Bright and Grey States in CdSe-CdS Nanocrystals Exhibiting Strongly Reduced Blinking

P. Spinicelli,[1] S. Buil,[2] X. Quélin,[2] B. Mahler,[3] B. Dubertret,[3,*] and J.-P. Hermier[2,†]

[1]*Laboratoire Kastler Brossel, École normale supérieure, Université Pierre et Marie Curie, CNRS UMR8552, 24 rue Lhomond 75231 Paris Cedex 05, France*

[2]*Groupe d'Étude de la Matière Condensée, Université de Versailles-Saint-Quentin-en-Yvelines, CNRS UMR8635, 45 avenue des États-Unis, 78035 Versailles, France*

[3]*Laboratoire Photons Et Matière, CNRS UPR5, ESPCI, 10 rue Vauquelin, 75231 Paris, France*

(Received 18 August 2008; published 30 March 2009)

When compared to standard colloidal nanocrystals, individual CdSe-CdS core-shell nanocrystals with thick shells exhibit strongly reduced blinking. Analyzing the photon statistics and lifetime of the on state, we first demonstrate that bright periods correspond to single photon emission with a fluorescence quantum efficiency of the monoexcitonic state greater than 95%. We also show that low intensity emitting periods are not dark but correspond to a grey state, with a fluorescence quantum efficiency of 19%. From these measurements, we deduce the radiative lifetime (45 ns) and the Auger lifetime (10.5 ns) of the grey state.

DOI: 10.1103/PhysRevLett.102.136801 PACS numbers: 73.63.Bd, 42.50.Ar, 73.22.−f

During the last decade, colloidal CdSe semiconductor nanocrystals (NCs) have attracted great attention. Their high quantum efficiency (QE) and high photostability at room temperature make them very promising emitters for a wide range of applications such as optoelectronic [1], biological labelling [2] or quantum cryptography [3]. However, at the single molecule level, CdSe colloidal NCs exhibit fluorescence intermittency: their fluorescence intensity switches between bright and dark states [4]. The dark periods follow slowly decaying power law distributions known as Lévy statistics [5] with nondefined variance and mean. The main consequence of Lévy statistics is that ''off'' events of the order of the observation time are observed and tend to dominate the fluorescence signal [6]. In the field of quantum cryptography and of biological labeling, these arbitrary long events represent the main restriction for the use of colloidal NCs.

The very origin of blinking is not completely established. However, it is commonly admitted that fluorescence intermittency is due to ionization of the NC [7]. One carrier of an electron-hole (e-h) pair is ejected from the NC core into the surrounding matrix or trapped at the NC surface. The ionized NC is nonfluorescent due to Auger process between the remaining carrier and any subsequent e-h pair. The NC becomes fluorescent again when charge neutrality is recovered.

First results to reduce fluorescence intermittency were obtained using organic molecules acting as charge compensators or charge mediators at the NC surface [8]. However, the obtained NCs still exhibit strong blinking. More recently, two groups have synthesized novel CdSe-CdS core-shell with very thick shells [9,10]. At the typical CCD observation rate of 30 Hz most of individual NCs do not blink. At faster acquisition rates (1 kHz), low emitting states are observed but their statistics duration is no longer a Lévy statistics. Mean values and standard deviation are defined and the longest low emitting period do not exceed 50 ms.

Compared to CdSe-ZnS NCs, CdSe-CdS NCs exhibit another important difference. In CdSe-ZnS NCs, electrons and holes are confined in the core of the NC. In the case of CdSe-CdS NCs, if the hole is also confined in the core, due to relative positions of CdSe and CdS conduction bands, the electron is delocalized in the whole structure. For this kind of NCs, the thicker the layer, the more the fluorescence is red shifted and the radiative lifetime is increased [9]. The delocalization of charge carriers also reduces Coulomb interactions, inducing an increase of Auger lifetime. Through a spectroscopic study of multiexcitonic processes in CdTe-CdSe NCs ensembles, for which localization of electrons and holes are different, Oron *et al.* also demonstrated that Auger lifetime does not scale with the volume as for CdSe-ZnS NCs [11].

In this Letter, we investigate the modification of low emitting periods due to the Auger lifetime increase. Using an original method to study the high and low emitting periods, we first demonstrate that bright periods correspond to single photon emission. The fluorescence QE of the monoexcitonic state, determined at the single NC level is also found to be nearly perfect. Next, we show that low intensity periods in CdSe-CdS NCs emission are not ''dark'' states as for CdSe-ZnS NCs. Under low power excitation, the grey state corresponds to a trion (one e-h pair in a ionized NC). We measure a fluorescence QE of the trion state equal to 19%. Comparing the QEs of ''on'' and ''grey'' periods, we deduce the Auger lifetime and radiative lifetime of the grey state.

