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Quantum dots: Using the known as well as exploring the unknown

Ron Tenne[*a], Osip Schwartz[a], Ayelet Teitelboim[a], Pazit Rukenstein[b], Jonathan M. Levitt[a], Taleb Mokari[b], Dan Oron[a]
[a]Department of Physics of Complex Systems, Weizmann Institute of Science, Rehovot, Israel 76100;
[b]Department of Chemistry and Ilse Katz Institute for Nanoscience and Nanotechnology, Ben-Gurion University of the Negev, Beer Sheva, Israel

ABSTRACT

Super-resolution microscopy, the imaging of features below the Abbe diffraction limit, has been achieved by a number of methods in recent years. Each of these methods relies on breaking one of the assumptions made in the derivation of the diffraction limit. While uniform spatial illumination, linearity and time independence have been the most common cornerstones of the Abbe limit broken in super-resolution modalities, breaking the 'classicality of light' assumption as a pathway to achieve super-resolution has not been shown. Here we demonstrate a method that utilizes the antibunching characteristic of light emitted by Quantum Dots (QDs), a purely quantum feature of light, to obtain imaging beyond the diffraction limit.

Measuring such high order correlations in the emission of a single QD necessitates stability at saturation conditions while avoiding damage and enhanced blinking. This ability was facilitated through new understandings that arisen from exploring the QD 'blinking' phenomena. We summarize here two studies that contributed to our current understanding of QD stability.

Keywords: Quantum Dots, Colloidal, Superresolution, Microscopy, Blinking, Gray state, Saturation

1. INTRODUCTION

Semiconductor nanocrystals, Quantum Dots (QDs), are excellent candidates to complement organic dyes and fluorescent proteins in optics and optical applications mainly due to their stability under continuous illumination. The optical research of colloidal-synthesized QDs has three interlocking branches: The first is the exploration into diversifying synthesis methods to achieve a higher variety and better quality. The second is exploring unanswered questions regarding mechanisms and dynamics and the third is the utilization of QDs as building blocks in optical applications such as lasers [1-3], microscopy [4] and solar cells [5]. Bellow we summarize three studies that, while easily divided into the former categories, show how the applications may benefit from the exploration of both novel synthesis and unknown dynamics in well studied QDs.

In Section 2 a PbS tip grown on CdSe\CdS core-shell nanorod (NR) [6] (Figure 1a) serves as a positive charge trap stochastically inducing single electron charging in the CdSe\CdS NR. Charging of QDs has special interest since one of the most common explanations for QD fluorescence intermittency (termed blinking) is the irradiative Auger-recombination of an exciton in a charged QD. We found that charging, in our case, resulted in an additional intermediate brightness state while the dark state was left unaffected by the addition of the PbS tip. This study joined a few recent works [7-10] that raised doubt regarding the mechanism behind QD blinking.

The question surrounding the mechanism responsible of intermittent darkening in single QD fluorescence has raised new interest into the exploration of the dark 'off' state. Section 3 summarizes a work [11] that uses a variation of a pump-probe experiment to show that a long lived, μs scaled, excitation exists. Second photon absorption, while at this long-lived state, results in longer dark periods and irreversible bleaching of QD fluorescence. A clear conclusion from these measurements is that QD can be used as stable emitters using a pulsed laser with lower pulse repetition rates even at high excitation intensities.

Using this notion one can excite QDs a with a photon flux that will generate on average one exciton in every pulse without causing irreversible damage to the QD. This pulse intensity is termed the saturation intensity. In section 4 we show that using a pulsed source with low repetition rate (1KHz) at saturation intensity we were able to measure 2nd and

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3rd order correlation of single QD fluorescence with a CCD camera [12]. As such high order correlation rely on coincidence of photon pairs and triplets (or their absence) it served as a method for super-resolution microscopy.

2. NEW DESIGN HINTS ON BLINKING MECHANISM

Single QD fluorescence measurements have a distinct feature of telegraph intensity fluctuations, termed blinking [13-14]. A QD's fluorescence intensity fluctuates between two distinct states: a bright "on" state and a dark "off" state. Since QD blinking was found to be robust to changes in the constituent materials and QD size, the notion of a universal model accounting for the dark "off" state, suggested by Efros and Rosen, was well accepted.[15] The dark state was claimed to be the result of QD charging, allowing non-radiative relaxation through a trion Auger process, whereby an exciton recombines while transferring its excess energy to the third spectator charge. Upon neutralization of the QD, radiative recombination is reconstituted and the exciton energy is released as a photon.

