Journal of Luminescence 131 (2011) 375–378

Contents lists available at ScienceDirect

Journal of Luminescence

journal homepage: www.elsevier.com/locate/jlumin

Intermediate intensity levels during the emission intermittency of single CdSe/ZnS quantum dots

Nicole Amecke, Frank Cichos *

Molecular Nanophotonics, Institute of Experimental Physics I, University of Leipzig, 04103 Leipzig, Germany

A R T I C L E I N F O

Available online 26 October 2010

Keywords:
Semiconductor
Quantum dot
Colloidal
Blinking
Single molecule
Optical microscopy

A B S T R A C T

We report on an intermediate intensity level in the emission intermittency of single CdSe/ZnS core shell quantum dots, which has been overlooked in previous experiments most likely due to its low quantum efficiency. The intermediate intensity level is observed in CdSe/ZnS quantum dots of large diameter (about 5 nm diameter) and appears to be independent of the general dark state power law dynamics. The dim emission periods are found to be exponentially distributed and thus correspond to similar findings in CdSe/CdS quantum dots, where their existence has been interpreted in terms of the emission of a positively charged trion.

1. Introduction

Single colloidal semiconductor quantum dots (QDs) show an intermittent emission on a timescale of milliseconds to several tens or hundreds of seconds [1], which limits to a large extent their application as markers or light sources [2,3]. The dynamics of this intermittency (or blinking) is very complex and in general well described by a power law distribution of the dark periods [4–9] even on a single quantum dot level. The power law indicates contributions from a wide distribution of relaxation rates to the blinking statistics, which is an intriguing observation for a nanoscale object. This intermittency is usually interpreted in terms of a photoinduced ionization process, which leads to a charged QD [10–13]. The free carrier in the QD can effectively quench the emission by a non-radiative Auger process. Therefore the QD is dark as long as it is ionized and the duration of the dark period monitors the lifetime of the ionized state itself. However, despite a vivid study of this phenomenon and a number of models [7,8,14,15] describing the origin of power law blinking, the physical details of it are not understood. Recent reports even rise doubts about the exclusive influence of Auger processes and thus pose new questions on the mechanism behind the quenched luminescence during the dark periods [16,17].

Further studies on single CdSe/CdS quantum dots have shown for the first time, that well defined intermediate intensity levels (so-called dim or grey states) occur, which are attributed to trion emission due to a localized charge at the CdS surface and a confined charge in the quantum dot core [23].

For CdSe/ZnS QDs on the other hand, continuously fluctuating intensity levels have been observed so far, showing no well defined intermediate levels. A linear correlation of the emission intensity with the excited state lifetime [18–21] directly indicates continuously fluctuating non-radiative decay channels which are often attributed to fluctuating charges at the surface of the quantum dot [18].

In this paper we report on the observation of a low lying, well-defined, intermediate intensity level for several CdSe/ZnS QDs in addition to the likewise observed continuous distribution. We find that it represents an additional pathway to and from the on- and off-states with exponentially distributed occupation period. This dim state emission is very weak and only observed for large CdSe/ZnS QDs (about 5 nm diameter). It has probably been overlooked due to low signal to noise ratio or time averaging with long exposure times, which are common in fluorescence widefield microscopy studies.

2. Experimental

Experiments have been carried out in a home-built inverted confocal microscope using a pulsed laser diode (Hamamatsu PLP-10, 470 nm, 88 ps) as excitation source. The light is coupled into the microscope by a dichroic mirror (Omega Filters) and focused onto the sample with an Olympus 100x/1.4 NA oil immersion objective (UPLanSApo). The light is collected from the sample mounted on a *XYZ* piezo translation stage (PI 517.C3) by the same objective and focused onto a 50 μm pinhole with a $f=20$ cm lens. The pinhole is imaged onto two avalanche photodiodes (APDs, MPD Picoquant) through a polarizing beam splitter by another lens of $f=10$ cm. The emission intensity is recorded by a single photon counting multichannel board (Becker & Hickl DPC 230).

* Corresponding author. Tel.: +49 341 97 32571; fax: +49 341 97 32598.
E-mail address: cichos@physik.uni-leipzig.de (F. Cichos).

0022-2313/$ - see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.jlumin.2010.10.026

All data is stored in form of single photon time traces involving a macro- and a micro- time corresponding to the time of the measurements as well as to the arrival time of the photon with respect to the subsequent excitation pulse.

Emission intensity time traces have been analyzed by binning the photons in bins of $\Delta t = 10$ ms. Emission intensity decay as well as photon correlations have been determined accordingly from the single photon time traces. Intensity-lifetime correlations were obtained by fitting the decay histogram of micro-times for each intensity bin with an exponential function. For the inter-photon correlation, similar to a Hanbury–Brown–Twiss setup [22], the delay times between photons from one detector and those of the other were summed up to a histogram.

The QDs studied in this paper were purchased by Evident Technologies (Evidots: 612 nm emission wavelength, 5 nm diameter) and upon dilution to 1 nM concentration spin coated in a polystyrene matrix on a glass substrate. They were excited at 0.4 kW/cm^2 (5 MHz repetition rate) corresponding to 0.6 absorbed photons per pulse.

