Multiexponential photoluminescence decay of blinking nanocrystal ensembles

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We investigate the relationship between the multiexponential photoluminescence (PL) dynamics of large nanocrystal (NC) ensembles and the intensity intermittency (blinking) characteristic of single NCs. A general model is developed and a simple fitting form derived for the analysis of PL decay curves allowing the extraction of both the intrinsic radiative recombination rate and an intensity intermittence parameter. The analysis is applied to the PL of a series of Si-NCs embedded in silicon oxide matrices yielding a good agreement between extracted and theoretical recombination rates. An excellent agreement is furthermore reported between the range of power-law exponents obtained and those previously determined through both single-NC experiments and current blinking mechanism theory. We suggest that a similar approach may well be fruitful in the analysis of time-resolved PL for a large variety of other carrier-confined materials.

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I. INTRODUCTION

It is well known that nanostructured Si materials such as porous Si,[1,2] Si quantum wells,[3] and Si nanocrystals (Si-NCs) (Refs. 4 and 5) exhibit greatly improved luminescent properties in comparison with those of the bulk. However, despite the long-held interest in these remarkable characteristics, the fundamental nature of carrier recombination in such systems remains highly controversial. This is particularly exemplified by the anomalous multiexponential form of photoluminescence (PL) decay.

It has been widely observed that the PL relaxation of carrier-confined Si ensembles exhibits a multiexponential or typically stretched-exponential form.[6–17] Such observations are a source of anomaly as populations of confined carrier densities emitting at a given energy are expected to ideally share a single recombination rate and thus decay according to a single exponential.[18] Multiexponential curves on the other hand imply either recombination rate dispersions or a recombination rate that is time varying.

The physical mechanisms that may be responsible for such behavior have been extensively debated. Three main models have been proposed to explain the elongation of PL dynamics in carrier-confined Si and these can be differentiated according to their assertions in regards to the escape of carriers from confined states.

The first model, proposed by Pavesi and Ceschini[19] to describe PL dynamics in porous Si, relies on the supposition that excited carriers can easily migrate to nearest-neighbor NC core states by tunneling through the intervening oxide potential barriers. A group of NCs is thus represented as an interconnected network of confined states where distributions of random delays impede the recombination of carriers. These delays determine the form of luminescence relaxation[7,20] and are introduced either by the occasional trap-release of carriers in the case of correlated (exciton) pairs[11,19,21] or, conversely, in the case of uncorrelated carriers[15,22] the unlikely spatial concurrence of an electron-hole pair. Evidence against such intercrystallite migration however has been reported in two separate works. Mihalcescu *et al.*[23] provide arguments based on resonant excitation while Guillois *et al.*[9] demonstrate the independence of PL dynamics on intercrystallite distances.

The second model to be considered, though it discounts any intercrystallite transport, asserts that PL decay is affected by the escape of confined carriers to nonradiative states located in much closer proximity to the NC.[16,17,24] The probability of escape is determined both by local disorder at the NC interface and the crystallites' immediate environment.[24] The variations between independent NCs within a sample thus result in distributions of escape rates and, consequently, *nonradiative* recombination rate dispersions.

The third mechanism arises from the notion that the PL relaxation of confined Si is determined by the independent and wholly migration-confined relaxation of core-state transitions which, it is suggested, result in dispersions of *radiative* rates.[6,9] Delerue *et al.*[6] assert that small variations in Si-NC structure may cause large variations in the overlap between electron and hole wave functions in k space. This, coupled with the multiphonon nature of confined-state transitions, would result in radiative rate dispersions for any ensemble of indirect-gap NCs.

Although each of these three models could hypothetically generate the required elongated or "stretched-exponential" decay form,[20,25–27] without further evidence, for example, a convincing agreement between theoretical and experimental recombination rates, no single model can be confirmed. However, perhaps due to both the theoretical complexities involved in the simulation of atomic clusters[28–30] and the difficulty in deriving physically meaningful conclusions based on aggregate behaviors of large NC populations with intrinsic polydispersity,[28,31,32] such information remains elusive.