In our experiments, a nanomolar solution of CdSe-CdS core-shell NCs ($\lambda = 620$ nm peak emission, FWHM of 30 nm) was spin coated on a glass cover slip. These NCs were synthesized as described in [9]. A CdSe core is surrounded by a CdS layer as thick as 5 nm. The fluores-

cence of individual NCs is collected by a confocal microscope with an oil immersion objective (NA = 1.4). Pulsed excitation comes from a 400 nm pulsed laser diode (Picoquant). The pulse duration (50 ps) is much shorter than the radiative lifetime (about 60 ns) in order to observe single photon emission. Photons are detected by a high sensitivity Hanbury Brown and Twiss setup consisting on two avalanche photodiodes (PerkinElmer, time resolution of 300 ps). The signal of the two photodiodes is sent to a data acquisition card (TimeHarp 200). In the following, two configurations were used. In the configuration 1 ($C1$), the card measures the delay between photons when this delay is lower than 4.7 μs. The time resolution is equal to 1.1 ns. For each pair of photons, the card also provides the arrival time of the first photon with a time resolution of 100 ns. After choosing a time bin t_b, these data enable us to know the evolution versus time of the number of photon pairs detected per time bin t_b. This number is proportional to the square of the fluorescence intensity. As the number of pairs recorded never exceeds 5×10^4 pairs per second, t_b must be greater than 1 ms to obtain a significant number of event per time bin. The repetition period was set to 400 ns, a period much longer than the fluorescence lifetime in order to avoid any overlap between the peaks observed in the histogram of the delays between photons (see Fig. 1). In the second configuration 2 ($C2$), the card records the delay between the photons detected by the avalanche photodiodes and the laser pulses. The arrival times of each photon is also recorded, which gives the evolution of the fluorescence intensity. In order to increase the fluorescence intensity, we could lower the repetition period to 200 ns without generating any systematic error in the photoluminescence (PL) decay fitting. Since the maximal measured intensity is of the order of 3×10^5 photons per second, t_b cannot be shorter than 0.1 ms for $C2$. The crucial point is that, using $C1$ and $C2$, we can select the photons detected for a specific fluorescence intensity level and characterize the corresponding photon delay statistics ($C1$) or PL decay rate ($C2$).

We first demonstrate that the bright state corresponds to single photon emission whatever the number of e-h pairs generated by each laser pulse may be. Only the monexcitonic state can recombine radiatively and we show that its QE, i.e., the probability that the e-h pair recombination

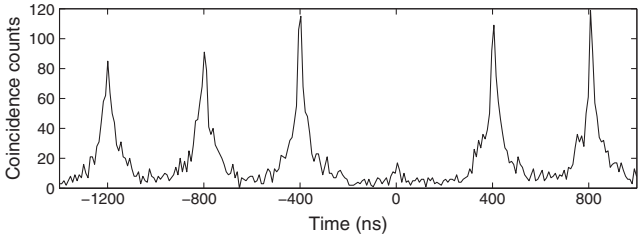

FIG. 1. Histogram of coincidence counts of the on state under high pulsed excitation.

generates a photon, is greater than 95%. Using $C2$, we recorded the fluorescence of an individual NC. Increasing progressively the pump power, we measured that the maximal intensity $I_{\max}$ is equal to 350 ± 20 kHz (35 photons per $t_b = 0.1$ ms). Let us now illustrate how $C1$ permits to characterize the delays between photons for the bright state emission. Performing another fluorescence recording, we define the on state threshold as half of the maximal number of photon pairs per time bin ($t_b = 1$ ms). Selecting the photons detected during the consecutive bright states, we can calculate the histogram of the delays between photons (Fig. 1). The absence of photon coincidences at zero delay proves that only single photon are emitted during on states. Considering the laser repetition rate for $C2$ (200 ns), we deduce that 7% of the laser pulses produce a single photon which is detected by our experimental setup. To evaluate the QE of the monoexcitonic state of our CdSe-CdS NCs, we measured the maximal collected intensity obtained with standard CdSe-ZnS NCs (2.5 nm core radius, $\lambda =$ 620 nm peak emission) of which QE has been measured independently [12] and found to be higher than 95%. In average, we found that the number of emitted and collected photons per pulse is equal to 7.1% ($\pm$ 0.4%), showing that the fluorescence QE of the monoexcitonic state of CdSe-CdS NCs is greater than 95%. To confirm that the QE is very close to 1, we considered the optical losses of each element of our setup (lenses, filters, microscope objective, photodiodes) and calculated that the collection efficiency of our setup cannot exceed 8,5%.

