} \gg \tau_1$) and at room temperature, determined by $2^*\tau_1=1300$ ps, (τ_{12}, $\tau_{21} \ll \tau_1$), is clearly seen. In the intermediate temperature range (see decay curves at 150 and 250 K), apparently a "plateaulike" structure, followed by a fast decay, can be seen in the experiment, not reproduced by the model calculations.

Although the structures are nominally undoped, we suggest that one has to consider charged excitons here. An electron or hole trapped, e.g., in a QD or a defect state might escape by thermalization and undergo a carrier transfer[15,27] to a neighboring QD [with a transfer time τ_{trans} of several 100 ps (Ref. 27)]. If the latter is already occupied by a DE or BE, this exciton will be converted to a trion. Trions, however, do not have the dark-bright fine structure, and thus exhibit a purely monoexponential decay with an expected rate of about $1/\tau_1$. Especially for the dark excitons that principally occupy a QD for a long time, this transfer can open an efficient recombination channel. Note, that the thermalization process will not be active at low temperatures and will also be of minor importance at room temperature because at high temperatures the dark-bright-exciton transfer might become considerably shorter than τ_{trans}. For "intermediate" temperatures, however, this process is be expected to be significant. In order to take into account these effects, we expanded the rate-equation system [Eq. (2)] by a third equation $dn_3/dt=(n_1+n_2)/\tau_{trans}-n_3/\tau_1$, where n_3 is the trion population, and extended the first and the second rate equation of the system by the transfer channels $-n_1/\tau_{trans}$ and $-n_2/\tau_{trans}$, respectively. Assuming for instance a transfer time $\tau_{trans}=500$ ps at 150 K, this extended model is in very good agreement with the experimental findings (dashed line in Fig. 4).

In conclusion, we have been able to elaborate the impact of fine-structure effects on the radiative recombination dynamics in a zero-dimensional solid-state system all the way up to room temperature. While the suppressed spin flip between bright- and dark-exciton states occurring at low temperatures in our specially designed self-assembled quantum dots allows for a direct experimental access to the radiative lifetime τ_1 of the bright exciton, at room temperature an exponential decay with $2^*\tau_1$ is found as a consequence of the thermal equilibrium between bright- and dark-exciton states. These findings confirm zero dimensionality up to room temperature and confirm theoretical predictions. Moreover, experimental evidence of a significant accumulation of dark excitons is given that represents a hidden reservoir, which influences the transient decay of the photoluminescence signal.

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