The observation of single NCs is therefore needed to provide basic information for the understanding of PL in confined systems. Recently, advances in single-NC spectroscopy have furnished excellent results relating to the characteristics of single particulates.[28] However, though single-particle behavior inevitably affects the characteristics of large ensembles, it is not immediately obvious how the attributes of single NCs can be combined for the interpretation of experimental results for large populations.[33]

In this work, we broach a deeper analysis into the link between the characteristics of single NCs and the luminescent behavior of systems comprising large NC distributions. In particular, we suggest that the widely observed phenomenon of intensity intermittence, or "blinking," in single fluorophores[34,35] is likely to play an important role in the multiexponential nature of PL relaxation for a large range of luminescent materials.

Under continuous excitation, single NCs are observed to exhibit intermittent and discrete luminescence intensity levels resulting in a series of alternating on- and off-periods.[28] This phenomenon, observed for a large variety of systems, is now thought to be exhibited by single fluorophores of almost all light sources.[34,35] Interestingly, the distribution of on- and off-periods for many nanoscale systems (NCs, nanorods, nanowires, and some organic molecules) appears to be characterized by power-law behavior with exponent values in the vicinity of 1.5, irrespective of the nanoparticle material.[28,34–40]

We propose that the blinking mechanism, producing sudden changes in PL intensity during continuous excitation, is furthermore likely to affect carrier recombination during PL relaxation and, consequently, must be significant in the evolution of decay curves for NC ensembles.

We begin with the development of a general model describing the interaction of relaxing carrier populations with the blinking mechanism and subsequently derive a simple fitting procedure which allows the deconvolution of intrinsic recombination rates and extrinsic blinking effects. This analysis is then applied to relaxation curves recorded for a series of Si-NCs embedded in Si oxide, which were synthesized using reactive pulsed laser deposition (rPLD). Good agreement is obtained between extracted recombination rates with energy and theoretical values reported in the literature.[6] In addition to this, we achieve excellent agreement between power-law blinking parameters thus obtained and the range of values expected for the blinking statistics power-law exponent according to both experimental[28] and theoretical[41] works.

II. EXPERIMENT: METHOD AND RESULTS

Si-NCs were synthesized using the experimental procedure described by Riabinina *et al.*[42] in which Si-rich Si oxide films are deposited using rPLD and are subsequently annealed. Samples were hydrogen passivated in 5% forming gas at 500 °C for 1 h. X-ray diffraction (XRD) and high resolution transmission electronic microscopy (HRTEM) were used to determine the average size of Si-NCs embedded in the Si oxide matrix.[43] Time-resolved PL output light was recorded using a photomultiplier tube with a typical resolution of 1 μs. Samples were excited using a diode laser pulse of 30 μs at 405 nm. The observation energy is selected within the range 1.2–1.9 eV using optical filters.

As previously reported[42] significant PL is obtained from Si-NCs embedded in Si oxide synthesized by rPLD. Figure 1(a) shows the continuous excitation PL spectra of four Si-NC samples A, B, C, and D. The average NC diameters were found to be 4, 2.5, 2, and 1.5 nm, respectively.[43] As expected,[44] the peak positions of the PL spectra are size dependent. These peaks are centered at 1.35 (A), 1.51 (B), 1.57 (C), and 1.63 eV (D) with an average full width at half maximum (FWHM) equal to 0.3 eV. Time-resolved PL decay curves were recorded as a function of emission energy for all four samples and typical decay curves are shown in Fig. 1(b) where one sees multiexponential behavior with slope magnitudes changing by a factor of 2 or more.