During the past few years several works displayed experimental results challenging Auger-based blinking models [7-10]. One of these innovative measurement techniques employs electrochemistry to measure in situ fluorescence during QD charging.[9, 10]. The main finding of these studies is that the quantum yield (QY) of a negatively charged QD is often not sufficiently low to account for the drastically reduced emission measured in the "off" state. Qin et al. [10] combined that realization with previous observation of a "gray" (intermediate QY) state in CdSe/CdS QDs [16] and arrived at the conclusion that the "gray" state, and not the "off" state, is the result of negative charging of a QD.

We tried a different approach to induce charging [6]; a fully inorganic NR heterostructure that is essentially composed of two isolated QDs separated by a tunneling barrier. One serves as an optical emitter while the other serves as a controlled charge carrier trap. The particular system realized is based on a CdSe/CdS seeded NRs onto which a PbS tip was grown (Figure 1a) [17]. The tip component serves as a localized hole trap, facilitating the effective charging of the optically active QD core. Such architecture allows for examination of QD blinking under stochastic charging conditions resulting from the designed trap state.

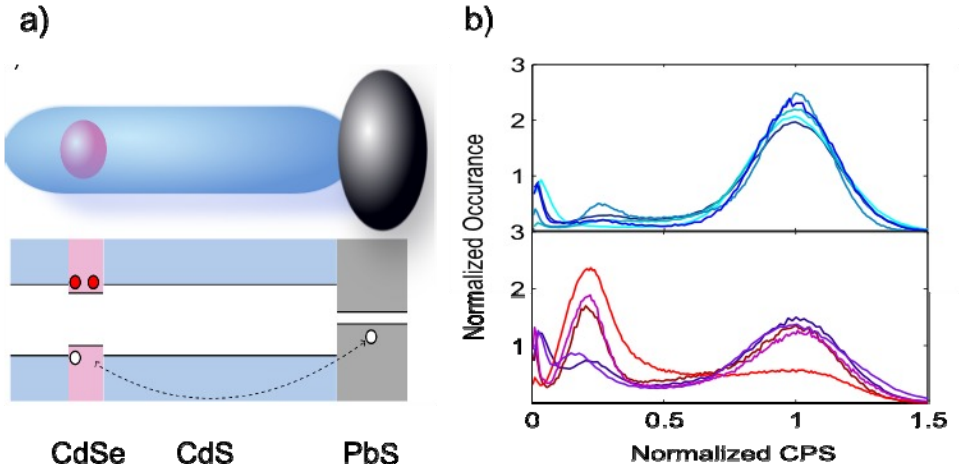

Figure 1: (a) Top: The structure of the PbS tipped NRs investigated here. A core of CdSe (pink) is capped by a shell of thick CdS. On its tip was grown a PbS nano-crystal (gray) . Bottom: Energy level diagram for the structure shown on top. (b) Fluorescence intensity histogram for 5 measured NR without a tip (top) and 5 measured PbS tipped NRs (bottom). On the bottom histograms one can see the high occurrence of the intermediate intensity "gray" state. (Image reproduced with permission from [6])

Figure 1b compares normalized intensity distribution functions for single bare NRs (upper panel) with those of single PbS-tipped ones (bottom panel). One can clearly see that the addition of the PbS hole trap enhanced an already scarcely pronounced state with an intermediate intensity such as the "gray" state reported earlier. To provide a graphic visualization of the variance between particles, five curves of each are shown. The x values of the curves were normalized so that the "on" state peak center occurs at unity in order to compensate for the distribution of absorption cross sections. One can notice that while some of the bare NRs' curves exhibit a small "gray" state peak, the PbS-tipped NRs spend an appreciable amount of time in the "gray" state. This observation was quantified for an ensemble of 9 bare NRs and 21 PbS tipped NRs for which we analyzed the proportion of time spent in the "gray" state. While the bare NRs

spent less than 20% of the measurement time in the "gray" state, the PbS-tipped NRs spent, on average, 40% at the intermediate intensity state.

