

Bunching and antibunching in the fluorescence of semiconductor nanocrystals

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The fluorescence of single-colloidal CdSe quantum dots is investigated at room temperature by means of the autocorrelation function over a time scale of almost 12 orders of magnitude. Over a short time scale, the autocorrelation function shows complete antibunching, indicating single-photon emission and atomiclike behavior. Over longer time scales (up to tens of seconds), we measure a bunching effect that is due to fluorescence intermittency and that cannot be described by fluctuations between two states with constant rates. The autocorrelation function also exhibits nonstationary behavior related to power-law distributions of ON and OFF times. © 2001 Optical Society of America

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The realization of single-photon sources and generation of nonclassical states of light is of great interest in quantum optics, especially in quantum cryptography, where secure transmission requires that one and only one photon be sent at a given time.¹ To obtain a single-photon source, one should use the fluorescence emission of single-quantum systems, and several potential sources have already been studied. Antibunching has been observed in the fluorescence of atoms,^{2,3} organic molecules,^{4–6} AlGaAs quantum dots (QDs),^{7,8} and single nitrogen vacancy centers.^{9,10} Colloidal CdSe–Zns QDs have also attracted much attention, since they can be used at room temperature, present remarkable photostability, and have a high quantum efficiency. Michler *et al.*¹¹ and Lounis *et al.*¹² recently showed that the fluorescence light of such QDs exhibits partial or complete antibunching. However, the fluorescence emission of QDs is known to exhibit intermittency¹³ resulting from physical mechanisms that remain to be fully elucidated. In this Letter the photophysical properties of individual QDs are investigated over a large time scale (from nanoseconds to tens of seconds) by use of the autocorrelation function (ACF), providing a more-comprehensive description of QDs as light emitters.

We prepared the samples by spin coating a nanomolar solution of QDs (1.8-nm radius, 570-nm peak emission) in butanol and a thin film of poly methyl(methacrylate) on a glass coverslip. The excitation light comes from the 514-nm line of a cw Ar⁺ laser whose beam is focused to the diffraction limit (waist, ~300 nm) by a high-N.A. objective (Apochromat; N.A., 1.4; oil immersion) of a confocal microscope. The fluorescence photons are collected by the same objective and sent to a high-sensitivity Hanbury-Brown–Twiss detection scheme composed of a 50/50 nonpolarizing beam splitter followed by two (start and stop) single-photon avalanche photodiodes. The pulses from the photodiodes are simultaneously sent to various data acquisition systems. First, a picosecond time analyzer (PTA; EG&G 9138) pro-

vides histograms of time delays between photons for delays ranging from hundreds to tens of microseconds. The PTA functions similarly to a conventional time–amplitude converter, except that it registers all the stop events during a time interval triggered by a start pulse and gives direct access to the ACF. To investigate negative correlation times, we introduce a constant delay (~200 ns) in the stop channel. The single-photon avalanche photodiode pulses are sent in parallel to a correlator (Malvern 7932) that calculates the ACF for delays greater than 1 μs. Finally, the absolute arrival time of each detected photon is recorded by a counting board with a 12.5-ns time resolution.

The normalized ACF of the fluorescence intensity is a tool suited to exploration of emission properties over large time scales. It is defined as

$$g^{(2)}(t, t + \tau) = \frac{\langle I(t)I(t + \tau) \rangle}{\langle I(t) \rangle \langle I(t + \tau) \rangle}, \quad (1)$$

where $I(t)$ is the fluorescence intensity and $\langle \rangle$ indicates ensemble averaging. In practice, this quantity is calculated by use of time averaging, with implicit assumptions of ergodicity and stationarity. As explained below, calculating this quantity is of great importance in our measurements. Both the PTA and the correlator give the number of coincidence counts, $n(\tau)$, as a function of the time delay between photons. The normalized ACF can be deduced by calculation of $g^{(2)}(\tau) = n(\tau)/I_A I_B \Delta t T$, where I_A and I_B are the mean intensities on the start and stop channels, Δt is the time resolution, and T is the total acquisition time.

