

Fluorescence Decay Time of Single Semiconductor Nanocrystals

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We present fluorescence decay measurements of single ZnS covered CdSe nanocrystals. It is shown that the fluorescence decay time is fluctuating during the investigation leading to a multiexponential decay even for a single nanocrystal. In combination with measurements of the fluorescence blinking behavior we find that a high fluorescence intensity is correlated with a long fluorescence decay time. This is consistent with a model of fluctuating nonradiative decay channels leading to variable dynamic quenching processes of the excited state.

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The detailed understanding of the photophysics of semiconductor nanocrystals (NCs) is of major importance for both fundamental research and future nanoengineering. Because the size of these colloidal particles can be adjusted by wet chemical methods between 1 and 10 nm, the electronic properties can change considerably. For example, the emission color of CdSe particles can be tuned over almost the whole visible range as a function of size which could lead to several nanotechnological devices such as light emitting diodes, NC-bio labels, or even nanocrystal lasers [1].

While the photoabsorption of the NCs is now fairly well understood [2,3], the emission of the particles is still puzzling. Especially the technique of single nanocrystal fluorescence spectroscopy has revealed many novel photophysical properties, which could never have been seen in ensemble experiments [4]. A very intriguing phenomenon is the blinking behavior of the particles, i.e., the fluorescence fluctuation under cw excitation. It was observed that this blinking depends on several experimental parameters such as excitation intensity [5] or temperature [6]. As a physical reason it is discussed that charges in and around the particles are responsible for the dark periods of the particles [7]: apparently (positively) charged particles do not fluoresce because the excitation energy promotes the excess charge in an excited state which in turn undergoes radiationless relaxation, a process which is called Auger quenching [8]. On the other hand, it has also been shown that even the surrounding gas environment influences the blinking of colloidal nanocrystals [9] whereas Stranski-Krastanow quantum dots which are epitaxially embedded in a solid matrix blink only very infrequently [10]. Therefore it is very likely that fluorescence fluctuations can also be caused by “structural” changes in the environment of the dots.

However, any analysis of the blinking behavior so far relies only on the assumption that the particles are either *on* or *off*. Intensity fluctuations during the *on* periods are explained by *off* times that are shorter than the observation interval. In fact, it has been shown that the *off*-time distribution follows an inverse power law behavior which

covers at least 5 orders of magnitude [11]. For the *on*-time distribution, a similar behavior could be seen [12] but the time resolution is always limited by the minimum width of the time bins, which is at least several ms. Extrapolation of this behavior to much shorter time scales might lead to the assumption that the observed intensity fluctuations result only from short *off* times which cannot be resolved in the cw experiments. In that sense, the fluorescence fluctuations would result only from static quenching processes which in general occur when there is ground state interaction between the fluorophor and the quencher [13]. As a dark particle is already charged in its ground state it might absorb but not emit a photon. On the other hand, it has also been demonstrated in low temperature experiments, where the intensity fluctuations are strongly reduced, that a long off time is often followed by a change of luminescence spectrum and intensity [14,15]. Here it was speculated already that this behavior could be explained by a fluctuating environment of the particles which might lead to a change of the quantum efficiency or even to a change of the fluorescence lifetime of individual dots.

In this Letter we will address this problem by employing time correlated single photon counting (TCSPC) on a single nanocrystal level. We will show that the fluorescence decay time of colloidal single dots in a polymer matrix is indeed not uniform but strongly correlated to the fluorescence intensity fluctuations which might be an effect of a fluctuating environment. This would also explain the multiexponential fluorescence decay dynamics of colloidal ensembles of semiconductor nanocrystals [16], while the fluorescence decay of nanocrystals embedded in a glass can be almost monoexponential [17].

The optical experiments were performed with a home built laser scanning microscope where the focus of the microscope objective (NA = 1.25, 60 \times) can be scanned over a range of 50 \times 50 μ m, using galvano driven mirrors and a telecentric lens system. For excitation we used the second harmonic of Ti-sapphire oscillator (458 nm) in ps-(3 ps) or fs-(200 fs) mode with a cw intensity between 50–500 nW, i.e., 20–200 W/cm² in the focus of the microscope objective. With a repetition rate of 4.7 MHz

this results in a pulse energy of 10–100 fJ, and a peak power of 4–40 mW in ps mode and 60–600 mW in the fs mode. The fluorescence of the particles is collected with the same microscope objective, separated from the scattered laser light by Notch and/or color glass filters and guided to an avalanche photodiode (APD) and/or to a spectrograph equipped with a charge-coupled device (CCD) camera. The output signal of the APD is split such that the cw-fluorescence intensity, i.e., the fluorescence transient and the fluorescence decay curve can be recorded simultaneously. Moreover, by using a beam splitter to guide 70% of the fluorescence light to the APD and 30% to the CCD camera we could observe fluorescence transients, decay curves, and spectra at the same time. The ZnS covered CdSe nanocrystals were prepared after standard methods [18,19] and spin cast in a thin (50 nm) polymer film, which was either Polystyrene or Zeonex®.

