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Microscopic investigation of the emission efficiency of nanostructures

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Emission efficiency of individual nanoparticles

On the single-particle level, the emission efficiency is determined by PL blinking, i.e. the periodic switching between an emissive ON and a dark OFF state. Here we employ single-QD microscopy to study the PL blinking of bu:Si-QDs. By careful consideration of the effect of photo-degradation on the blinking dynamics, we determine the duty cycle - the fraction of time that each QD is in the ON state. We find that, in contrast to CdSe QDs, bu:Si-QDs are mostly OFF with a duty cycle below 4%. This shows that for efficient emission with organically passivated Si-QDs, blinking needs to be significantly suppressed, most likely to be achieved through a better surface passivation. Potentially, the short ON events with high PL intensity could make bu:Si-QDs interesting for super-resolution microscopy techniques.

4.1 Introduction

Almost all types of quantum emitters exhibit PL intermittency or PL 'blinking', which is a random switching between an emissive (ON) state and a non-emissive (OFF) state. PL blinking emerges at the single-particle level and can significantly reduce the overall emission efficiency of emitters, when these are frequently trapped in an OFF state. For many applications, PL blinking is therefore detrimental, motivating the search for pathways to suppress it [17]. On the other hand blinking also provides opportunities. For example, blinking can be used to overcome the diffraction limit of optical imaging, as is done in super-resolution microscopy techniques such as photo-activated localization microscopy (PALM) [136], stochastic optical reconstruction microscopy (STORM) [137] and bleaching/blinking assisted localization microscopy (BALM) [138]. These techniques rely on the precise localization of separate emitters - within a denser ensemble - that are temporarily switched ON. In this way, a high resolution image can be reconstructed from a series of images, which sample a different subset of the emitters in the field of view. Also in this case, the blinking dynamics are crucial [139], i.e. the duration of the
ON events, and determine the spatial and temporal resolution of the imaging system.

There are two widely used models to explain the two types of PL blinking commonly observed in semiconductor QDs: A and B type blinking [19]. The charging model by Efros and Rosen [16] is used to explain A-type blinking by assuming that in the OFF state, the QD is charged as a result of trapping of one of the photo-excited carriers on the surface. Due to the remaining carrier in the core (electron or hole), a subsequent excitation of an electron-hole pair results in an increased recombination rate due to non-radiative Auger processes and hence in a low IQE. The ON state is restored when the trapped carrier returns to the core. The intensity fluctuations in A-type blinking are thus accompanied by changes in the PL decay rate. The model by Galland et al. [19] is used to explain B-type blinking, which manifests itself by intensity fluctuations without a change in the PL recombination rate. This model assumes the reversible introduction of a surface state, which serves as an efficient non-radiative recombination channel for hot carriers. Hence the number of carriers that end up in the bottom of the conduction band is reduced, but the PL recombination rate in the ON and OFF state is not affected. In both models, the surface assumes an important role and therefore full control over PL blinking lies in the surface design. Indeed a significant suppression of PL blinking in CdSe QDs was demonstrated as a result of growing an inorganic shell around the QD [128, 140], achieving duty cycles up to 100%.

The blinking dynamics of Si-QDs have been studied by multiple groups: both for Si-QDs with an SiO₂ passivation (O:Si-QDs) [141–144] and for organically passivated Si-QDs [145, 146]. O:Si-QDs can exhibit stable blinking over extended periods of time [143, 144], with duty cycles approaching 100% [144]. For C:Si-QDs, short ON periods with respect to the long-lived OFF states are typically found [145, 146], suggesting low duty cycles. The difference in the blinking behavior between both types of surface passivation suggests a critical role of the surface also for Si-QDs. Here we will study the blinking of individual bu:Si-QDs, to investigate if the duty cycle can be the cause for the discrepancy between the ensemble QY and IQE found in Chapters 2 and 3.

