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Nonclassical Radiation from a Single Quantum Dot

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We report the experimental observation of photon antibunching in the photoluminescence of a chemically synthesized CdSe/ZnS quantum dot (QD) at room temperature and from a single self-assembled InAs/GaAs QD at 4 K. These results prove that a single quantum dot acts like an artificial atom, with a discrete anharmonic spectrum. Using the quantum regression theorem, we find that the normalized second-order correlation function $g^{(2)}(\tau)$ can be described by a single exponential function in the weak-laser excitation regime. From this model we derive that the time constant of the photon antibunching signal is determined by the effective incoherent pump and recombination rates of the nonresonant optically pumped QD.

Introduction A solid-state nonclassical light source which is able to generate single photon states is of great interest in quantum optics research. The observation of photon antibunching demonstrates the nonclassical nature of radiation and provides direct evidence that the emission source is a single two-level quantum emitter since this nonclassical effect is washed out if the number of emitters is larger than unity. The physics of photon antibunching is easy to understand: After a photon is emitted from a single two-level emitter at time $\tau = 0$, it is impossible for the system to emit another one immediately after, since it is necessarily in the ground state. The next photon can only be emitted after a waiting time, which is determined by the excitation and relaxation rates. First, photon antibunching has been observed in the resonance fluorescence of a single atom in an atomic beam [1] and from a single ion which has been stored in a radiofrequency trap [2]. The extension of these studies to single molecules has been reported from Basché et al. [3]. Recently, photon antibunching was demonstrated for a single nitrogen-vacancy center in diamond [4, 5].

In this contribution, we report our recent observations of photon antibunching in the fluorescence of a chemically synthesized CdSe/ZnS QD at room temperature [6] and

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from a single self-assembled InAs/GaAs QD at 4 K [7]. The measurements prove that a single self-assembled QD and a chemically synthesized QD can be considered as strongly anharmonic quantum emitters. Our results thus show that QDs have a high potential for applications in the fascinating field of quantum information science. For example, a QD can be used as an active emitter of a single photon source [8]. Such a source is of interest for future applications in quantum computing [9] and quantum cryptography [10].

Experimental The CdSe/ZnS (core/shell) QDs were synthesized following the high temperature organometallic methods described in the literature [11–13]. The resulting nanoparticles were capped with the organic ligand trioctylphosphine oxide (TOPO) and had a distribution with an average diameter of 4.1 nm and a root-mean-square (rms) width of 0.33 nm (8% size distribution). The single QD samples were prepared by spin-casting 30 μl of a 0.5 nM solution of the QDs dissolved in hexanes onto a bare glass coverslip, which resulted in a mean separation of the QDs of approximately 1 μm.

The InAs/GaAs QDs were grown by molecular beam epitaxy (MBE) using the partially covered island technique [14] with a gradient in the QD density reaching from $\leq 10^8$ cm^{-2} to $\sim 10^{10}$ cm^{-2} across the sample wafer. The QDs possess a diameter of $\approx$40–50 nm and a height of $\approx$3 nm, emitting in the wavelength range from 920 to 975 nm.

Our experimental setup combines a diffraction-limited scanning optical microscope (SOM) for spatially resolved photoluminescence (PL) spectroscopy and a standard Hanbury Brown-Twiss (HBT) setup for photon correlation measurements.

Both types of QDs were excited with a continuous wave laser generating the electron–hole pairs in the excited states of the QDs (CdSe/ZnS) and in the barrier layers (InAs/GaAs). The PL of the QDs is collected by a microscope objective. In the case of the CdSe/ZnS QDs the light is passed through a spectral filter to block scattered laser light. In contrast, the InAs/GaAs QD luminescence was passed through a monochromator to spectrally filter the excitonic ground state transition.

To measure the photon statistics of a selected QD the collected light is split with a 50/50 nonpolarizing beam splitter and the resulting two photon beams were focused onto the active areas of two single-photon-counting avalanche photodiodes (SPAD). The pulses from the two SPADs were used to start and stop a time-to-amplitude converter (TAC) whose output is stored in a multichannel analyzer (MCA). An electronic delay (53 ns (12 ns) for CdSe (InAs)) was introduced into the stop channel in order to check for the symmetry of the photon correlation around $\tau = 0$. The time resolution of the HBT setup was 420 ps. The resulting histograms yield the number of photon pairs $n(\tau)$ with arrival time separation of $\tau = t_{\text{stop}} - t_{\text{start}}$. The measured photon count distribution $n(\tau)$ was normalized to the expectation value for counting completely uncorrelated photons obeying a Poissonian arrival time distribution. The normalized measured distribution is equivalent to the correlation function $g^{(2)}(\tau)$ as long as the measured time separation τ between photon pairs is much smaller than the mean time ΔT_{D} between detection events [15], which was always the case for our measurements.