As standard CdSe-ZnS NCs, CdSe-CdS exhibit on periods with a fluorescence QE of the monoexcitonic state close to 1 [12]. The growth of a ZnS thin shell on a CdSe core permits to obtain nearly perfect QE, but blinking characterized by long off events is observed. In the case of a thick CdS shell, a QE close to 1 and quasisuppression of blinking are simultaneously obtained.

Saturation of monoexcitonic emission is reached for very high pump power for which many e-h pairs are created by the same laser pulse. As for standard CdSe-ZnS NCs, we observe the absence of signal at zero delay in the coincidence histogram. This demonstrates that, if more than one e-h pair are generated by a single pulse excitation, Auger recombination is the preferential energy relaxation channel until only one electon hole pair remains.

We now analyze the fundamental properties of low emitting and bright states. In order to avoid any multiexcitonic process, we choose a pump power for which the probability to generate several e-h pairs by one pulse is low. In the following, we adjust the pump power to a value μ to get the mean intensity of the on state equal to 54 kHz. The probability to create at least 1 e-h pair by pulse is then equal to $I/I_{\max} = 15.4\%$. Since the laser wavelength is much shorter than the emission wavelength, an e-h pair is always created in a highly excited state belonging to a quasi continuum. No blockade effect [13] can occur and

we can assume that the probability to generate an e-h pair does not depend on the presence of e-h pairs in the NC. The generation of each e-h pairs is an independent process and the number of e-h pairs excited by an individual laser pulse follows a Poissonian statistics. Let us call $P(n)$ the probability to have n e-h pairs after one pulse. If $\sum_1^\infty P(n) = 15.4\%$, we deduce $P(1) = 14.2\%$ and $\sum_2^\infty P(n) = 1.2\%$. The probability to excite multi e-h pairs is much lower than the probability to create a single e-h pair [14].

In Fig. 2(a), we plotted a zoom of the intensity trace ($t_b = 1$ ms, total time recording = 180 s) we obtained and the corresponding intensity histogram [Fig. 2(b)]. The emission of a dark region without any NC has been recorded for the same pump power. The corresponding signal has a mean value equal to 1.35 photons per ms. The crucial point is that the low emitting states are not dark states as in the case of standard CdSe-ZnS NCs. Their intensity are well above the background signal (1.35 photons per ms). For the high and low emitting states, we call I_h and I_l the intensity values corresponding to the maximum of the two peaks. Using the data of Fig. 2, we find $I_h = 54$ photons per ms and $I_l = 10$ photons per ms. For each peak, if we consider a Poissonian distribution having the same mean value, we find a standard deviation of the order of 65% of the fluctuations experimentally observed. This suggests that the low and high emitting states can be mostly described by two states.

Selecting the photons detected for intensity ranging from 50 to 58 photons per ms [range B of Fig. 2(b)], we plotted the PL decay time of the bright periods [Fig. 2(c)]. For the range [0–200 ns], which corresponds to the delay between each laser pulse, the decay is described by a monoexponential curve corresponding to a lifetime of 62($\pm$1) ns. For the low emitting state (intensity ranging from 8 to 13 photons per ms, range A of Fig. 2(b)], we find also a monoexponential decay for the first decade with a lifetime of 8.5($\pm$0.5) ns. Finding monoexponential decays for each intensity level confirms the possibility to describe the NC fluorescence by two emitting states. The bright state corresponds to the monoexcitonic neutral state of the NC. As for standard CdSe-ZnS NCs, we suppose that low emission is observed when the NC is ionized. The hole being well confined in the CdSe core while the electron is delocalized in the whole structure, the ionization process most probably occurs when the electron escapes from the NC. We can consider that the excited NC is then described as a trion.

For the same pump power μ, we also recorded the delays between photons using $C1$ ($t_b = 10$ ms, total time recording = 180 s). In Fig. 3(a), we plotted the number of photon pairs per 10 ms time bin detected during 2 s and the thresholds we used to define the grey and on states. Figure 3(b) [respectively, Fig. 3(c)] represents the histogram of delays between photons for the on state (respectively the low emitting state). The complete absence of peak at zero delay demonstrates that the fluorescence of the bright and grey states correspond to single photon emission. The decays of the histogram peaks is in agreement with the values of the lifetime decays measured with the configuration $C2$ [15].