Together with further analysis regarding the switching dynamics between the "gray" and "on" state, these results present additional evidence that in some cases the "gray" state rather than the "off" state is the result of an extra electron charging. This study joined former studies in the field [7-10] that doubted the universality of the Efros and Rosen blinking model and claimed that at least in some systems darkening was not the result of charging.

3. AVOIDING BLEACHING AND BLINKING AT SARURATION CONDITIONS

The fact that the universal model of QD blinking was not a full description of the phenomenon, led us to new thoughts as to how to explore and prevent blinking. The explanation Auger-assisted quenching during the "off" state implies that the dynamics of darkening are as fast as the Auger recombination lifetime, which in QDs is usually sub-nanosecond. If this is the case then the QD returns to its charged ground state within a few Auger lifetimes after the excitation pulse arrive.

Unlike this fast relaxation dynamics, in organic dyes re-absorption while at an intermediate long-lived triplet state is a main route for bleaching a dye molecule and therefore the stability of fluorescence is highly dependent upon the excitation repetition rate [18-19]. As a close analogy we suspected that re-absorption during an un-relaxed excitation in a QD might be a route for QD blinking and bleaching. We examined this hypothesis by using a pulsed source illumination with tunable pulse repetition rate (Edinburgh EPL470) as an excitation source for single CdSe\CdS\ZnS QDs (synthesized following [20]), a variation of a pump-probe experiment. In order to investigate this behavior under various pulse energy regimes, including saturation intensity, we oscillated the excitation pulse energy in a triangular wave pattern.

We then analyzed the results to produce signal versus excitation power scatter plot diagrams per each repetition rate shown in Figure 2. Each scatter plot is shown together with a histogram of the QD brightness probability distribution corresponding to a given range of excitation power. The figure shows data from two typical QDs studied at repetition rates ranging from100 kHz to 1 MHz.

At low pulse energy and low repetition rates, most data points fall on the same line. With increasing pulse energy, the scatter increases significantly. Nevertheless, at low repetition rates, most data points cluster around a clear saturation curve. As the interpulse intervals are decreased, more and more data points are shifted downward from the curve due to more frequent occurrence of the "off" state, so at the highest repetition rate the time-averaged signal almost disappears. The fluorescence intermittency dependence on the repetition rate is seen clearly in the QD brightness histograms. At the lowest repetition rate, the histograms demonstrate a wide peak corresponding to the on state, occasionally also featuring a narrow off state peak at zero signal, which corresponds to almost continuous emission with moderate blinking. As the repetition rate is increased, the brightness distributions become wider and shift to lower signals, corresponding to increased fluorescence intermittency, while the zero-signal peak grows. At the highest repetition rate of 1 MHz, the QDs spend a significant fraction of time in the off state, and the average signal per excitation pulse is drastically reduced compared to the signal at low repetition rates.

One conclusion to be made from these experiments is that bellow the saturation intensity the pulse repetition rate makes only a small difference and QDs spend most of their time in the "on" stat. At higher intensities, at the vicinity of the saturation point, stability and blinking are strongly dependent upon the pulse repetition rate. While at high rates the signal is almost completely darkened by the occurrence of an "off" state and irreversible damage, at low rates QDs remain stable even at pulse energies beyond the saturation point.

