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X Brokmann[1], G Messin[1], P Desbiolles[1], E Giacobino[1], M Dahan[1] and J P Hermier[1,2]

[1] Laboratoire Kastler Brossel, École normale supérieure, Université Pierre et Marie Curie et CNRS, 24 rue Lhomond, 75231 Paris Cedex 05, France
[2] Fédération de Recherche Matériaux et Phénomènes Quantiques, Université Denis Diderot, 2 place Jussieu, 75251 Paris Cedex 05, France
E-mail: hermier@lkb.ens.fr

Abstract. The fluorescence of colloidal CdSe/ZnS nanocrystals at room temperature exhibits a perfect antibunching under continuous or pulsed excitation. In this paper, we discuss the consequences of fluorescence properties of CdSe nanocrystals on the generation of single photons. In particular, we examine the role of Auger processes in the inhibition of multiexcitonic emission. We also discuss the relationship between Auger processes and the fluorescence intermittency of CdSe quantum dots. Altogether, features discussed here indicate that CdSe/ZnS nanocrystals are promising single-photon sources.

Contents

1. Introduction

Single-photon emission has been demonstrated using the fluorescence of single emitters such as atoms [1], ions [2], organic molecules [3], semiconductor quantum dots [4]–[6] and nitrogen vacancy centres [7]. In the field of quantum information processing, single-photon sources could be used for quantum cryptography or optical quantum computation [8, 9].

Colloidal CdSe/ZnS core-shell nanocrystals have also been the focus of great attention because of their high quantum yield and high photostability at room temperature. These features make them promising emitters not only for quantum information but also for biological labelling [10] or the realization of devices such as thin-film LEDs or nanocrystal quantum dot (QD) lasers [11]–[13]. When observed individually, CdSe QDs exhibit remarkable properties. The fluorescence is known to exhibit fluorescence lifetime fluctuations [14], spectral shifts [15] and fluorescence intermittency resulting in the alternance of dark and bright periods [16]. Compared with atoms or molecules, CdSe/ZnS QDs provide opportunities to investigate new phenomena as well. The nanometre size of these QDs (radius <5 nm) permits the investigation of interactions between efficient multi-carriers known as Auger processes. Their effect on the fluorescence properties of CdSe QDs have previously been examined in detail for optical gain generation and lasing from CdSe QDs [11]–[13].

In this paper, we investigate the generation of single photons by colloidal CdSe/ZnS QDs under continuous (cw) and pulsed excitation, the latter being the regime used in quantum information protocols. First, we show that perfect antibunching can be obtained. Next, the nature of Auger processes and their role in single-photon emission are discussed. We show that the efficiency of these processes in nanometre-sized CdSe QDs is a clear advantage for triggered single-photon generation since it makes the light emission properties of CdSe nanocrystals similar to those of individual quantum systems such as single atoms or molecules. Finally, we discuss the implications of recent results concerning the fluorescence intermittency of colloidal CdSe QDs.