Figure 1(a) shows an ensemble absorption and fluorescence spectrum (dotted lines) and two typical single nanocrystal fluorescence spectra (I and II). The single particle emission spectrum II was recorded at the same time as the fluorescence decay curve in Fig. 1(b). The simultaneous recording of fluorescence spectra and decay curves is important because it allows one to judge the size of the particles. Of similar importance as the position of the fluorescence band is its width since it corroborates that the fluorescence stems from a single nanocrystal instead of an aggregate of particles. For example, from Fig. 1(a) it can be seen that the width of the nanocrystal ensemble is 100 meV whereas the width of single emitters can be as narrow as 50 meV at room temperature. This linewidth is still broadened by spectral diffusion effects since we could observe spectral fluctuations up to 20 meV by taking consecutive spectra of the same particle. However, from the about 100 fluorescing entities investigated we show only results where the linewidth was below 60 meV to have an indication that the fluorescence comes only from a single nanocrystal.

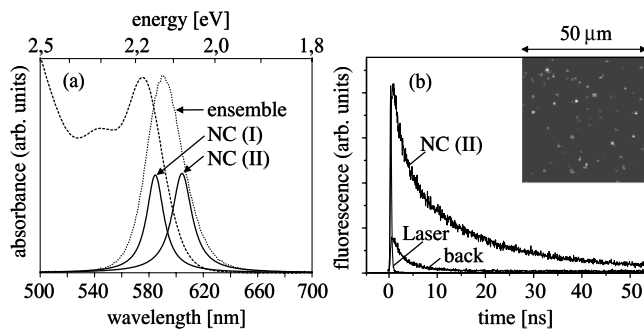


FIG. 1. (a) Absorption and fluorescence spectra of ZnS covered CdSe nanocrystal ensembles (dotted lines) and fluorescence of single nanocrystals I and II (solid lines). (b) Fluorescence decay curve of a single nanocrystal II and background fluorescence (<10%) together with the laser pulse. The inset shows a laser scanning fluorescence image of single emitters illuminated with pulsed excitation.

In Fig. 1(b) the fluorescence decay of nanocrystal II in Fig. 1(a) is shown. The background intensity is of the order of 10% of the total fluorescence intensity and is most likely due to matrix impurities. In our experiments the background was always acquired back-to-back to the nanocrystal fluorescence under the same experimental conditions and subsequently subtracted in the time domain before further data processing. The time resolution is limited by the APD which is better than 350 ps. Because the decay times are several ns, no deconvolution techniques were performed at this point.

Figure 2(a) shows the decay curves of three different nanocrystals (III, IV, and V) with a fluorescence band centered between 610 and 640 nm, i.e., a core diameter of approximately 5–6.5 nm. These decay curves were taken with ps excitation, while the data in Fig. 3 were taken with fs excitation and a similar average intensity. Obviously the decay characteristics among different nanocrystals can be very diverse even though the particles are of a similar size. Also, no obvious difference could be seen between ps and fs excitation at this point. Therefore, with the limited data set taken so far, we can neither judge about any size dependency or decay time statistics, nor about the influence of ps vs fs excitation or even excitation power upon