4.2 Single-QD microscopy

PL imaging

Insight into the emission inefficiency of individual QDs is obtained by employing single-dot microscopy. For this we use an inverted microscope coupled to an electron-multiplying CCD (EMCCD) camera in a wide-field scheme, as shown in Figure 4.1 (for more details, see the Materials & methods section). Using a long-pass filter, the scattered excitation light is filtered out, which enables the imaging of the PL of the sample. Compared to schemes employing a single-photon detector, the wide-field scheme has a limited time-resolution, but has the advantage that it enables to study multiple QDs simultaneously and thus the extraction of representative material properties in heterogeneous samples.
4.2. Single-QD microscopy

Figure 4.1: (a) Schematic of the wide-field single-dot microscopy setup. The PL of the spatially separated QDs is excited by a de-focused continuous wave laser in a wide-field scheme. We use either an oil immersion objective (NA = 1.4) or an air objective (NA = 0.75) to collect the emitted light, which is imaged using an EMCCD camera. (b) Example of a wide-field PL image of CdSe QDs under 488 nm excitation using an air objective.

The spatial resolution for optical imaging is given by Abbe’s diffraction limit: \( d = \frac{\lambda}{2 \cdot NA} \), i.e. the wavelength of the imaged light divided by the numerical aperture of the collection lens, with typically \( d > 250 \) nm. To resolve individual particles, we spatially separate the imaged QDs beyond this limit by drop-casting them from highly diluted dispersions onto a clean quartz substrate (Figure 4.1b). To excite and collect the PL of the sample, we either use an oil immersion objective with a high NA of 1.4 (Figure 4.1b), or an air objective lens with a NA of 0.75 in a dark-field illumination scheme, where we excite the sample from outside of the microscope (Figure 4.1c). The former setup has the advantage of improved spatial resolution and collection efficiency due to the high NA lens, whereas the latter has the advantage of a more homogeneous excitation spot and of a reduced background signal from the optical elements in the objective, the immersion oil and the substrate.

PL blinking

To quantify the PL switching, we record a sequence of images and extract the PL intensity of different diffraction limited bright spots in the field of view (FOV). For this we locate pixels that are characterized by a significant intensity with respect to the surrounding pixels. Examples of resulting time traces \( I(t) \) are shown in Figure 4.2 for CdSe-based QDs (CdSe525 - see Chapter A.1). The PL signal is not continuous, but reversibly switches between bright ON periods and dark OFF periods. The occurrence of such two-level blinking is indicative of single quantum emitters and shows that the emitters are most-likely individually dispersed. Intensity traces of small ensembles of emitters within the same diffraction limited spot will show multiple bright intensity levels, resulting from different subsets of the small ensemble that reside in the ON state.

To distinguish the two intensity levels, we define an intensity threshold \( I_{TH} \) (Figure 4.3). In frames in which the PL intensity exceeds this threshold the QD is considered to be ON, and is considered to be OFF otherwise. For \( I_{TH} \) we use the definition of Kuno et al. [147] and set \( I_{TH} \) to a multiple of the standard deviation of the background intensity.
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From the number of ON and OFF occurrences the duty cycle is evaluated:

$$\delta = \frac{T_{ON}}{T_{ON} + T_{OFF}} = \frac{T_{ON}}{T_{TOT}}.$$  (4.1)

Here $T_{ON}$ and $T_{OFF}$ are the total time spent in the ON and OFF state respectively and $T_{TOT}$ the total time.

![Figure 4.2](image1)

**Figure 4.2:** Examples of PL intensity traces of CdSe QDs (red) under 488 nm cw excitation ($\sim$70 W/cm$^2$) compared to the background intensity (black). Traces are shifted for presentation purposes.

![Figure 4.3](image2)

**Figure 4.3:** (a) PL intensity trace of CdSe QD (red) under 488 nm cw excitation ($\sim$70 W/cm$^2$) compared to the background intensity (black) and to the intensity threshold (blue horizontal line). (b) Histogram of the measured intensities in (a).

**Photo-degradation**

For the majority of fluorescence proteins, dyes and semiconductor QDs, the ensemble PL intensity is found to decrease over time, when exposed to laser irradiation. This has been observed for many materials and is typically the consequence of a decreasing number of emissive particles. The PL intensity of an ensemble of CdSe QDs is shown in Figure 4.4a.