A histogram of the coincidence counts on a short time scale given by the PTA shows a dip centered at $\tau = 0$ (Fig. 1). The antibunching of the fluorescence finds its origin in the quantum nature of the emitter: A QD in its ground state needs to absorb an excitation photon before spontaneously emitting a fluorescence photon. Since both these processes take a finite time, two photons cannot be emitted simultaneously. The dip can be described by an exponential curve $a[1 - b \exp(-|\tau|/\tau_0)]$. For

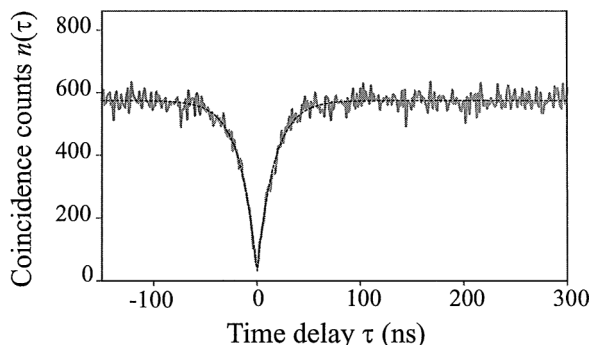


Fig. 1. Histograms of coincidence counts obtained from the PTA (time resolution, 600 ps) and corrected from the time delay. The solid curve is a fit by an exponential curve $a[1 - b \exp(-|\tau|/\tau_0)]$, with $a = 577.5$, $b = 0.95$, and $\tau_0 = 20.1$ ns.

an excitation intensity I well below the saturation limit ($20\text{--}80\text{ kW/cm}^2$),¹² the value of τ_0 is essentially determined by the excited-state lifetime. In our experiments, it is found to be 17.5 (2.0) ns, similar to direct lifetime measurements. In contrast with Michler *et al.*,¹¹ but in agreement with Lounis *et al.*,¹² we found that the measured value of b usually exceeds 0.9, independently of the excitation power. When it is corrected from the background noise that is due to scattered excitation light,¹⁰ the amplitude is even greater than 0.99.

This complete antibunching is a clear indication of single-particle measurement, since two (or more) independent QDs would emit uncorrelated photons and contribute to the histogram at $\tau = 0$. As we repeatedly observed, this complete antibunching is the only non-ambiguous criterion, rather than fluorescence intermittency, for experiments at the single QD level. In our experiments, for I of $\sim 1\text{ kW/cm}^2$, we could collect up to 30×10^6 photons with average detected emission rates of $10\text{--}30\text{ kHz}$. Compared with single molecules at room temperature,⁶ QDs appear to be superior in terms of the number of emitted photons before photodegradation. In addition, the large absorption spectra of QDs make them compatible with a pulsed blue laser diode, opening the way to compact single-photon sources.

The stability of such a source over time is an issue that has seldom been addressed so far. It has been repeatedly observed that QDs exhibit fluorescence intermittency, possibly because of Auger ionization, after creation of multiple electron-hole pairs.^{13,14} This effect manifests itself as an alternation of bright (ON) and dark (OFF) periods with durations of up to tens of seconds.

To link short- and long-term behavior, we measured the ACF from hundreds of picoseconds to tens of seconds. We obtained this time scale, which is to our knowledge unprecedentedly large, by joining the normalized data from the PTA and the correlator without any further adjustment (Fig. 2). The ACF is nearly constant from 100 ns to 100 μs , with a value of a_{norm} that indicates an absence of intermittency on this time scale. To a good approximation, $1/a_{\text{norm}}$ represents the fraction of time spent by the emitter in the ON state.

Beyond 100 μs , the ACF decreases slowly over several time scales before falling more abruptly at a time close to the measurement duration, T . Strikingly, we do not observe a time scale over which the ACF reaches an asymptotic value of 1, even for measurements with a duration of more than 1000 s.

To grasp this particular observation fully, it is useful to compare it with a two-state model in which a system jumps back and forth between an ON and OFF states with constant rates, k_{on} and k_{off} , respectively. Such a model, often employed to represent the fluctuations of fluorescent systems, successfully describes, for instance, bunching in organic molecules as a result of shelving in the triplet state.⁵ In this case, the ACF is stationary and $g^{(2)}(t)$ varies as $1 + [(1 - p)/p]\exp(-t/t_0)$, where $t_0 = 1/(k_{\text{on}} + k_{\text{off}})$ and $p = k_{\text{off}}/(k_{\text{on}} + k_{\text{off}})$. This exponential decay from $1/p$ to 1 implies that, for t much larger than the characteristic time scale t_0 , the ACF is constant (equal to 1). Efros and Rosen actually developed a model for the fluorescence of individual QDs that leads to this kind of behavior.¹⁴

Our ACF measurements cannot be described by an exponential decay. To understand the origin of this discrepancy, we considered the intensity time trace obtained by binning the incoming pulses [Fig. 3(a)]. We obtained the distributions of ON and OFF periods by setting a threshold (equal to a couple of times the background signal) and comparing the intensity with this value. Instead of following exponential laws (as would be the case in the two-state model), the densities of probability of ON and OFF periods, calculated for more than 100 individual QDs, exhibit a power-law dependence $1/t^{1+\mu}$, with μ in the range $0.3\text{--}0.7$.¹⁵ The origin of this dependence, first observed and discussed by Kuno *et al.* for OFF times,¹⁶ has yet to be understood fully. However, its occurrence has several consequences for the shape and the meaning of the ACF.