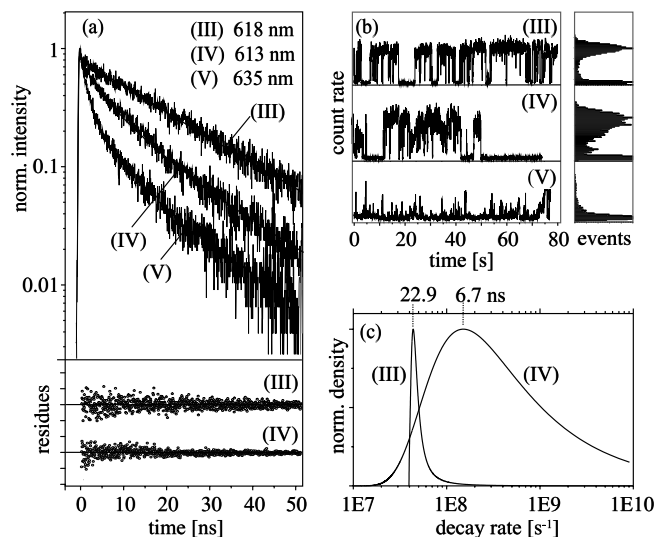


FIG. 2. (a) Fluorescence decay curves of three different individual nanocrystals [(III), (IV), and (V)]. The decay curves of (III) and (IV) are fitted with a stretched exponential function revealing multiexponential dynamics. (b) Fluorescence transients and count rate histograms for (III), (IV), and (V) recorded at the same time as the decay curves in (a). Particle (III) shows a defined on-level with a maximum count rate of 200 counts/20 ms. The count rate distribution is much broader for particle (IV) while particle (V) fluoresces only periodically. (c) Distribution of fluorescence decay rates as calculated from the stretched exponential fit functions in (a). The almost single exponential decay of (III) results in a narrow rate distribution ($\tau_{\max} = 22.9$ ns), whereas the strong bending of logarithmic decay curve from particle (IV) correlates with a broad rate distribution ($\tau_{\max} = 6.7$ ns). Note the similar shape of the decay rate distribution and the corresponding count rate histogram.

the measurements. Consequently this study focuses on the analysis of the decay characteristics and possible reasons for the strong deviations.

For nanocrystal (III), the linear appearance of the logarithmic decay curve indicates an almost single exponential fluorescence decay with a lifetime of about $\tau_{(1/e)(III)} = 20$ ns. At the same time the corresponding fluorescence transient in Fig. 2(b) shows an almost binary blinking behavior, i.e., this particle is either *on* or *off*. Most of the particles investigated, however, behave like particle (IV) where the decay curve is multiexponential. Here the fluorescence intensity decays to $\frac{1}{e}$ of its initial value in about 7 ns and at the same time the count rate distribution of the transient becomes broader. The correlation between the “bending” of the logarithmic decay curve and the fluorescence intensity fluctuations is even more evident when looking at particle (V). This is one of the worst fluorescing particles investigated because it luminesces only periodically and no distinct on/off behavior can be seen in the transient. The decay curve of this particular particle is obviously multiexponential and the lifetime is even shorter than in (III) and (IV). However, the subtracted background was of the order of 30% of the total signal in this case which is not sufficient for any detailed data analysis.

To get a more quantitative measure of the decay behavior we fitted the background corrected decay curves for nanocrystal (III) and (IV) with a Kohlrausch-William-Watts (KWW) function, commonly known as stretched exponential:

$$I(t) = I_0 \cdot e^{-(t/\tau_{1/e})^\beta}. \quad (1)$$

This function describes the exponential decaying fluorescence intensity $I(t)$, which drops to $1/e$ of its initial value I_0 after the decay time $\tau_{1/e}$ for any value of the stretching exponent β ($0 < \beta \leq 1$). This stretching exponent is basically a measure of the relaxation rates involved in the fluorescence decay process where a smaller β means a broader rate distribution. For the decay of nanocrystal (III), which is almost single exponential we observed $\tau_{(1/e)(III)} = 19.9$ ns and $\beta_{III} = 0.97$, whereas for nanocrystal (IV) we observed $\tau_{(1/e)(IV)} = 6.5$ ns and $\beta_{IV} = 0.66$.

An average lifetime $\langle \tau \rangle$ can be calculated from the fit functions by

$$\langle \tau \rangle = \left(\frac{\tau_{1/e}}{\beta} \right) \Gamma\left(\frac{1}{\beta} \right), \quad (2)$$

where Γ represents the gamma function [20]. We calculated $\langle \tau_{III} \rangle = 20.2$ ns and $\langle \tau_{IV} \rangle = 9.0$ ns for particles (III) and (IV), respectively.

Obviously, every particle shows a multiexponential fluorescence decay with $\beta < 1$. The underlying distribution of rates can be calculated in principle by a direct inverse Laplace transformation of a given decay curve or its fit function. Since the inverse Laplace transform has only analytical solutions for discrete values of β we employed

the technique of series expansion and saddle point calculation [20]. The rate distributions calculated from the fit functions for (III) and (IV) are shown in Fig. 2(c).

It should be mentioned at this point that the recovery of rate distributions from decay curves is an ill-conditioned problem. There will be many different rate distributions which could describe the corresponding decay curve equally well. For example, any decay curve can be reasonably fitted with a sum of four discrete exponentials [21]. Therefore the straightforward approach of inverse Laplace transformation, which results in a continuous distribution of rates, is very sensitive to the quality of the underlying fit. In any case we could observe a distribution of rates which is much broader for nanocrystal IV than for III. As can be seen from Fig. 2(c) there is at least 1 decade of rate space with a maximum amplitude at 1.43×10^8 s⁻¹ involved in the fluorescence decay of IV, whereas the rate distribution for III is considerably narrower with a maximum at 4.35×10^7 s⁻¹. The lifetimes corresponding to the maximum amplitude τ_{\max} represent a third value which is characteristic for a nanocrystal. Here the maximum amplitudes for (III) and (IV) correspond to $\tau_{\max III} = 22.9$ ns and $\tau_{\max IV} = 6.7$ ns, respectively.