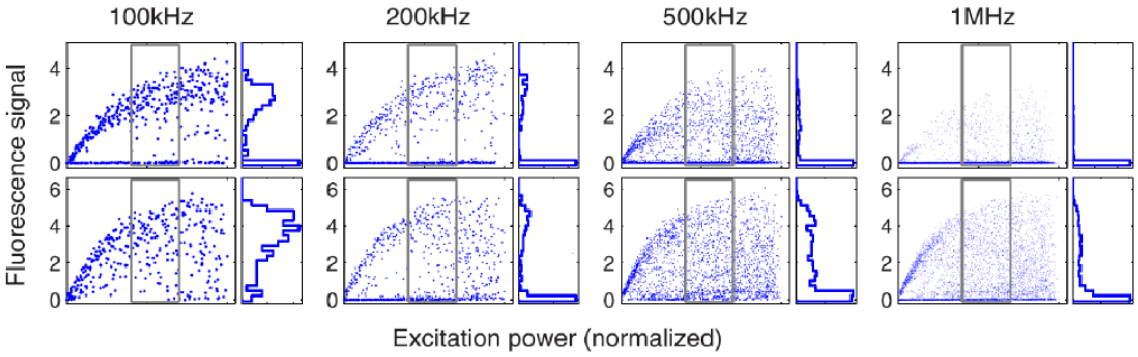

Figure 2: Saturation of fluorescence intensity vs. excitation power for two single CdSe\CdS\ZnS QDs. The two lines represent two specific QDs while each column shows a curve compiled at a different laser repetition rate. (Image reproduced with permission from [11])

4. SUPERRESOLUTION MICROSCOPY WITH QUANTUM EMITTERS

With the understanding that one can illuminate QDs with saturation intensity at low repetition rates without compromising their stability, we set out to utilize these typical and well-studied CdSe\CdS\ZnS QDs as fluorescent markers in a new super-resolution modality.

The optical diffraction limit restricts the resolution of far-field optical microscopes to approximately half the wavelength of light. Abbe's description of the imaging system [21] is based on the laws of classical linear optics, applied to stationary objects. Correspondingly, there are three loopholes in the argument, concerning the linearity, stationarity, and classicality assumptions. In the last two decades, super-resolution imaging methods were developed based on nonlinear optical effects such as stimulated emission [22] optical shelving [23] and fluorescence saturation.[24,25] More recently, sub-diffraction limited imaging was achieved by another class of microscopy methods, making use of non-stationary emission of fluorescent markers caused either by photo-switching [26,27] or by intrinsic brightness fluctuations.[28,29]

The remaining loophole for overcoming the diffraction barrier, resorting to quantum optics, has received a lot of attention in the recent years [30-37] and some method utilized higher order quantum interference effect to receive image entanglement [38], sub shot-noise images [39], as well as tomography with improved depth resolution. At the same time sub-diffraction limited quantum imaging has not yet been experimentally demonstrated.

The common element of most proposed quantum super-resolution schemes is illuminating an absorptive sample with a non-classical state of light. An alternative approach, proposed theoretically by Hell et al [40] relies on non-classical properties of light emitted by the sample itself, while using regular laser light for illumination. It was shown in this work that a hypothetical quantum emitter producing photons only in pairs (or groups) can be imaged using coincidence detection with a resolution increase similar to that attainable in two-photon (multi-photon) microscopy.

Here, we extend the idea of multi-photon detection put forward by Hell et al [40] by utilizing fluorophores in which emission of more than one photon is suppressed. Emitters, such as organic dyes and QDs, commonly used in fluorescence microscopy are single photon emitters by nature. In QDs, for example, the non-radiative Auger recombination rate is faster by 2-3 orders of magnitude than the competing radiative recombination rate. As a result once a multi-exciton is generated it is highly more likely that only a single photon would be emitted, or in other words a multi-photon event would be missing in comparison to Poissonian statistics. Quantifying the missing N-photon coincidence events gives a signal equivalent to N-photon detection signal, narrowing the effective point spread function by a factor of $\sqrt{N}$ [41]. In this work, we detect photon statistics in the image plane of a wide-field fluorescence microscope, determine the spatial distribution of missing two- and three-photon coincidence events, and reconstruct second and third order super-resolved images.