2. Experimental setup

In our experiments, colloidal CdSe/ZnS core/shell nanocrystals are chemically synthesized semiconductor nanoparticles with a mean radius of 1.7 nm and a peak wavelength emission about 560 nm. To collect the fluorescence of a single nanocrystal, samples are prepared by spin coating a nanomolar solution of quantum dots in butanol on a cleaned glass coverslip. After deposition, the mean distance between two nanocrystals is about 1 μm. The fluorescence emitted by a single nanocrystal under continuous or pulsed excitation is collected by a confocal microscope. For continuous wave excitation we used the 514 nm line of an Ar-ion laser. The pulsed excitation comes from a 400 nm pulsed laser diode whose pulse duration ($\tau_p = 50$ ps) is much shorter than the fluorescence lifetime $\tau_{rad} = 20$ ns of our CdSe QDs to suppress two-photon emission as far as possible. The energy per pulse could be continuously set from 0 to 5 pJ, and the pulse repetition period was set at 100 ns, a duration much longer than τ_{rad} to avoid the overlap of triggered photons generated by consecutive pulses. The fluorescence photons are collected by a high numerical apperture (NA) oil immersion objective (Olympus $\times$100, apochromatic, NA $= 1.4$), which also focuses the excitation beam to the diffraction limit (waist $\sim$250 nm). Photons are then sent to a standard high sentisitivity Hanbury-Brown and Twiss setup. It consists of a 50/50 non-polarizing
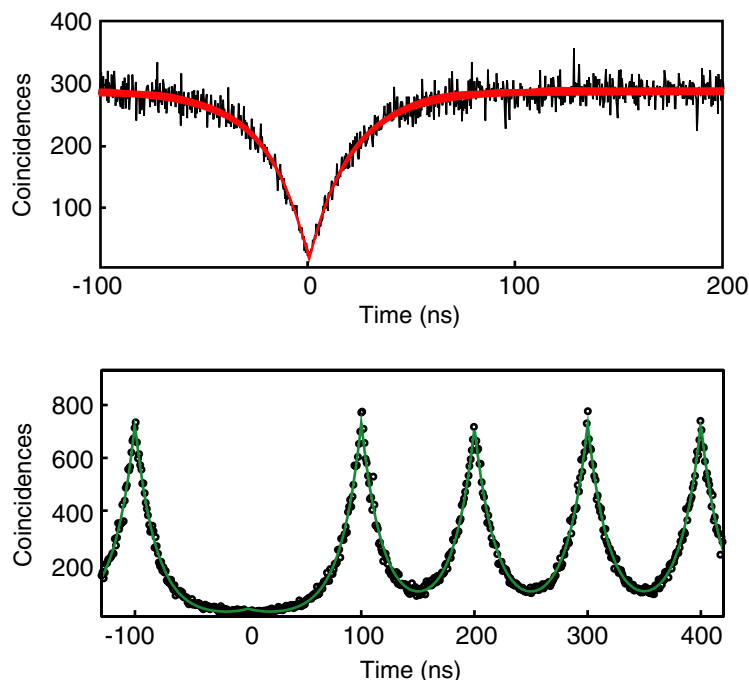
Figure 1. Histogram of coincidence counts of single QDs' fluorescence (○) after background correction under continous (a) or pulsed (b) excitation. (a) The red solid line is a fit yielding a 20 ns excited-state lifetime for this nanocrystal. (b) The blue solid line is a fit of the data, yielding a 22 ns excited-state lifetime for this nanocrystal.

beamsplitter and two (start/stop) photon avalanche photodiodes (APDs) with a time resolution of 300 ps. A picosecond time analyser (PTA, EG&G 91 38) provides the histogram of time delays between photons. We also introduced a delay of 200 ns in the stop channel to record the signal at negative correlation times.

3. Results

3.1. Fluorescence antibunching

First we analyse the autocorrelation function of the emitted light under pulsed or continuous excitation. Under cw excitation, our data are in agreement with [17]. The histogram of coincidence counts at short time scale given by the PTA exhibits a dip centred at zero delay (figure 1(a)). After correction for the background noise due to photodiodes, the antibunching amplitude is found to be greater than 99%. The adjustment of our experimental data lead to a value of $\tau_{rad} = 20$ ns. Under pulsed excitation, the autocorrelation function also shows few coincidence counts at zero delay (figure 1(b)). For all accessible pumping power, the value of the zero delay peak area is less than 0.05, systematically droping close to zero after substracting the background due to the APD dark counts. As for cw excitation, the value of τ_{rad} deduced from our experimental data is of the order of 22 ns.
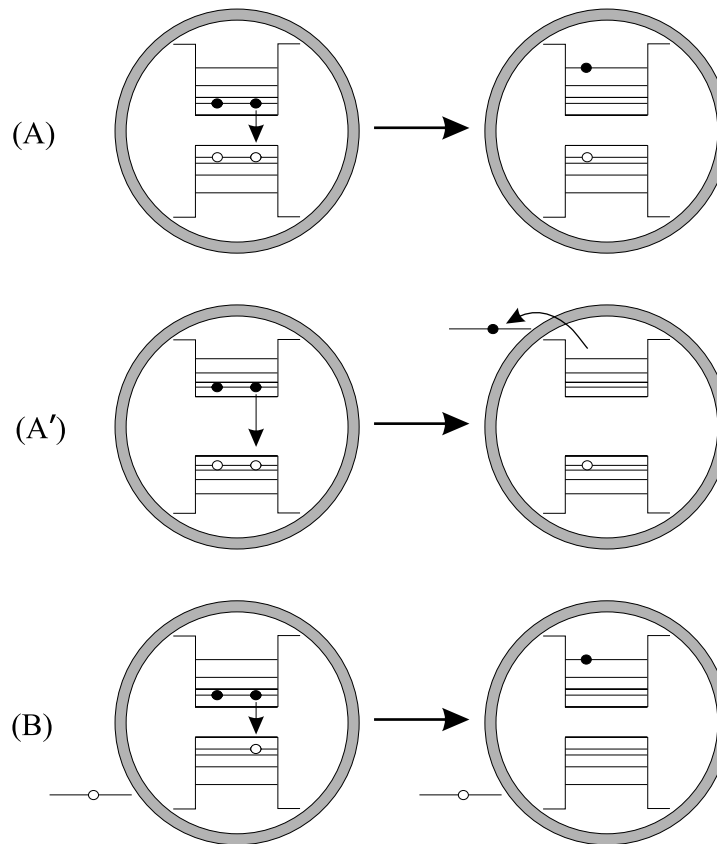
Figure 2. Scheme presenting Auger effects considered in this paper. In each process, one electron/hole pair does not decay radiatively. The energy recombination is transferred to the remaining carrier. (A) Auger relaxation of a biexciton in a neutral QD. The remaining excited carrier is still confined in the nanocrystal. (*A'*) Autoionization of a neutral QD by Auger process. The remaining excited carrier is ejected from the QD. (B) Auger relaxation of a bi-exciton in a ionized QD leading to the QD extinction.

