Chemical Physics 406 (2012) 9–14

Contents lists available at SciVerse ScienceDirect

Chemical Physics

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

Change point analysis of matrix dependent photoluminescence intermittency of single CdSe/ZnS quantum dots with intermediate intensity levels

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ARTICLE INFO

Article history:
Available online 3 March 2012

Keywords:
Photoluminescence intermittency
Semiconductor quantum dots
CdSe/ZnS
Change point analysis
Intermediate intensity levels
Hydroxyl groups
Polymers
Trap states
Hole trapping

ABSTRACT

Blinking dynamics of single CdSe/ZnS quantum dots are analyzed by change point analysis, which gives access to intermediate photoluminescence (PL) intensities observed during PL intermittency. The on-times show systematic deviations from a (truncated) power law. This deviation is manifested in variations of the PL intensity distribution and is related with well defined PL intensity jumps. Varying the matrix from polystyrene (PS) to polyvinyl alcohol (PVA) changes the on-time blinking dynamics and reveals coupling of the QDs either to OH-groups of the SiO_x interface or to OH-groups of PVA. Analysis of dwell times in respective intensity correlated traps reveals that OH-related traps are strongly stabilized with much longer dwell times as compared to otherwise broadly distributed trap states.

1. Introduction

Since the introduction of single molecule spectroscopy blinking or luminescence intermittency was observed in many single quantum systems like organic molecules, proteins, colloidal and epitaxial semiconductor quantum dots (QDs), but also large organic systems like single conjugated polymer chains, polymer nanoparticles and J-aggregates. Recent reviews and publications give an overview on these phenomena including statistics such as the presence of power-law distributed times [1–5]. Even diamond nanocrystals [6] or Ag nanoparticles [7] show blinking. It is generally assumed that these phenomena are caused by photoejection of charges, probably electrons, which can be trapped at the interface between the quantum object and the environment or even in the environment (polymer, substrate) itself. For this reason it is not surprising that the general features of blinking depend on the QD interfaces (ligands, shell) [8–10] and the embedding matrix [11] or substrate [12]. Generally, so called on- and off-times of the luminescence are broadly distributed between ns and minutes and are very often described by inverse power-laws with power-law coefficients between roughly −1 and −2 [1–3]. The intriguing, since obviously very general blinking behavior has been intensively investigated for more than 15 years. Various models have been set-up to interpret the basic observations [1–3,13–15]. However, the understanding is still far from being complete.

In the course of time experiments have become more sophisticated. In parallel, the sensitivity has been increased resulting nowadays in detection of on- and off-time probabilities distributions covering about 6 orders in probability and about 4 orders in timescale [2,3,12]. Thus more and more subtle effects are unraveled and related to the microscopic nature of the quantum system coupled to an inhomogeneous environment. Many laboratories have reported that the power-law behavior turns over into an exponential process at long times. This seems to be more pronounced for on-times as compared to off-times. A power-law for off-times can be readily rationalized, since it is related to a process, which involves the return of a photoejected charge from an inhomogeneous environment to the quantum object. In contrary, the on-time dynamics should be exponential, no matter how many accessible (trap-) states are envisaged. Therefore, in case of on-times a power-law behavior is thus still not yet explained basically.

For this reason we have started to perform detailed investigations of the on-time dynamics of semiconductor quantum dots as a function of the matrix [16] or the interface [12]. From these experiments we find that the power-law is truncated by a strongly matrix dependent exponential cut-off [16] and/or that this combined behavior is superimposed by an additive (exponential) process, which can be related to coupling of the exciton of the QD to specific surface states (e.g. silanol groups on SiO_x interfaces) of the substrate [12]. To further elucidate this more and more complex

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doi:10.1016/j.chemphys.2012.02.018

situation we will make use of a recently reported analytical tool, the change point analysis (CPA) [17]. This method takes not only (totally) on- or off photoluminescence (PL) intensities into account, but also handles the rich features of intermediate intensities. In this paper we report, how CPA can reveal the influence of the matrix on the on-times of CdSe/ZnS as a prototype QD with respect to the polarity of two very different polymers, namely polystyrene (PS) and polyvenylalcohol (PVA).

2. Experimental and methods

To investigate single semiconductor nanocrystals, a stock dispersion (10^{-6} mol/l in decane) of TOPO capped CdSe/ZnS quantum dots (Invitrogen, $\lambda_{\max}$ = 565 nm, which corresponds to a core diameter of about 4 nm with about a 1 nm thick ZnS shell) was diluted in spectroscopic toluene down to a concentration of approximately 2×10^{-11} mol/l. After this, the solution was spin coated onto cleaned (Piranha treatment) silicon wafers with a 100 nm thermally grown oxide layer (Centre for Microtechnologies, Chemnitz University of Technology) at 5000 rpm for 10 s. In the case of polystyrene (PS) measurements, approximately 50 mg of high purity polystyrene (M_W = 116000...118000 g/mol, Polymer Standards Service) were dissolved in the QD toluene mixture. After spin coating, this results in typically 20 nm thick layers of PS with embedded QDs. For measurements in polyvinyl alcohol (PVA) a solution (10 % mass fraction) of high purity PVA (Sigma Aldrich) in deionized water was spin coated onto the wafers prior to depositing quantum dots.