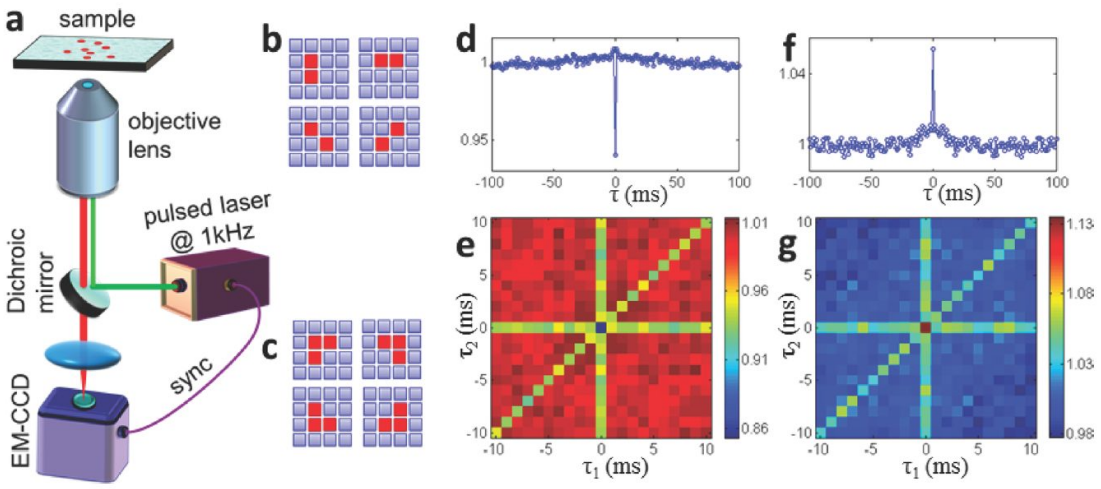

Figure 3: Detecting non-classical correlations in fluorescence microscopy. (a) A schematic of the experimental setup used for correlation imaging. (b,c) The pixel configurations used for second and third order correlation detection, respectively. (d) A typical second order intensity correlation function from an eight-pixel region on the CCD covering an image of a single emitter, computed as $g^{(2)}(\tau) = \Sigma_{i\neq k}[\langle n_i(t)n_k(t+\tau)\rangle]/[\langle n_i\rangle\langle n_k\rangle]$, where the sum runs over all pixel pairs in the relevant region and angle brackets indicate averaging over t. The graph features an antibunching dip. Panel (e) demonstrates a two-dimensional plot representing third order autocorrelation $g^{(3)}(\tau_1,\tau_2) = \Sigma[\langle n_i(t)n_k(t+\tau_1)n_m(t+\tau_2)\rangle]/(\langle n_i\rangle\langle n_k\rangle\langle n_m\rangle)$, where the sum runs over all three-pixel combinations within the same region of interest. (f) A correlation function computed for the same region on the CCD illuminated with a classical light source with a bunching peak at zero delay. (g) The third order correlation measured with classical signal demonstrates behavior opposite to antibunching: it has ridges at $\tau_1 = 0$, at $\tau_2 = 0$, and at $\tau_1 = \tau_2$ and a peak at $\tau_1 = \tau_2 = 0$. (Image reproduced with permission from [12])

For the proof of principle demonstration of antibunching imaging, we used test samples consisting of CdSe\CdS\ZnS core\shell\shell colloidal quantum dots (QDs), commonly used as labels in fluorescence microscopy. The QDs were embedded in a thin polymer film spin-coated onto a glass slide.

The observation of antibunching was done by using an EMCCD camera in a regular microscope setup (Figure 3a) as a multi-pixel single photon detector. Each frame was taken after a single pulse illumination (at 1KHz) and each captured image was then discriminated by a threshold value to decide whether or not a photon arrived. Under these conditions, if a single photon emitter's emission is spread over a few pixels their intensity would be anti-correlated, that is, if one pixel would detect a photon the others should remain dark.

Since the frequency of image acquisition is limited by the camera electronics, a high probability of generating multiexcitons per pulse and therefore pulse energies above the saturation point are imperative to receive measurable signal levels. Fortunately, our previous experiments [11], shown above, have hinted that indeed at lower repetition rates QDs can be worked as stable emitters at saturation intensity, enabling us to work at detection rates of 0.1 photon per pulse (approximated as our detection probability).

First, we set out to confirm that photon antibunching can be observed in our setup by measuring $g^{(2)}(\tau)$, the second order correlation of the electric field. This correlation function is commonly detected by using a pair of single photon detectors in a Hanbury Brown−Twiss configuration and computed as the normalized coincidence probability [42,43]. In this setup any pair of neighboring pixels served as the two detectors. A typical correlation function shown in Figure 3d exhibits the characteristic antibunching dip at zero delay.