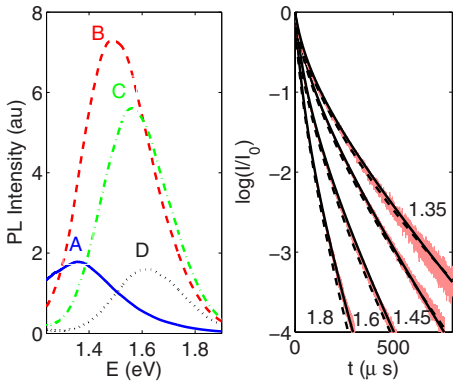

FIG. 1. (Color online) (a) Continuous stimulation PL curves for samples of embedded NCs with mean diameter 4 (sample A), 2.5, (sample B), 2 (sample C), and 1.5 nm (sample D). (b) Typical decay curves measured for sample B at emission energies between 1.35 and 1.8 eV. Each decay curve is fit with both the derived blinking form (continuous line) and the common stretched-exponential form (dashed line).

III. BLINKING MODEL OF LUMINESCENCE DECAY

A. Overview

In this section, we develop a model which explains the multiexponential nature of pulsed stimulated decay curves by including the effects of the single-NC blinking phenomenon. In this model, we consider a collection of NCs that, having turned "on" at some preceding time, are in an "on-state" at the termination of pulse stimulation.

While in an on-state, carriers excited by the stimulus recombine according to an intrinsic recombination rate which represents a sum of the available radiative and nonradiative recombination pathways. However, during PL relaxation, one by one, each of the radiators turn off irreversibly via a strong Auger-type recombination pathway. The peculiar characteristics of the power-law blinking process mean that the longer a NC is in an on-state, the less likely it is to turn off within a following interval.

As a result, the signal intensity initially drops much faster than it would have according to intrinsic mechanisms alone, due to the time-dependent turn-off rate of the emitters. This effect, however, is not as straightforward, nor as abrupt, as the power-law duration distribution, given that NCs taking part in the decay process have already spent some undetermined duration in the on-state.

Evidently, the total instantaneous rate of change per carrier for a segregated carrier population is not constant in time, implying that the members of any exponential decom-

position of the relaxation curve are not necessarily directly characteristic of the available recombination pathways. The challenge, then, is to determine how the PL behavior of NC ensembles may be analyzed to extract the basic information concerning both carrier recombination and the blinking phenomenon.

B. Development

Intensity intermittence in single quantum dots (QDs) was first reported by Nirmal *et al.*[45] in 1996, who observed that under constant excitation the fluorescence of single CdSe QDs exhibit sudden and discrete changes in intensity resulting in a series of alternating on/off periods. This phenomenon, now commonly referred to as blinking, has since been reported for various other NC materials including InP,[36] CdS,[46] CdTe,[47] and PbS,[48] in addition to both Si QDs (Ref. 38) and porous Si particulates.[37] In this section we consider how this phenomenon may contribute to the recombination of excited carrier populations during PL relaxation.

It is now widely accepted[34,35,49] that the luminescence quenching responsible for such two-state behavior is caused by the sporadic transition of an excited carrier to localized trap states external to the NC. The net charge left on the NC as a result of local electron or hole deficiency opens an additional strong Auger recombination pathway, whereby, recombination energy is transferred to another carrier rather than to the emission of a photon. Subsequent radiative recombination events are thus rendered highly improbable until the luminescence is reenabled by the trapped carrier returning to the NC core.[50]

The ionization of the NC may occur in one of several ways.[28] First, at high excitation intensities, an Auger assisted process may occur if multiple excitons are present in the conduction band simultaneously. As one of the excitons recombine, it may release its energy to one of the remaining excited carriers, effectively reducing the interface potential barrier seen by that carrier and thus increasing the probability of escape. However, as the nonradiative relaxation of multiexciton states to single exciton states is expected to take place on the picosecond scale,[51] it is unlikely that this process will be significant for systems such as embedded indirect-gap NCs due to the low photon absorption rate. Another possible ionization mechanism, however, involves the direct tunneling of single excited carriers to nearby external trapped states. Cichos *et al.*[37] calculate that the tunneling of carriers to states external to the NC may be efficient for Si-NC systems where trapped states are located within a few nm of NC cores. As the tunneling mechanism does not rely on the presence of multiexcitons or on continuous excitation, it is likely that NC ionization (and consequently nonluminescent states) will occur even during PL relaxation after pulse excitation.