After the laser is switched on, the PL intensity decreases roughly exponentially, within an average time of $\sim$920 s. The decreasing PL intensity is linearly proportional to the number of emitting QDs $N_{ON}$ (Figure 4.4b), confirming that the loss of PL intensity is due to the discrete switching OFF of individual QDs and not due to the continuous
4.2. Single-QD microscopy

decrease in their PL intensity, which would happen e.g. through the gradual oxidation of the QD core [148].
The decreasing number of emissive particles is commonly interpreted in terms of irreversible photo-degradation of the individual emitters [149]. Most likely, it is related to photo-chemical reactions, e.g. through photo-oxidation effects [148], which introduce efficient non-radiative channels that quench the PL of the emitter (e.g. bottom two traces in Figure 4.2). In most cases this process is irreversible, or at least not detectable on the time-scales on which we measure, and leads to the permanent decrease of the emitting fraction and total PL intensity. Importantly, photo-degradation complicates the estimation of the efficiency associated with the reversible de-activation of the individual emitters, i.e. with blinking, as the permanent dark state resulting from photo-degradation is indistinguishable from a long temporary OFF state. Photo-degradation during the measurement leads to an overestimation of the total time spent in the OFF state \( T^{OFF} \) and therefore to an underestimation of the duty cycle.

![Figure 4.4: (a) PL intensity integrated over 262 CdSe QDs against time under 488 nm cw excitation (~70 W/cm²). The solid red line indicates an exponential fit yielding an average decay time of 920 s. (b) Integrated PL intensity versus the number of QDs in the ON state. The solid red line indicates a linear fit, showing that the decrease in PL intensity is the consequence of a decreasing number of emitting QDs.](image)

To quantify the photo-stability, we determine the survival time \( T^S \) [149], given by the time period before the last time at which the QD is observed to be ON (green shaded area in Figure 4.6a). The surviving fraction \( F_S \), i.e. the fraction of dots that are either ON or temporary switched OFF, but still emitting at a later point in time, is shown for CdSe QDs in Figure 4.5. During the first 1500 s of the measurement \( F_S \) decreases exponentially (red dashed line) with an average survival time of 1400 s, close to the decay time of total PL intensity in Figure 4.4. Towards to the end of the measurement this exponential behavior changes and \( F_S \) decreases more rapidly. This is the consequence of an increasing amount QDs with OFF events that are not followed by ON events as these are cut-off by the experimental time window. In this time period the surviving fraction underestimates the stability of the material, although this effect can be avoided by measuring sufficiently long.

The duty cycle \( \delta_i \) of each QD against the survival time \( T^*_i \) is shown in Figure 4.6. During
the measurement of $\sim 2600$ s, $\delta$ assumes values between 0 and 60%, but the highest values are found only for QDs that survive towards the end of the measurement. For QDs that only appear shortly after the laser is switched on the duty cycle is close to zero, indicating that their duty cycle is underestimated as a consequence of photo-degradation. The average duty cycle $\overline{\delta}(t)$ of the surviving fraction (red line) indeed increases with time up to a value of $\sim 25\%$, the average duty cycle of the QDs that survive the entire measurement, and are not affected by photo-degradation. We assign this value to the average duty cycle associated with the PL blinking of this material.

Figure 4.5: (a) PL intensity trace of CdSe QD (red) under 488 nm cw excitation ($\sim 70$ W/cm$^2$) compared to the background intensity (black). The green area indicates the survival time, i.e. the time window $T_s$ in which the QD is observed. The horizontal dashed lines indicates the intensity of the ON state. (b) Histogram of the measured intensities in (a). (c) Surviving fraction obtained by analysis of 262 QDs during a measurement of $\sim 2600$ s. The red dashed lines indicates an exponential decay fitted to the first part of the data, yielding an average survival time of 1400 s.

Figure 4.6: (a) Duty cycle obtained for 262 individual CdSe QDs against the survival time, i.e. the time at which the dots last appear ON. The red line indicates the average duty cycle of the surviving fraction of QDs. (b) Distribution of the duty cycle.