Furthermore, we were able to detect antibunching features in the third order intensity correlation function, ant correlation of three neighboring pixels, depending on two discrete delay times τ_1 and τ_2. A two-dimensional plot of a typical third order temporal correlation function is shown in Figure 3e. The plot features depressed lines at $\tau_1 = 0$, at $\tau_2 = 0$, and at $\tau_1 = \tau_2$, which represent the lack of two-photon coincidence events. The central data point of this plot, at $\tau_1 = \tau_2 = 0$, which is depressed even further, corresponds to the missing three-photon coincidence events.

The observed magnitude of the antibunching features is reduced due to frame-to-frame fluctuations in the CCD readout circuitry, leading to apparent bunching of detection events. Our data processing offsets the antibunching signal to account for this effect.

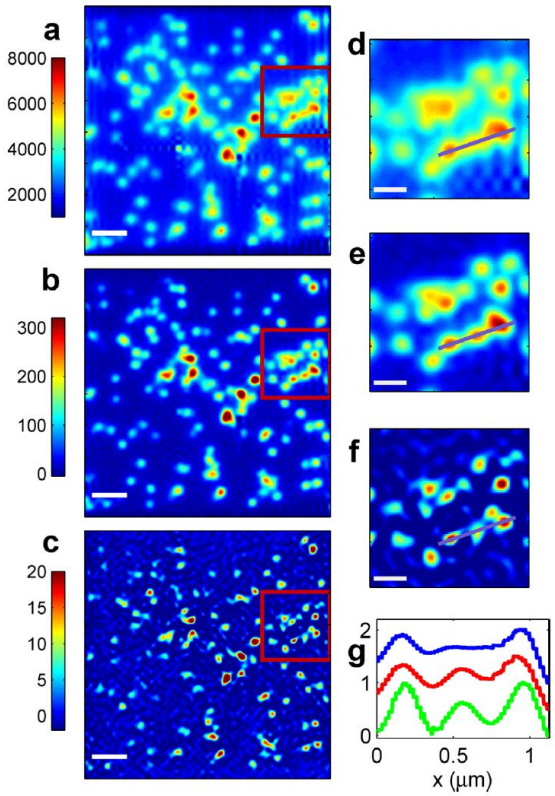

Figure 4: Fluorescence antibunching imaging. Panels (a–c) show a regular fluorescence image, second and third order antibunching images, respectively. Scalebar length is 1 μm. (d–f) Magnified views of the boxed areas in the images (a–c). Scalebar is 400 nm. The graph presented in panel (g) shows a cut of the magnified images (in normalized units) along the line indicated in panels (d–f). The blue line corresponds to regular fluorescence image and the red and green lines represent the second and third order antibunching imaging, respectively. The lines are vertically shifted for visibility. (Image reproduced with permission from [12])

Using these anti correlations of neighboring pixel at zero delay times we constructed images (see technical details at [12]). A typical super-resolved image set is shown in Figure 4. A regular fluorescence image and the second and third order antibunching images of the same area, presented in Figure 4a–c, demonstrate consecutive improvement of resolution. The magnified view of a small region (Figure 4d–f) illustrates the initially unresolved features of QD distribution revealed by antibunching imaging. Enhanced resolution is also evident in the line scan plotted in Figure 4g.

Quantitatively, the resolution defined as the full width at half-maximum of the point spread function improves from 272 nm in regular images to 216 nm in the second order and 181 nm in the third order, corresponding to a resolution enhancement by a factor of 1.5 (see Supporting Information of [12] for resolution quantification and additional antibunching images).

5. CONCLUSIONS

The main connecting link for the three studies we have summarized above is the research and application of QDs in optical methods. In this context we would like to point out the manner in which one study feeds the next one. Synthesis of novel QD heterostructures was the basis of the work shown in section 2. This work contributed to an existing doubt in our understanding of the mechanism behind QD blinking which led us to perform a version of pump-probe experiment, presented in section 3. Its conclusion, that QDs can be used as stable fluorophores under saturation illumination

conditions as long as the pulse repetition rate is low, has enabled us to carry-out a new method for gaining super-resolution images from ubiquitous emitters by breaking the classicality of light assumption in Abbe's diffraction limit.

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