By comparing the respective count rate histograms and decay rate distributions of Figs. 2(b) and 2(c) it can be seen that the corresponding functions are of similar shape. The narrow transient count rate histogram of (III) corresponds with a narrow fluorescence decay rate distribution while for (IV) both distributions are considerably broader. Moreover, it can be argued that a high fluorescence count rate goes along with a long fluorescence lifetime and vice versa.

Therefore we performed an experiment where several fluorescence decay curves were measured from a single nanocrystal at different count rate thresholds. Figures 3(a), 3(b), and 3(c) show transients of an individual nanocrystal (II) on different time scales, the fluorescence spectrum and overall decay curve of which is shown in Fig. 1. This particular nanocrystal shows very strong intensity fluctuations but could be investigated for more than 1000 s enabling us to detect decay curves at several arbitrary count rate levels (i, ii, and iii) in Fig. 3(d). After background subtraction, the decay curves were fitted with stretched exponentials as shown in Fig. 3(e). It can clearly be seen that the fluorescence decay changes considerably depending on the temporary fluorescence intensity even for a single nanocrystal. This is not a background effect because the subtracted background was carefully weighted with the dwell time in the respective count rate level. The inset in Fig. 3(f) shows the corresponding lifetime distributions which were calculated as described above. Here it can clearly be seen that a lower count rate is indeed associated with a shorter fluorescence decay time.

The fact that even a single nanocrystal changes its excited state lifetime during the measurement clearly demonstrates that fluctuating dynamic quenching processes can

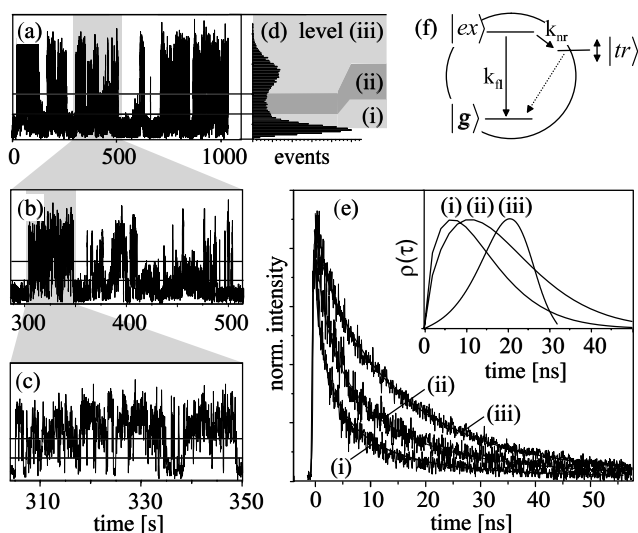


FIG. 3. (a),(b),(c) Fluorescence transient of a single nanocrystal on different time scales. This particular nanocrystal shows strong intensity fluctuations with a count rate histogram shown in (d). (e) Fluorescence decay curves (i, ii, iii) at different count rate levels as depicted in (d). The maximum of the decay time distribution $\rho(\tau)$ is shifted to longer times at higher count rates. (f) Sketch of the energy levels and transition rates in a nanocrystal.

occur. In light of former experiments, this is most likely due to acceptor levels on the surface of the particle, such as temporarily adsorbed molecules or dislocations in the surrounding matrix, which could lead to nonradiative decay channels as sketched in Fig. 3(f). When a particle is excited from the ground state $|g\rangle$ to the excited state $|ex\rangle$ there are radiative and nonradiative channels for relaxation. The decay observed in the time resolved fluorescence experiments k_{obs} is only a sum of the radiative k_{fl} and the nonradiative k_{nr} decay: $k_{obs} = k_{nr} + k_{fl}$. Additional acceptor levels $|tr\rangle$, will open up new nonradiative decay channels which will lead to a decrease of the fluorescence intensity and at the same time to a decrease of the excited state lifetime. Therefore, a fluctuation of the nonradiative decay channels k_{nr} will necessarily lead to a broadening of the observed fluorescence decay time distribution. Further measurements in a defined environment, e.g., at low temperature in helium atmosphere, are needed to explore whether an intrinsically charged “dark particle” is indeed totally dark or if the quenching rate can also be resolved by time resolved fluorescence measurements.

In conclusion, we have shown that the fluorescence decay time of single semiconductor nanocrystals is fluctuating in time. The distribution of fluorescence decay rates correlates strongly with the fluorescence intensity fluctuations where a high fluorescence intensity is associated with

a long fluorescence decay time. This is compatible with a model of fluctuation dynamic quenching processes of the emissive state due to a fluctuating electronic and/or structural environment of individual particles.

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