PL images of the CdSe/ZnS nanocrystals were obtained by scanning the QD-covered glass plate through the laser focus and recording the number of counts with one of the SPADs.

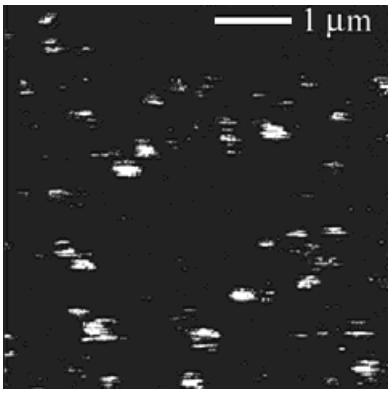

Fig. 1. PL image of CdSe/ZnS nanocrystals on a glass plate, acquired by raster scanning the particle-covered glass plate through the laser focus ($\lambda = 488$ nm, FWHM = 300 nm) and collecting the PL onto a single-photon-counting avalanche photodiode. This 256×256 pixel image (4.9 ms/pixel) represents a $5 \times 5\ \mu m^2$ field of view

Results Figure 1 shows a typical confocal image ($5 \times 5\ \mu m^2$) of CdSe/ZnS nanoparticles on a glass plate. Each bright spot corresponds to the luminescence from either a single CdSe/ZnS QD or a cluster of several QDs. However, it is important to note that the smallest spot size (≈300 nm) is defined by the resolution of the SOM. As can be seen, bright spots with different sizes are visible and the smallest spots appear to blink "on" and "off" during the course of a scan [16]. This behavior is thought to be the result of QD ionization which is discussed elsewhere [6].

Figure 2 shows a comparison between a PL spectrum (300 K) of an ensemble of CdSe/ZnS nanoparticles (a) and of a strong blinking nanoparticle (b) and therefore likely a single QD. As expected, the ensemble spectrum shows a broad (≈133 ± 0.4 meV) and smooth spectrum due to averaging over many individual nanocrystal spectra. The spectrum of the strong blinking nanoparticle is spiky and exhibits a somewhat smaller linewidth (≈111 ± 7 meV). This line shape is thought to arise from rapid shifting of the emission wavelength (spectral diffusion) on a time scale that is fast relative to the measuring time [17]. In contrast, the PL spectrum of a self-assembled InAs QD at low temperature (4 K) shows a single, resolution limited (70 μeV) line due to single exciton recombination (1X) (see Fig. 3).

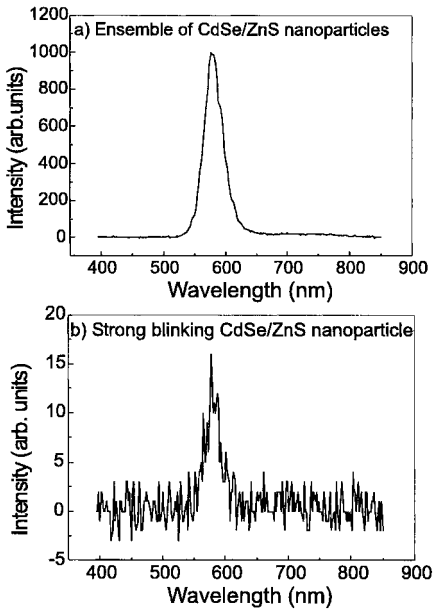

Fig. 2. PL spectrum of a) an ensemble of CdSe/ZnS nanoparticles and b) of a strong blinking CdSe/ZnS nanoparticle at $T = 300$ K, respectively

However, the observation of strong blinking and discrete emission lines in the spectrum cannot be taken as an evidence that the observed system consists of a single nanoparticle. It cannot be ruled out that several QDs contribute to the PL spectrum. In contrast,