The results obtained with the two configurations show that the CdSe-CdS can be pictured as a system randomly switching between the two states represented in Fig. 4. In the bright state, the recombination of an e-h pair is purely radiative. The radiative lifetime is equal to $1/k_{\mathrm{rad}} = 62$ ns. In the grey state, two ways of recombination are in competition. The e-h pair can recombine radiatively giving rise to a single photon (rate k'_{rad}). Through an Auger process (rate k_A), it can also transfer its energy to the hole remain-

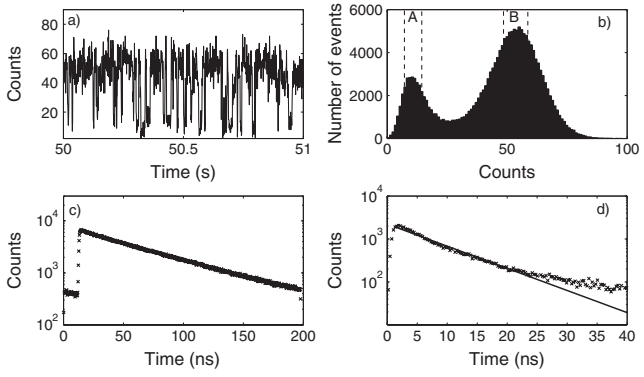

FIG. 2. (a) Fluorescence intensity of a single CdSe-CdS NC (configuration $C2$, zoom of 1 s). The pump power is adjusted to have a probability to excite the NC by one laser pulse equal to 15.4%. (b) Intensity histogram corresponding to (a). (c) PL decay of the ''bright'' state [range B of (b)]. (d) PL decay of the grey state [range A of (b)]. The line is an exponential decay with a lifetime of 8.5 ns.

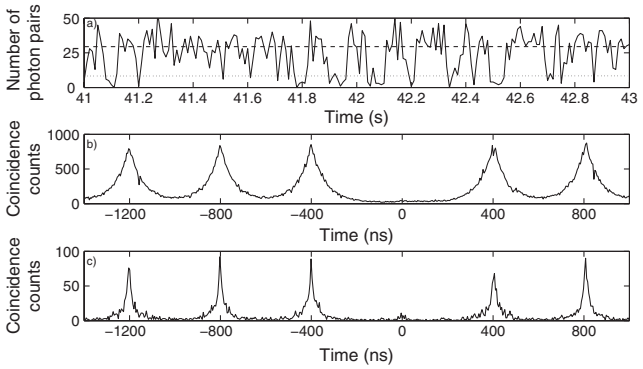

FIG. 3. (a) Number of photon pairs per time bin ($t_b = 10$ ms) (configuration $C1$, zoom of 2 s). The intensity excitation μ is the same as the one of Fig. 2. The dotted line represents the threshold for the grey state, and the dashed line corresponds to the threshold for the on state. (b) Histogram of coincidence counts for the on state. (c) Histogram of coincidence counts for the grey state.

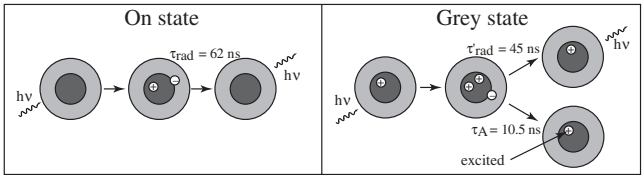

FIG. 4. Scheme presenting the on and grey states. (a) For the on state, the absorption of one photon results in the emission of one fluorescence photon. (b) For the grey state, two recombination processes of an *e*-*h* pair are possible. The first one corresponds to a radiative process. In the second one, the *e*-*h* pair energy is transferred to the remaining carrier.

ing in the core of the NC. The desexcitation rate k of the PL is the sum $k'_{\mathrm{rad}} + k_A$ of the two processes rates.