3.2. Effects of Auger processes over single-photon emission

The absence of photon coincidences at zero delay under pulsed and continuous excitation proves that colloidal CdSe QDs are perfect single-photon emitters at room temperature. The antibunching exhibited by the fluorescence of these solid-state sources is similar to that of a single quantum system such as an atom. QDs are often called artificial atoms since the three-dimensional confinement results in a discrete, atomic-like energy spectrum. Perfect antibunching strengthens this analogy. However, QDs exhibit an important difference with atoms or molecules. Multi-electron/hole pairs can be created by the excitation laser. The crucial point is that multi-excitonic states recombine non-radiatively due to the Auger effect as shown schematically in figure 2 (type *A* Auger effect). In this process, a ground-state bi-exciton decays to an excited monoexcitonic state without any photon emission. Subsequently, the excited carrier rapidly relaxes to its ground state in a couple of ps [19]. Recent experimental and theoretical results showed that, for CdSe QDs with radii ranging between 1.2 and 3.6 nm, the Auger process occurs in less

than 100 ps [18, 19], much faster than $\tau_{rad} \sim 20$ ns. Auger recombination is thus the dominating relaxation process for multiexcitonic states.

Auger processes are much more efficient in nanometre-sized structures than in bulk materials for two reasons. First, for the bulk case, the maximum density of excitons corresponds to one exciton per excitonic volume $V \sim a_B^3$, where a_B is the Bohr radius of the exciton. Above this density, carriers do not form an exciton gas but a metallic plasma and strong screening effects reduce Coulomb interactions. In nanocrystals with a radius lower than a_B, several excitons can occupy a volume smaller than V, without the possibility of dynamic screening because of strong carrier confinement. The overlap between carrier functions is increased and Coulomb interactions are enhanced. Second, there is no wave vector carrier momentum conservation in QDs because of their nanometre size. Due to this non-conservation, which may be interpreted in terms of translation-symmetry breaking, Auger transitions which exhibit a low probability in bulk material are very efficient in QDs. Accurate calculations of Auger rates [19] confirm this picture.

The influence of the efficiency of Auger processes on colloidal CdSe QD fluorescence antibunching has already been invoked [17] for continuous excitation to explain the multiexcitonic emission suppression. Under pulsed excitation, the absence of the zero delay peak confirms that if the QD contains more than a single electron/hole pair after a pulse excitation, non-radiative recombination via process A is the preferential energy relaxation channel until a single electron/hole remains. Only the last pair can recombine radiatively and no more than one photon can be emitted after one pulse excitation.

The absence of multiexcitonic emission for high pumping power is specific to colloidal CdSe QDs. For epitaxially grown QDs, the suppression of radiative bi-exciton recombination requires low pumping. Close to saturation of the monoexcitonic emission, which is the regime called for efficient single-photon generation, radiative recombination of bi-excitons is always observed [6, 20]. As a result, epitaxially grown QDs require the use of spectral filtering which isolates the first exciton emission of a single QD from the bi-excitonic emission but also introduces optical losses. In terms of photon collection efficiency, a crucial parameter for the realization of a practical single-photon source [8], monoexcitonic emission thus provides a specific advantage to CdSe QDs. This benefit is reinforced by the high quantum yield of CdSe QDs at room temperature. Working at room temperature allows the use of high-NA immersion objective, leading to simple and efficient light collection. A detailed analysis [21] of the collection efficiency of our setup showed that 12.5% of the emitted photons were collected and detected, and that the probability to detect a photon per pulse was equal to 3%, much higher than the rate of 0.1% obtained for epitaxially grown QDs [22].