In general, the durations of both PL-on- and PL-off-periods for nanoparticles (ξ_{on} or ξ_{on} referred to henceforth as $\xi_{on/off}$), as measured using single-NC photospectroscopy, are found to be statistically distributed according to an inverse power law, $P_{\xi_{on/off}}(t) \propto t^{-\alpha_{on/off}}$, where $P_{\xi_{on/off}}(t)$ represents the probability that the duration $\xi_{on/off}$ is equal to t. Such behavior is often characterized by power-law exponents α_{on} and α_{off} that are approximately equal to 1.5 or fall within the range $1 < \alpha_{on/off} < 2$.[28,52] Various authors have had some success in explaining these observations in terms of physical models.[34,35,49]

Duration statistics have been shown to be well described by the inverse power law for an extremely wide range of time values, where cutoff points are often determined by experimental limitations.[28,49] However, due to the physically unacceptable infinite short-time behavior of the inverse power law, the duration statistics must deviate from the overall tendency as a result of some intervening mechanism (likely to tend toward zero at $t=0$) at some short cutoff time ξ_{min}. Where ξ_{min} is sufficiently small, the probability $P(\xi_{on/off} < \xi_{min})$ is negligible in comparison with $P(\xi_{on/off} \geq \xi_{min})$. As there is some evidence to suggest that power-law behavior extends toward short times even into the nanosecond regime[49,53,54] and few works[47] have reported any deviation in statistics for long durations, despite several decades of observation, it can be assumed that $P(\xi_{on/off} < \xi_{min})$ is effectively equal to zero.

For simplicity, we assume the short-duration cutoffs for both on- and off-periods to be equal and constant ($\xi_{min,on} = \xi_{min,off} = \xi_{min}$). Long-time cutoffs ξ_{max}, if they exist, are furthermore expected to be many orders of magnitude greater than both the excitation-pulse duration T_p and expected confined carrier lifetimes.[49,53,54] For the purposes of decay analysis, it is therefore safe to neglect long duration cutoffs and assume that $\xi_{max} = \infty$.

Inverse time power-law behavior presents many formal problems for analysis.[55] To begin with, the expectation value of the relation $P_{\xi_{on/off}}(t)$ is infinite for $\alpha_{on/off} < 2$. This implies that an average value calculated from experimental data is dependent on the maximum observation time and, consequently, cannot be characteristic of any physical process. The conditional probability $P(t+s|s)$ in addition, unlike purely random (exponentially distributed) variables is *not* simply equal to $P(t)$. As a result, the probability for a NC to remain in a given state for some additional t after a time s depends on the length of time s that the NC has previously passed in that state. Given the counter-intuitive nature of blinking statistics, the interpretation of both single particle and ensemble behavior requires particular care.

The *cumulative distribution function* (CDF), of blinking durations $\xi_{on/off}$, is determined by first applying the normalization $\int_{\xi_{min}}^{\infty} P_{\xi_{on/off}}(t)dt = 1$ to the inverse time power-law form and subsequently integrating over time from ξ_{min} to time t,

$$F_{\xi_{on/off}}(t) = 1 - \left[\frac{t}{\xi_{min}}\right]^{-(\alpha_{on/off}-1)}. \quad (1)$$

Here, we employ the useful notation $F_X(x)$ to represent a CDF that describes the probability that the random variable $X < x$. The corresponding probability density function (PDF) is denoted by $f_X(x)$.

Figure 2 summarizes the sequence of events that are likely to contribute to relaxation curves measured under pulse excitation for large NC ensembles. As is shown in the

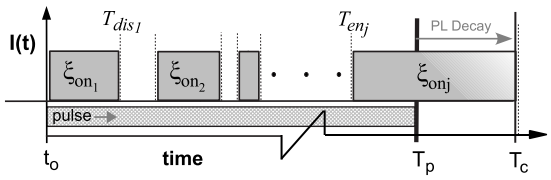

FIG. 2. Schematic representation of PL intensity vs time for the pulse excitation of a single intermittent NC. The blinking NC undergoes a series of statistically distributed ξ_{on} and ξ_{off} intervals before the termination of the laser pulse at T_p. While undergoing natural relaxation processes after T_p, the decay may be cut short at some time T_c due to a final disabling blinking event occurring at T_{dis_j} (i.e., at the end of jth on-period). If excited carriers remain in the NC at time T_c, they will be lost nonradiatively.