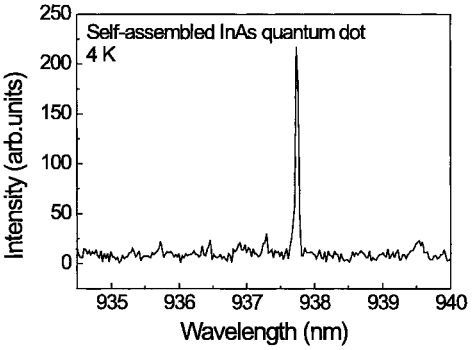

Fig 3. Photoluminescence spectrum of a self-assembled InAs quantum dot, obtained at 4 K at a pump intensity of 66 W cm^{-2}

photon correlation measurements, such as those reported below, provide a reliable method for deciding whether or not the observed system is a single two-level quantum emitter.

The measured *raw data* photon correlation signals from a cluster of several CdSe/ZnS QDs and a single CdSe/ZnS QD are shown in Fig. 4. In order to minimize the generation of two electron–hole pairs simultaneously we used a low excitation intensity of $\approx$250 W/cm^2. Typically, a QD is excited every $\sim$1–10 μs [17], whereas the PL decay time is on the order of 30 ns. Thus the probability of generating two electron–hole pairs is small. The single QD data shows a minimum of coincidence counts $n(\tau)$ around $\tau = 0$, and an exponential increase of $n(\tau)$ for negative and positive τ. This is a clear signature of nonclassical photon antibunching [1, 18]. In contrast, the photon correlation signal of the CdSe/ZnS cluster is flat. In this case many independently radiating QDs contribute to the signal.

The measured photon count distribution $n(\tau)$ for the 1X transition of the InAs QD is shown in Fig. 5 for two different pump intensities. These intensities correspond to an excitation of the QD well below saturation (a) (see also Fig. 3) and at the onset of saturation (b). Saturation is defined here as the pump intensity at which the 1X line reaches its maximum intensity [19]. Traces (a) and (b) exhibit also a clear dip in the correlation counts for a time delay $\tau = 0$, indicating a strong photon antibunching. For comparison, trace (c) of Fig. 5 shows the correlation for multiple emission lines of many QDs in a high-density region of the sample. As expected, this correlation is flat over the complete measurement time and its normalized value of 1 corresponds to Poissonian photon statistics.

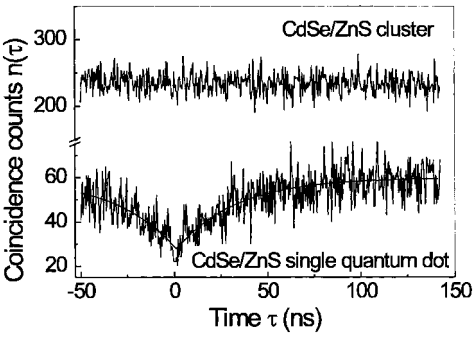

Fig. 4. Measured distribution $n(\tau)$ of photon pair separation times τ for a CdSe/ZnS cluster and a single quantum dot at 300 K. The full line represents a fit to an exponential law and is described in the text

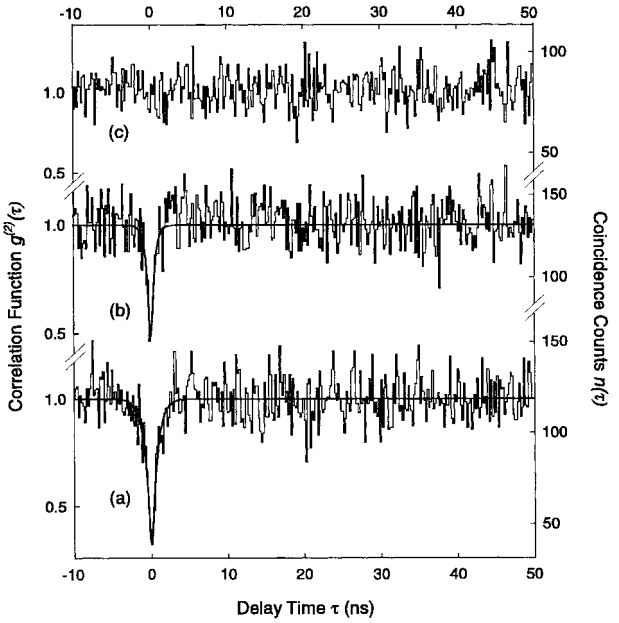

Fig. 5. Measured distribution of coincidence counts $n(\tau)$ and fit of the correlation function $g^{(2)}(\tau)$ (solid line) for a single InAs QD at 4 K, obtained at two different pump intensities: 66 $\mathrm{Wcm^{-2}}$ (trace (a)) and 252 $\mathrm{W\,cm^{-2}}$ (trace (b)). Trace (c) shows the coincidence counts for many QDs in a high density region of the sample