3. Results and discussion

Fig. 1 shows an example of a recorded emission intensity time trace of a single CdSe/ZnS core/shell quantum dot ($\lambda_{em} = 612$ nm) embedded in polystyrene together with a histogram of the emission intensity taken over the whole time trace. Both graphs display a strongly fluctuating intensity, which displays a well defined *on* and *off* state as well as an almost continuous distribution of intermediate intensity levels.

Such continuously varying emission intensities have been reported and analyzed before [18–21]. They are either due to non-resolved blinking, when binning of photons to intensities, or due to a fluctuating non-radiative rate modulating the total excited state decay. Both effects are indicated in Fig. 2 showing on the left an intensity–lifetime correlation. The linear relation at the upper left edge displays the fluctuating non-radiative rate, while the vertical intensity fluctuations at about 24 ns excited state lifetime correspond to non-resolved blinking. The non-radiative rate fluctuations have been related in previous reports to fluctuating surface charges even though the existence of these surface charges is in general only anticipated [18–20].

The new observation in this study is, however, that for several QDs the emission intensity fluctuations reveal a low-lying well defined intensity level (dim state). Note that this dim intensity level cannot be due to non-resolved blinking, since Fig. 2 (left) demonstrates, that such blinking would cause a wide distribution of intensity levels. The dim state, however, is clearly visible in the intensity histogram and well separated from the background intensity due to a high signal to noise ratio of our measurements. We suppose that it has been overlooked so far as many of the studies use wide field CCD based detection with lower signal to noise ratio, where the emission of low quantum yield states cannot be separated from the background. In addition, we find the intermediate intensity level only to be present in emission time traces of larger CdSe/ZnS ($\lambda_{em} = 612$ nm) quantum dots. This suggests that decreasing the quantum dot size further

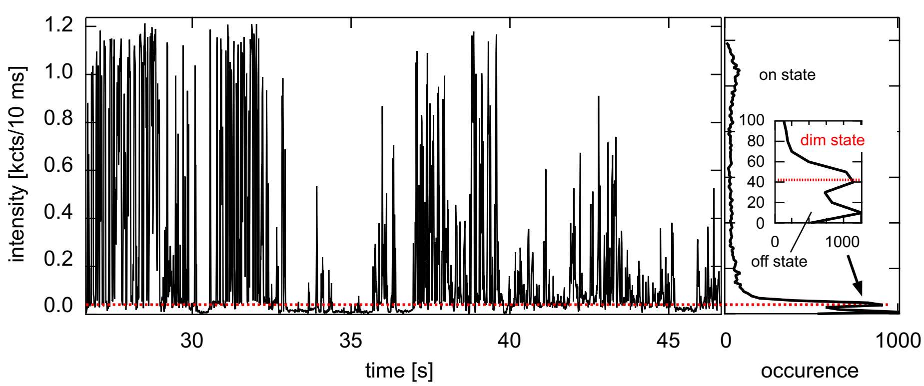

Fig. 1. Emission intensity time trace of a single CdSe/ZnS core shell quantum dot ($\lambda_{em} = 612$ nm) embedded in a polystyrene film. The quantum dot shows a discrete intensity level marked with the red line, which is also visible from the intensity histogram attached to the right of the time trace. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

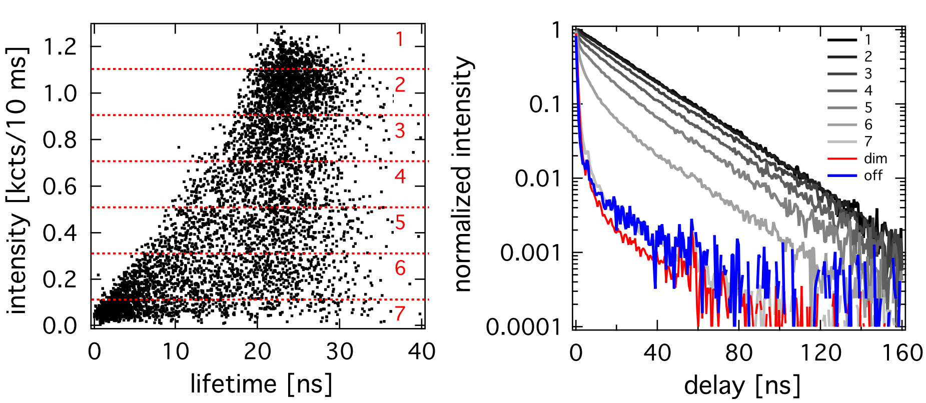

Fig. 2. *Left:* Emission intensity of a single quantum dot as a function of its emission lifetime. The emission lifetime was extracted for 10 ms bins of the time trace by a single-exponential fit. *Right:* Emission decay for various intensity intervals of the emission time traces. The dashed lines in the left graph mark the intensity intervals for the grey curves. The red line represents the observed dim level (30–70 cts/bin), the blue one the background intensity (< 30 cts/bin). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)