The single QD fluorescence was recorded using a homebuilt confocal microscope under excitation of a ps-pulsed diode laser at 465 nm with a cw-power of about 500 nW. A high numerical aperture objective (100*x*/0.9NA, Zeiss) focused the laser light onto the sample and collected the fluorescence light. A long pass filter at 480 nm (Omega Optical 3rd Millennium) separated the reflected excitation light from the fluorescence which was detected by an avalanche photodiode (Picoquant GmbH MPD, PDM Series) allowing for single photon counting via a TCSPC-board (Becker & Hickl SPC-630). In this way, both the macro time, relative to the beginning of the measurement, and the micro time, relative to the excitation pulse, was recorded for each detected PL photon.

The time tagged, time resolved single photon counting data were binned to obtain a fluorescence time trace (binning time t = 1 ms) on the one hand and analyzed by the Change Point Analysis (CPA), developed by Watkins and Yang [17], on the other. This method takes advantage of the Poisson statistics of photons, emitted by a single photon emitter, to estimate states of constant PL intensity directly from a set of arrival times, photon by photon. Because no binning is needed, the occurrence of "false", binning related, intermediate intensities is suppressed. While CPA is able to detect states of constant PL intensity, the intensity itself is uncertain, depending on the number of photons the state emits. This leads to continuously distributed intensity levels. To correlate these intensity levels to a finite number of states in the QD, a clustering algorithm, also developed by Watkins and Yang [17], is applied to the CPA data. As a result, all states of constant PL intensity with a similar distribution of photon arrival times are attributed to one of a finite number of intensity levels.

3. Results

The probability distribution for on-times of a single CdSe/ZnS QD embedded in PS and its representative intensity time traces with 1 ms binning time are shown in Fig. 1(a) and (b). The distribution reveals basically a power-law at early times (<20 ms) followed by an exponential superposition at medium times (30–800 ms) and finally an exponential cut-off. The overall behavior can be described by Krasselt et al. [12]:

$$P(t_{\mathrm{on}}) = A\, t_{\mathrm{on}}^{-\alpha} \cdot \exp(-\Gamma t_{\mathrm{on}}) + B \exp(-\gamma t_{\mathrm{on}}). \tag{1}$$

The relative contribution of each of the 3 constituents varies from QD to QD [12,16]. While a (truncated) power law behavior (first summand) is reported quite often [1–3] the additive exponential term (second summand) is only observed under certain conditions, e.g. the coupling to well defined trap states such as silanol groups of the supporting substrate [12].

The power of CPA is, that it follows intensity jumps whenever they occur leading to a higher time resolution compared to binned time traces (of less than 1 ms in the present case). From this analysis one obtains a probability distribution for the magnitude of PL intensity jumps ΔI (Fig. 1(d)). This distribution reveals two features: a sub-distribution centered at small intensity jumps and two side peaks, symmetric with respect to the centre $\Delta I = 0$, at about $\Delta I \approx \pm 20$ kcps. These large intensity jumps are only present if the according on-time distribution (see Fig. 1(a)) contains the superimposed exponential decay, while the magnitude of the jumps depends on the individual QD. Using a clustering algorithm [17], which attributes the distributed PL intensities gained by CPA to the "real" emitting state intensities of the QD results in the histogram of clustered intensities shown in Fig. 1(c). This distribution also shows very distinct features, that is a wide range of almost equally spaced intensities, only very few (2–3) highest intensities and a bunching of intensities at very low and medium to high intensities. Furthermore, all intensity levels show a similar occurrence. This is an evident difference to classical intensity histograms constructed from binned time traces which represent not only the occupation of certain intensity levels, but also their length. Again, bunching of clustered intensities in the medium to high range comes only about, when the superimposed exponential term (Fig. 1(a)) shows up in combination with the side peaks shown in Fig. 1(d). We conclude that all these three observations are a consequence of coupling QD states to very well defined trap states [12].

In Fig. 2 we compare the respective ΔI distributions for three representative QDs in each of the matrices PS and PVA. Three observations immediately emerge. Firstly, the distributions are quantitatively different for each single nanocrystal in one and the same matrix. Secondly, the distribution is much broader and exhibits more pronounced side peaks for QDs on PVA compared to PS. Third, the general behavior of all distribution is, that they consist out of a strong central peak (containing also contributions from noise), which corresponds to small intensity jumps and symmetric side peaks, whose ΔI values vary from crystal to crystal and among the matrices. While the shape of the central peak is clearly non-Gaussian, it is of more Gaussian type for the side peaks. For PVA we never observed only the central distribution, while for PS all types of distribution show up without any preference.

A comparison of the behavior of intensity jumps in the two different matrices reveals the widths of the respective (central or side peak) distributions in PS to be smaller by about a factor of two as compared to PVA. Moreover, the side peak amplitudes and the respective separations $|\Delta I|$ from the central peak are much more pronounced for PVA. Fig. 3 depicts the "conventional" probability presentations of on-times for the same 6 QDs presented already in Fig. 2. A clear correlation emerges between the on-time distributions and the intensity jump distributions. In PS we observe almost a power-law over the total observation time with an (from left to right) increasing deviation from a truncated power law. On PVA we did not find nearly-power-law type dynamics but always a more complex behavior (see Eq. (1)). Due to the exponential deviation from the truncated power law the exponential cut-off can often not be determined with high accuracy, but it is close to 1s in PS