To model our photon correlation experiment, we use a three-state model for the QDs. We assume that the excited electron–hole pair relaxes incoherently before spontaneously emitting a photon: this relaxation process between the excited state and the radiatively active upper state is much faster than other relevant rates [20–22]. In addition, we have introduced a fast, elastic dephasing rate for the coherences between the ground and excited states. Using quantum regression theorem, we derive an expression for the normalized second-order correlation function [18] $g^{(2)}(\tau) = \langle : I(t)I(t+\tau) : \rangle / \langle I(t) \rangle^2$ (: : indicates normal ordering and $I(t)$ is the measured intensity) in the weak-laser excitation regime

$$g^{(2)}(\tau) = 1 - \mathrm{e}^{-(\Gamma + W_\mathrm{p})\tau} . \tag{1}$$

Here Γ is the spontaneous emission rate and W_p is the effective pump rate into the radiatively active upper state. The fast dephasing of the emitting transition has no effect on $g^{(2)}(\tau)$ of a single QD. In contrast, for an ensemble of QDs, the bunching effect decays with the dephasing time, which is estimated to be at least 10 ps using the narrowest observed linewidths [23]. This result indicates that with the time resolution of our experiment $\tau_\mathrm{res} = 420$ ps, one expects to find uncorrelated photon counting events for an ensemble of QDs (i.e. $g^{(2)}(\tau) = 1$).

The single QD data are fitted by

$$g^{(2)}(\tau) = 1 - a\,\mathrm{e}^{-\tau/t_\mathrm{d}} , \tag{2}$$

where $t_\mathrm{d} = 1/(\Gamma + W_\mathrm{p})$ is the antibunching time constant and a is introduced to take care of background light. Both t_d and a are fit parameters.

In the case of the CdSe/ZnS dot, we obtain $t_\mathrm{d} = 32 \pm 2$ ns which directly determines the radiative decay time under our experimental conditions ($W_\mathrm{p} \ll \Gamma$). This value is on

the same order of magnitude as independent lifetime measurements on ensembles of QDs. The fit also gives an estimate of $g^{(2)}(0) = 0.47 \pm 0.02$, which is a clear signature of nonclassical photon antibunching from a single anharmonic quantum system. The measured correlation function $g^{(2)}(0)$ does not reach its theoretical minimum of zero because of the presence of residual stray-light and biexciton luminescence. The biexcitonic contribution in the luminescence should be small due to the low excitation power. In addition, the fast Auger rate in this type of QDs also reduces the probability of biexcitonic recombination.

In order to correct for the time resolution of our setup the InAs single QD data were fitted with the normalized count distribution, Eq. (2), convolved with a gaussian time distribution with 420 ps full width half maximum. The resulting fitted $g^{(2)}(\tau)$ is shown as solid line in Fig. 5. The values of $1 - a = g^{(2)}(0)$ obtained from the fit are 0.23 and 0.34 for traces (a) and (b). The fact that $g^{(2)}(0) < 0.5$ in both traces unambiguously indicates that the measured photon antibunching from the 1X transition stems from a single, anharmonic quantum emitter. However, $g^{(2)}(0)$ does not reach its ideal value of zero due to the presence of background straylight. The correlation function $g_{\mathrm{b}}^{(2)}(\tau)$ expected in the presence of a background radiation is $g_{\mathrm{b}}^{(2)}(\tau) = 1 + \rho^2(g^{(2)}(\tau) - 1)$, where $\rho = S/(S + B)$ is the ratio of signal S to background B counts [5]. From the optical emission spectra of the single QD we can determine ρ for the 1X transition for the two pump intensities to be 0.9 and 0.83, respectively. The resulting values of $g_{\mathrm{b}}^{(2)}(0)$ are 0.18 and 0.30, which are in good agreement with $g^{(2)}(0)$ values determined by the fits. The antibunching time constants t_{d} obtained from the fit of $g^{(2)}(\tau)$ are 736 ps and 444 ps for traces (a) and (b). Thus the t_{d} decreases with increasing pump power in accordance with our model. Using these pump-intensity-dependent time constants and a simple three-level rate equation model taking into account exciton and biexciton transitions we can determine the lifetime of the single exciton ground-state transition to be 900 ± 100 ps. Details of the analysis can be found in Ref. [7]. This value is comparable to lifetime values found in the literature [24].