4.3 Results: bu:Si-QDs

PL blinking

To study the duty cycle of C:Si-QDs, we investigate bu:Si-QDs, drop-cast from a dilute dispersion in ethanol on a quartz substrate. An example of a PL image used for blinking analysis is shown in Figure 4.7a, recorded using a NA=1.4 oil immersion objective. To
4.3. Results: bu:Si-QDs

account for the inhomogeneity in the excitation spot, we measure the excitation intensity
distribution on a dense layer of QDs (Figure 4.7b). From the QD positions, excitation
intensity distribution and measured laser power, we obtain the power density at each emitter’s position.

![Figure 4.7: (a) Wide-field PL image of bu:Si-QDs under 488 nm (∼0.8 mW) excitation. (b) The measured excitation intensity distribution.](image)

Typical examples of intensity traces of bu:Si-QDs are shown in Figure 4.8. The intensity traces are characterized by short ON periods that typically last only a few seconds and long OFF periods that last up to 1000’s of seconds. In contrast to CdSe QDs, each trace consists only of a few ON events, the vast majority of which appears in the first part of the measurement, shortly after the laser is switched on (Figure 4.9, green triangles). Only a fraction of the QDs appear ON towards the end of the measurement.

![Figure 4.8: (a) Representative examples of PL intensity traces of bu:Si-QDs (red) under 488 nm cw excitation (∼28 W/cm²) compared to the background intensity (black). In total 120 traces were recorded. Traces are shifted for presentation purposes.](image)

Interestingly, the fraction of bu:Si-QDs in the ON state $F_{ON}$ decays within ∼250 s, whereas the surviving fraction $F_S$ decays much slower within ∼1000 s (Figure 4.9, black circles). This shows that apart from photo-degradation, additional photo-induced changes occur in the sample, causing QDs to have a higher probability to be emissive in the first part of the measurement.
**Duty cycle**

To estimate the fraction of time spent by each QD in an emissive state, we extract the duration of the ON and OFF events from the intensity traces and compute the duty cycle using the procedure outlined in Section 4.2. For this, we quantify the survival time and duty cycle of 120 bu:Si-QDs during the total measurement time of ~2600 s (Figure 4.10a). The duty cycle appears between 0 and 30%, with the most frequently observed value around a few percent. Like for CdSe QDs, the duty cycle estimate for bu:Si-QDs that appear only in the first part of the measurement is close to zero. However, in contrast to CdSe QDs, bu:Si-QDs that survive towards the end of the measurement also have a low duty cycle, typically less than 4%. The average duty cycle \( \bar{\delta}(t) \) (red line in Figure 4.10c) is roughly constant between 2 and 4% and is independent of the survival time.

To understand the decay in the fraction of the emissive QDs, \( F_{ON} \), we separate the contribution of photo-degradation from other photo-induced changes. For this we evaluate the surviving ON fraction, i.e. the fraction of QDs that are still alive (and will appear at a later point in time) and are in the ON state at some point in time: \( F_{ON}^S(t) = F_{ON}(t)/F_S(t) \). The surviving ON fraction is shown in Figure 4.10b (black symbols). At the start of the measurement \( F_{ON}^S \) is around 30%, but decreases roughly exponentially within ~300 s to a value of around 4%. This value is close to the average duty cycle \( \bar{\delta}(t) \) (red curve).

The high surviving fraction of QDs in the ON state at the start of the measurement indicates that bu:Si-QDs are in a different equilibrium state before laser irradiation [139]. A potential reason for this could be that most QDs are initially uncharged and thus emissive [150]. Only upon laser irradiation does \( F_{ON}^S \) reach an equilibrium dictated by the blinking dynamics. This occurs even though we keep the excitation intensity as low as possible, and shows that the initial decrease of the fraction of emissive QDs (Figure 4.9, green) is for a large part governed by the PL blinking rather than due to the irreversible photo-degradation (Figure 4.9, black).
4.3. Results: bu:Si-QDs

Figure 4.10: Estimated duty cycle against the survival time of bu:Si-QDs under 488 nm excitation (∼28 W/cm²). (b) Distribution of the obtained duty cycle values. (c) Average duty cycle (red, left axis) and surviving ON fraction (black, right axis) and against time. The surviving ON fraction is roughly 30% right after the laser is switched, but decays within ∼300 s, as indicated by the solid black line.