In addition to antibunching observed under continuous or pulsed excitation, light emission by single electron/hole pair recombination successfully explains the fluorescence saturation of a single emitter. Under continuous excitation, measurements on the fluorescence saturation were consistent with a two-level system [17]. Under pulsed excitation, we investigated the probability σ to excite the emitting transition versus the pump pulse power, knowing that this probability is crucial for the efficient generation of triggered single photons. To deliver a single photon per pump pulse, the probability σ to excite the emitter must be close to 1. Our results [21] showed that the variation of the photon emission intensity versus the excitation intensity can be fitted by an effective two-level model and an excitation probability greater than 0.95 can be obtained.
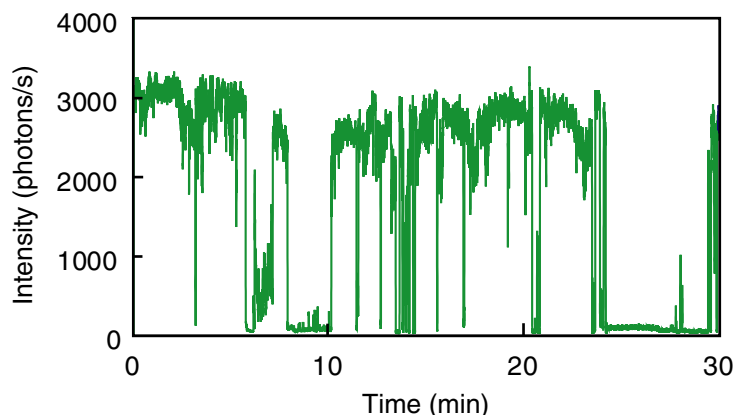
Figure 3. Time trace of a single QD fluorescence registered over 30 min with 100 ms time bins. 'On' and 'off' events with duration of the order of the acquisition time are likely to be observed due to power-law distributions.

3.3. Fluorescence intermittency

Due to Auger process *A*, colloidal CdSe QDs are similar to a two-level system in terms of single-photon generation and fluorescence saturation. However, the overall fluorescence properties of colloidal CdSe QDs are not identical to a simple two-level system. Resonant excitation is not required since efficient excitation has been observed for many wavelengths. CdSe QD fluorescence is also known to exhibit intermittency resulting in the alternance of dark and bright periods (figure 3) [16]. A statistical analysis of the intermittency reveals power-law distributions of the 'on' and 'off' times [23]–[25]. Consequences of these statistics have been analysed. Statistical aging and ergodicity breaking have been reported [26, 27]. In the field of quantum cryptography, the main problem is the random duration of bright and dark periods. 'On' and 'off' times have no mean value and very long 'off' events are observed (figure 3). These long dark periods are the main restriction for the use of colloidal CdSe QDs as single-photon emitters.

The origin of fluorescence intermittency has been studied in detail [24, 25, 28]. It is now commonly admitted that blinking arises from rare ionization events that eject a carrier from the QD [24, 25]. For simplicity, we will consider in the following that the hole is the ejected carrier. The ionized QD is non-fluorescent due to a multiparticle process between subsequent exciton and the remaining electron as shown schematically in figure 2 (type *B* Auger effect). An Auger ionization model was proposed earlier by Efros *et al* [28] to explain the QD fluorescence intermittency. The relaxation of a bi-exciton following the Auger process presented in figure 2 (type *A'* Auger effect) was assumed to lead to ionization of the QD, which consequently became non-fluorescent. According to this model, single-photon emission and fluorescence intermittency would then be intimately linked, as suggested in [17]. However, recent results showed that process *A'* is probably not involved in the QD ionization [24, 25]. Ionization process *A'* would lead to a mono-exponential probability distribution of 'on' events [28], which is not consistent with the power-law distributions and the large dynamic range of time scale observed experimentally (from $100 \, \mu s$ to $100 \, s$). Actually, electron or hole tunnelling to a fluctuating environment of trap sites is more probably at the origin of blinking [24, 25].

Although fluorescence intermittency has long been considered as an intrinsic property of CdSe QDs, very recent results [29] demonstrated that the intermittency of single QDs could be

significantly reduced by chemical processes. Surrounding the QDs with a concentrated solution of molecules containing thiol groups (such as betamercaptoethanol or DTT) suppresses the blinking. This suppression is presumably due to the passivation of surface traps by thiol groups, which also confirms that Auger process A' is not the cause of QD ionization.

4. Conclusion

In conclusion, we have analysed the generation of single photons by colloidal CdSe QDs. At room temperature, due to the efficiency of Auger processes, the fluorescence of colloidal CdSe QDs exhibits a perfect antibunching under continuous or pulsed excitation. The collection of single photons is also both simple and efficient. The main drawback of colloidal CdSe/ZnS is their fluorescence intermittency although recent results showed that it could be partly suppressed. Auger processes also take part in the blinking mechanism but are probably not at the origin of the effect. Overall, CdSe/ZnS QDs appear as promising single-photon sources.

Acknowledgments

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