Summary In summary, we showed that the photoluminescence from a single self-assembled InAs QD and from a single chemically synthesized CdSe/ZnS QD exhibits photon antibunching. We have demonstrated that a CdSe quantum dot behaves as an anharmonic emitter even at room temperature and is therefore a potential candidate as an active emitter for a single photon source. The observation of nonclassical radiation in various types of QDs opens the way for different applications in the field of quantum information science and cavity-QED experiments.

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References

[1] H. J. KIMBLE, M. DAGENAIS, and L. MANDEL, Phys. Rev. Lett. **39**, 691 (1977).
[2] F. DIEDRICH and H. WALTHER, Phys. Rev. Lett. **58**, 203 (1987).
[3] TH. BASCHÉ, W. E. MOERNER, M. ORRIT, and H. TALON, Phys. Rev. Lett. **69**, 1516 (1992).
[4] C. KURTSIEFER, S. MAYER, P. ZARDA, and H. WEINFURTER, Phys. Rev. Lett. **85**, 290 (2000).
[5] R. BROURI, A. BEVERATOS, J.-P. POIZAT, and P. GRANGIER, Opt. Lett. **25**, 1294 (2000).

[6] P. MICHLER, A. IMAMOGLU, M. D. MASON, P. J. CARSON, G. F. STROUSE, and S. K. BURATTO, Nature **406**, 968 (2000).
[7] C. BECHER, A. KIRAZ, P. MICHLER, A. IMAMOGLU, W. V. SCHOENFELD, P. M. PETROFF, LIDONG ZHANG, and E. HU, Phys. Rev. B **63**, 121312(R) (2001).
[8] P. MICHLER, A. KIRAZ, C. BECHER, W. V. SCHOENFELD, P. M. PETROFF, LIDONG ZHANG, E. HU, and A. IMAMOGLU, Science **290**, 2282 (2000).
[9] E. KNILL, R. LAFLAMME, and G. J. MILBURN, Nature **409**, 46 (2001).
[10] D. BOUWMEESTER, A. EKERT, and A. ZEILINGER, The Physics of Quantum Information, Springer-Verlag, Berlin 2000.
[11] C. B. MURRAY, D. J. NORRIS, and M.G. BAWENDI, J. Am. Chem. Soc. **115**, 8706 (1993).
[12] M. A. HINES and P. GUYOT-SIONNEST, J. Phys. Chem. **100**, 468 (1996).
[13] B. O. DABBOUSI et al., J. Phys. Chem. **101**, 9463 (1997).
[14] J. M. GARCIA, T. MANKAD, P. O. HOLTZ, P. J. WELLMAN and P. M. PETROFF, Appl. Phys. Lett. **72**, 3172 (1998).
[15] R. HANBURY BROWN and R.Q. TWISS, Nature (London) **178**, 1447 (1956).
[16] M. NIRMAL et al., Nature **383**, 802 (1996).
[17] M. NIRMAL and L. BRUS, Acc. Chem. Res. **32**, 407 (1999).
[18] D. F. WALLS and G. J. MILBURN, Quantum Optics, Springer-Verlag, Berlin 1994.
[19] E. DEKEL, D.V. REGELMAN, D. GERSHONI, E. EHRENFREUND, W.V. SCHOENFELD, and P.M. PETROFF, Phys. Rev. B **62**, 11038 (2000).
[20] V. I. KLIMOV and DUNCAN W. MCBRANCH, Phys. Rev. Lett. **98**, 4028 (1998).
[21] S. RAYMOND et al., Phys. Rev. B **54**, 11548 (1996).
[22] T. F. BOGGESS, L. ZHANG, D. G. DEPPE, D. L. HUFFAKER, and C. CAO, Appl. Phys. Lett. **78**, 276 (2001).
[23] S. EMPEDOCLES and M. BAWENDI, Acc. Chem. Res. **32**, 389 (1999).
[24] E. DEKEL et al., Solid State Commun. **117**, 395 (2001).