Power-dependence of the duty cycle

Finally, we study the influence of the excitation power on the blinking dynamics of bu:Si-QDs, by recording intensity time traces for ∼120 QDs at lower excitation power densities of 18 and 11 W/cm². To quantify the change in blinking behavior, we compute the probability distribution of the recorded ON and OFF times. For this, we extract the duration of all ON and OFF periods in each trace \( \{t_{i}^{ON}\} \) and \( \{t_{i}^{OFF}\} \) and compute the associated probability densities \( P(t^{ON}) \) and \( P(t^{OFF}) \):

\[
P(t) = \frac{N(t)}{N_{tot} \Delta t}.
\]

Here, \( N(t) \) is the number of ON(OFF) events of length \( t \) and \( N_{tot} \) the total number of ON(OFF) event. The weighting-factor \( \Delta t \) represents the average time difference to correct for the low data density in the tail of the distribution, following the scheme proposed by Kuno et al. [147]. Furthermore, to obtain proper statistics, we compute the joint probability density by combining the time traces of 120 QDs.

\( P(t^{ON}) \) and \( P(t^{OFF}) \) are shown in Figure 4.11a and b. Both the ON and OFF times roughly follow a power-law \( P \propto t^{-m} \), as evident from the linear-dependence on a double-logarithmic scale (Figure 4.11). The power-law dependence holds over the full experimental time range for the OFF-times, whereas for the ON times it is truncated around ∼300 s. To estimate the power coefficients, we use a maximum likelihood estimation (MLE) method described by Hoogenboom et al. [151]. In this approach, an estimate for \( m \) is obtained by comparing the detected ON and OFF times with the probability distribution function of a power-law (for more details see References [151, 152]):

\[
p(t) = \frac{m-1}{t_{min}} t^{-m}.
\]

Here, \( t_{min} \) is the lower bound of the range in which the power-law dependence holds.
For the ON and OFF times we obtain $m_{ON} \sim 2.0$ and $m_{OFF} \sim 1.4$. Importantly, the exponents are independent of the excitation power density (Figure 4.11c). We also determine the average duty cycle (Figure 4.11d), by averaging the duty cycles obtained for QDs that survived at least the first 1000 s in each measurement (Figure 4.11c). Also in this case, we observe no clear dependence on the excitation power density. From this we conclude that the character of the PL blinking is not significantly influenced in the excitation power regime studied here and that the associated single-QD emission efficiency is unaffected.

**Figure 4.11**: (a,b) Composite probability density of the ON (a) and OFF times (b) for three different excitation power densities. In each curve the histograms are obtained by combination of 120 intensity traces. Solid lines show fits using a pure power-law (OFF times). Curves are shifted vertically for presentation purposes. (c) Power law exponents as estimated using a MLE approach. (d) Estimated average duty cycle against excitation power. $\delta$ was obtained by averaging the duty cycles obtained for QDs that survived at least the first 1000 s of the measurement.

### 4.4 Discussion & conclusion

In conclusion, using single-QD microscopy we study the PL blinking duty cycle of bu:Si-QDs. We demonstrate that bu:Si-QDs exhibit short emissive ON periods, but are most of the time OFF and are characterized by a duty cycle of $\sim 4\%$ for the timescales studied here ($\sim 2600$ s). This estimate might in fact be an upper limit of the duty cycle, since for longer measurements the probability of being trapped in a long OFF state increases as a result of the the power-law nature of the OFF times [153, 154]. Our finding thus suggest major implications for the emission efficiency of ensembles of bu:Si-QDs. However, for a direct comparison of ensemble and single-QD measurements, careful consideration of the excitation conditions in both cases is required, since typically much higher excitation powers are necessary to resolve the PL of individual emitters. Moreover, the dense packing of QDs in QD ensembles was shown to influence the blinking properties [145, 155]. In particular, both clusters of CdSe QDs and C:Si-QDs were observed to exhibit longer collective ON periods when compared to ensembles of isolated QDs [145, 155].