Since they have no mean values and are dominated by fluctuations, power-law distributions with exponents $1 + \mu$ smaller than 2 stand apart from conventional statistical laws.^{17,18} Because of the long tails of these broad distributions, events with a duration of the order of the acquisition time are likely to occur, as is visible in the trace in Fig. 3(a). Consequently, there is no characteristic time scale over which the fluorescence intensity can be averaged. A stochastic process driven by a broad distribution,

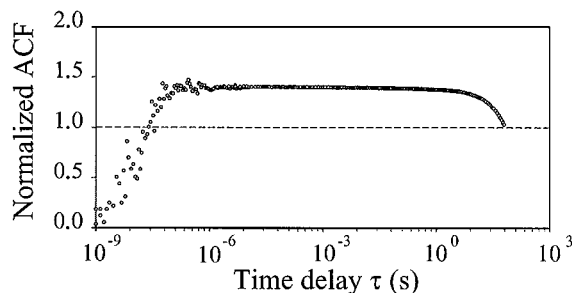


Fig. 2. Normalized ACF from 1 ns to 100 s, measured by the PTA and the Malvern correlator ($T = 900$ s, $I = 2\text{ kW/cm}^2$, $a_{\text{norm}} = 1.4$).

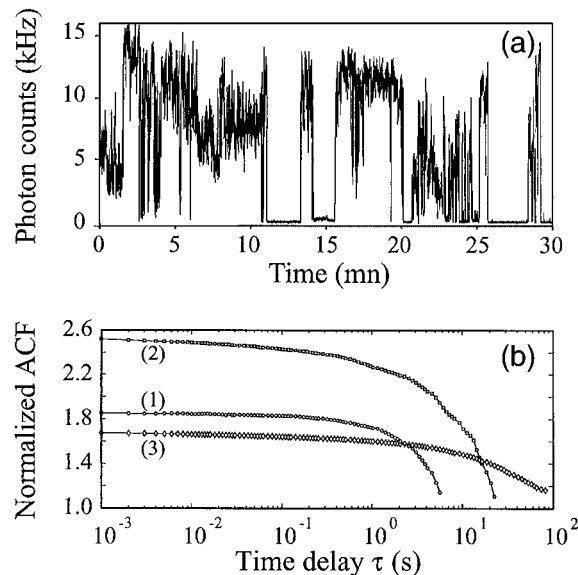


Fig. 3. (a) Time trace of the fluorescence intensity for a single QD (excitation intensity, 0.25 kW/cm^2). (b) Computations of the ACF for this trace. Curves (1), (2), and (3) correspond to time intervals of 18, 180, and 1800 s.

often designated as a Lévy flight, is intrinsically nonergodic: Ensemble and temporal averaging do not coincide.

This interpretation allows us to explain qualitatively the results of our ACF measurements. Since longer and longer ON and OFF events appear as the acquisition time increases, the value of the fraction of time spent in the ON state in the range $0-T$ (and consequently a_{norm}) does not reach an asymptotic value. The existence of ON and OFF times that are comparable to T also explains why the decay of the ACF always occurs on a time scale of the order of the measurement time. Both these properties are illustrated in Fig. 3(b). A significant and nonmonotonic change in the value at short time ($\sim 1 \text{ ms}$) as well as a progressive shift in the characteristic decay time can be observed. This effect is not due to statistical dispersion but is related to the sampling of the power laws during the particular time intervals. In contrast, for a two-state model, increasing the measurement time leads to a better single-to-noise ratio but does not induce any significant change of the ACF.

The nonergodicity induced by broad distributions implies that the temporal ACF does not equal the ensemble value. In particular, the ACF cannot be directly compared with recent analytical calculations of the ensemble correlation function.¹⁹ Nevertheless, the correlation measurements remain an appropriate tool for the study of fluorescence antibunching. Since the time scales of the fluorescence cycles (well below $100 \mu\text{s}$) and the intermittency are strongly decoupled, the coincidence histogram remains valid (and hence the values of b and τ_0). However, the normalized value a_{norm} has no general significance, as it depends critically on the acquisition time.

In conclusion, we have studied the fluorescence of single-colloidal quantum dots, using the ACF. At short time scales, we observed complete antibunching, demonstrating that, even though they have a crystalline structure, the emission properties of individual QDs are those of two-level atoms. At large time scales, because of the power-law dependence of the distributions of ON and OFF periods, QDs cannot be treated as stationary systems, meaning that standard analysis of the ACF should be used with care. This study also raises questions about the interpretation of single-molecule experiments when one is dealing with nonergodic systems.

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