From the histogram [Fig. 2(b)], we now deduce the QE $Q' = k'_{\mathrm{rad}}/(k'_{\mathrm{rad}} + k_A)$ of the grey state, i.e., the probability of the electron to recombine radiatively with one of the two holes. Since the laser excitation wavelength corresponds to an energy of 3.11 eV far above the band edge of CdSe and CdS, the absorption of the neutral and charged NCs are equal. Indeed, differences between the two absorptions spectra have been measured but only for energies corresponding to transitions implying the most confined levels of the hole and electron [16]. For optical transitions which do not correspond to any strong resonance, the NC absorption cross section can be theoretically described using the formalism of light scattering by small particles [17–19]. In this case, we can consider that the probability to excite the NC does not depend on its ionization state. Considering the perfect QE of the monoexcitonic bright state, the ratio between the grey state intensity I_l and the bright state intensity I_h is equal to the QE of the trion grey state. From data plotted in Fig. 2(b), we obtain $Q' = 0.19(\pm 0.01)$. Using the expresions of k'_{rad} and Q', we calculate $1/k'_{\mathrm{rad}} = 45(\pm 5)$ ns and $1/k_A = 10.5(\pm 0.7)$ ns.

In contrast with CdSe-ZnS NCs, Auger processes are less efficient in CdSe-CdS NCs due to delocalization of the electron in the shell. If photon emission of charged CdSe-ZnS NC is completly quenched by Auger interaction, we observe photoluminescence from a charged CdSe-CdS NC with a QE of about 19%. Our results also demonstrate the decrease of the radiative lifetime in case of ionization (from 62 to 45 ns). Such observation has already been made on charge and neutral biexcitonic emission of an ensemble of semiconductor NCs [20].

In conclusion, we used an original method to investigate the emitting states of CdSe-CdS NCs which are very promising due to their very reduced blinking. Measuring the delays between photons and the lifetime selectively for low and high emitting states, we first demonstrated that bright states correspond to single photons emission due to radiative monoexcitonic recombination. The QE of this process is close to unity. Under low excitation power, the low emitting state was found to be a grey state and not a dark state as for standard core-shell NCs. It corresponds to a radiative recombination of a trion exhibiting a QE of 19%. Finally, at the single molecule level, we investigated the consequences of the delocalization of the electron in the NC shell and the induced reduction of Auger processes efficiency. If Auger processes still prevent multiexcitonic emission of the on state, the trion can recombine radiatively. The reduction of the Auger effect results in non dark, low intensity emitting periods. Our results may be the first step towards nanocrystals characterized by an Auger recombination of the ionized nanocrystal less efficient than radiative recombination.

We thank P. Guyot-Sionnest for fruitful discussions. This work has been supported by CNANO Ile de France and the Agence Nationale pour la Recherche.

*benoit.dubertret@espci.fr
†hermier@physique.uvsq.fr

[1] V. I. Klimov *et al.*, Science **287**, 1011 (2000).
[2] X. Michalet *et al.*, Science **307**, 538 (2005).
[3] P. Michler *et al.*, Nature (London) **406**, 968 (2000).
[4] M. Nirmal *et al.*, Nature (London) **383**, 802 (1996).
[5] M. Kuno *et al.*, J. Chem. Phys. **112**, 3117 (2000).
[6] X. Brokmann *et al.*, Phys. Rev. Lett. **90**, 120601 (2003).
[7] M. Kuno *et al.*, J. Chem. Phys. **115**, 1028 (2001).
[8] S. Hohng and T. Ha, J. Am. Chem. Soc. **126**, 1324 (2004).
[9] B. Mahler *et al.*, Nature Mater. **7**, 659 (2008).
[10] Y. Chen *et al.*, J. Am. Chem. Soc. **130**, 5026 (2008).
[11] D. Oron *et al.*, Phys. Rev. B **75**, 035330 (2007).
[12] X. Brokmann *et al.*, Phys. Rev. Lett. **93**, 107403 (2004).
[13] A. Imamoglu *et al.*, Phys. Rev. Lett. **72**, 210 (1994).
[14] In principle, we could decrease the pump power to a value lower than μ in order to increase the ratio $P(1)/\sum_2^\infty P(n)$. Yet, the pump power must be high enough to get the grey state intensity greater than the background signal.
[15] X. Brokmann *et al.*, Appl. Phys. Lett. **85**, 712 (2004).
[16] K. Shimizu, Ph.D. thesis, Massachusetts Institute of Technology, Boston, 2002.
[17] C. A. Leatherdale *et al.*, J. Phys. Chem. B **106**, 7619 (2002).
[18] van de Hulst and H. C. Light, *Scattering by Small Particles* (Dover Publications, New York, 1981), 2nd ed.
[19] S. Berciaud, Ph.D. thesis, Université de Bordeaux 1, 2006.
[20] C. Bonati *et al.*, Phys. Rev. B **71**, 205317 (2005).