diagram, assuming the ionization state is initially neutral, at the onset of laser-pulse excitation at t_0, each NC will be in an on-state (indexed 1) which will persist for some duration ξ_{on_1}. Within this duration, carriers are excited by the laser and recombine both radiatively and nonradiatively as determined by their potential environments.[56]

At some time $T_{dis,1}$, an instantaneous off event occurs, forcing the NC into a nonluminescent off-state of duration ξ_{off_1}. Any carrier excited by the stimulus will then recombine very quickly, but nonradiatively, via the supplementary Auger recombination pathway. Evidently, an alternating sequence of a statistically determined number of ξ_{on} and ξ_{off} periods will then ensue leading up to the termination of the pulse at T_p.

If it happens that the NC is in an off-state at time T_p, it will quickly and nonradiatively lose its excited population and consequently remain dark for the remainder of the PL decay. (This condition is not depicted in Fig. 2 as it does not contribute to PL decay as no photons are emitted after T_p.)

The behavior of interest, for a given NC, obtains only if the end of the pulse excitation at T_p,falls within a NC on-duration. In this case, the relaxation could either proceed normally until the excited carrier (likely to be singular) (Ref. 51) has been lost according to intrinsic mechanisms or the process may be cut short at some time T_c (the last T_{dis}) by a final terminal blinking off event. The otherwise intrinsic relaxation curve of any large ensemble of blinking NCs is therefore effectively altered by the distribution of cutoff times T_c.

The following four assumptions apply in the analysis: (1) the pulse duration $T_p \gg \xi_{min}$, (2) ξ_{on} and ξ_{off} are distributed according to Eq. (1) for $\xi_{min} \leq t < \infty$, (3) sequences of random variables $\xi_{on/off}$ are memoryless,[57] and (4) at a given emission energy, members of a sequence containing only either on- or off-periods $\{\xi_{on/off_1}, \cdots \xi_{on/off_n}, \cdots \xi_{on/off_j}\}$ are identically distributed for all n and j.

With these assumptions, and where PL is observed at a selected wavelength (constant emission energy), the intensity recorded at some time t is described by the joint probability that (i) a radiative recombination event occurs at t *and* (ii) that a NC in an on-state at time T_p is still in that state at time t. The PL intensity decay curve can then be represented as a two-term product

$$I(t) = I_{in}(t_d + T_p)\bar{F}_{T_c}(t_d), \tag{2}$$

where the time variable $t_d = t - T_p$ is referenced to zero at the pulse termination T_p, the first term $I_{in}(t)$ will be the result of the probability density of intrinsic band-band recombination mechanisms without any random termination,[58] and the blinking term $\bar{F}_{T_c}(t)$ is a CDF that describes the probability $P(T_c > t)$ that a decaying NC is yet to undergo a terminating off event at time t.

In the analysis described in the Appendix, stable distribution theory is applied to obtain a useful approximate form for the CDF $\bar{F}_{T_c}(t_d)$. We arrive at the simple expression

$$\bar{F}_{T_c} \propto \left(1 + \frac{t_d}{T_p}\right)^{-(\alpha-1)}, \tag{3}$$

where the blinking parameter α is related to the statistical power-law blinking exponents α_{on} and α_{off} through convolution. As remarked in the Appendix, the substitution of Eq. (3) into Eq. (2) can be used in the construction of fitting forms for experimentally obtained decay curves, where some small number of confined and/or bulk recombination mechanisms are assumed.

IV. RESULTS

In this section we evaluate the significance of the blinking model to multiexponential PL relaxation by applying a fitting form based on the concept that the luminescence decay of a NC ensemble is determined both by the density of intrinsic recombination events and by the probability distribution of terminal off events, as stated by Eq. (2) and discussed in the previous section. In the simplest case, a singular recombination rate k is assumed to dominate intrinsic recombination at a given emission energy (potentially addressing a group of NCs with similar size and geometry).[5,56,59] We furthermore assume that within this group of crystals, the power-law exponents α_{on} and α_{off} are also shared.