To ensure that we are in the same excitation regime with single-QD measurements, we limited the excitation fluxes below 30 W/cm². In this regime, the PL intensity of
4.5. Materials & methods

bu:Si-QDs in the ON state increases linearly with the excitation power as shown in Figure 4.12. Assuming an absorption cross-section of $10^{-16}$ cm$^2$ [2], this yields an average number of absorbed photons per QD $N_{abs} \ll 0.001$ per emission cycle for the excitation powers used here. The linear-dependence of the PL intensity and the low value of $N_{abs}$ thus shows that we are well within the linear regime and that we can exclude any non-linear effects such as Auger recombination due to multiple excitations per QD. Moreover, despite the increase of the collective ON times that were observed in literature for clusters of QDs, the same studies showed that the total intensity and duty cycle were not affected by particle interactions [145, 155]. This suggests that the duty cycles that we obtain here for bu:Si-QDs can be directly compared to ensemble efficiency measurements. Hence our findings show that the low duty cycle constitutes a critical limitation of the emission efficiency of bu:Si-QDs.

To be considered for most applications, there is therefore an urgent need to suppress blinking in bu:Si-QDs. This is most likely to be achieved through improved surface passivisation strategies, since the QD surface assumes a critical role in the blinking of QDs [17, 128, 129]. Alternatively, the short ON times could make bu:Si-QDs interesting for super-resolution applications, where materials with a low duty cycle are preferred [139].

![Figure 4.12](image.png)

**Figure 4.12:** Maximum ON intensity against the excitation power density for bu:Si-QDs. Each point is the determined by averaging over the traces of 15 QDs. The red solid line represents a linear dependence, with a slope of 1. On the top horizontal axis the estimated average number of excited electrons per QD is shown.

4.5  Materials & methods

**Single-dot microscopy**

Single-dot PL was detected using an inverted microscope (Zeiss, Axio Observer Z1) coupled to a spectrometer (Princeton Instruments, Acton SP2300) and a CCD (Princeton instruments, Pylon 400B) in a wide-field scheme. Samples were prepared by drop-casting QDs from a dilute dispersion on a quartz cover slip (Structure Probe Inc.). The cover slips were cleaned by sonication in an alkaline cleaning solution (Hellma Analytics, Hellmanex III) for 60 minutes, followed by sonication in and rinsing with demineralized water (30
minutes), drying by nitrogen flow and an ozone dry-cleaning procedure (UVP, PR-100) for ~20 minutes. Cw excitation is provided by the 488 nm Ar+ laser line (Spectra-Physics, Stabillite 2017) attenuated by a Glan-Thompson polarizer. The emitted light is collected using a 100x objective (Zeiss, Epiplan-Neofluar NA 0.75) or 100x oil immersion objective (Zeiss, Plan-Apochromat NA 1.4) and is filtered by a 490 long-pass filter (Semrock, 488 nm EdgeBasic) long pass filter to remove scattered excitation light. By selecting a mirror in the spectrometer, we then acquire a blinking movie by recording sequences of PL images of the sample. For the CdSe QDs we used an acquisition time of 0.5 s per frame, for the bu:Si-QDs we used 2 s. The read-out time of the CCD was set below 50% of the used acquisition time.

Data analysis

To extract the QD positions, we construct an image which contains the maximum intensity measured at each pixel throughout the entire stack of acquired images. QDs were located by searching for pixels characterized by a high intensity with respect to the neighboring pixels. We obtain the time traces $I_n(t)$ for each QD $n$ by integrating the intensity of 5 by 5 pixels centered at the QD position throughout the blinking movie. We do the same for a position close the QD that does not contain any bright spots to obtain the intensity time trace of the background $I_{n}^{\text{bg}}(t)$. The background intensity shows a slight decay during the measurement, which is most likely related to the emission from the optical elements in the microscope. We correct for this by fitting an exponential decay to the background intensity, which we subtract from the intensity time traces.