This, coupled with the CDF $\bar{F}_{T_c}$, as given by Eq. (3), results in the following fitting form:

$$I(t) = I_0(1 + t/T_p)^{-(\alpha-1)} \exp(-kt). \tag{4}$$

Here T_p is set to the pulse duration (30 μs), I_0 is the initial intensity, both the blinking characteristic exponent α and recombination rate k are fitting parameters, and time t is referenced to the termination of pulse excitation.[60]

By way of comparison, each of the experimental Si-NC decay curves [Fig. 1(b)] are also fitted with the conventional stretched-exponential form

$$I(t) = I_0 \exp[(-k_{st}t)^{\beta_{st}}]. \tag{5}$$

The common stretched-exponential form is a semiempirical construction that is often used to describe relaxation curves in disordered systems for various quantities, for example, magnetic or dielectric relaxation,[61–63] or dispersive transport in amorphous semiconductors.[26] Although the physical mechanisms that may be responsible for the behavior remain a source of intense debate,[20,25,26,58,64,65] the form has been

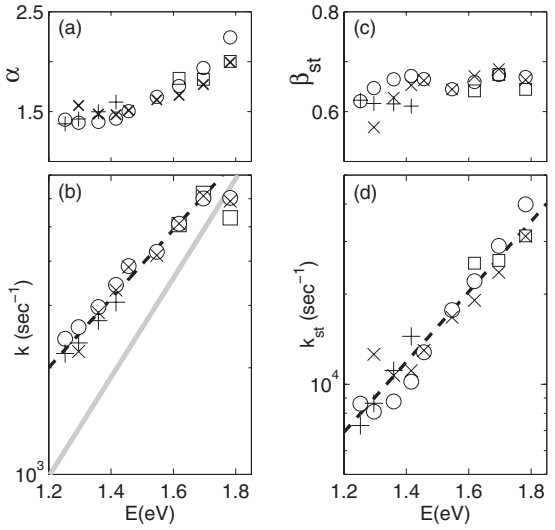

FIG. 3. Results of the analysis of time-resolved PL curves for Si-NC samples A (+), B (○), C (×), and D (□) using either the derived blinking form [(Eq. (4), Figs. (a) and (b)] or the stretched-exponential form [Eq. (5), Figs. (c) and (d)]. (a) Characteristic exponent "α" vs emission energy. (b) Intrinsic recombination rate "k" vs emission energy. The exponential tendency (black dashed) of experimental intrinsic recombination rates (symbols) is plotted to guide the eye [$k=A\exp(E/E_0)$, where $A=135$ sec^{-1} and $E_0=0.4$ eV]. Theoretical radiative recombination rates with energy (gray continuous) reported in the literature (Ref. 6) are included for comparison ($A=20.55$ sec^{-1} and $E_0=0.31$ eV). (c) Stretched exponential dispersion parameter "β_{st}" vs emission energy. (d) Stretched exponential rate parameter "k_{st}" vs emission energy showing exponential tendency (dashed) ($A=270$ sec^{-1} and $E_0=0.37$ eV).

frequently applied to time-resolved luminescence in nanostructured materials, where the fitting parameters β_{st} and k_{st} have sometimes been associated with dispersion and carrier lifetime, respectively ($k=1/\tau$).[10,11,66]

As shown in Fig. 1(b), both of these forms provide suitable fits for the experimental PL decay curves, however, for the highest photon energies (1.6 and 1.8 eV), the physically derived blinking form (continuous curve, Eq. (4)) provides a noticeably better agreement than the purely empirical stretched-exponential fit (dashed curve, Eq. (5)) shown on the same axis.

The intrinsic recombination rates k resulting from the blinking model fit of PL decay data are presented in Fig. 3(b) with observation energy for all four samples (A, B, C, and D). This tendency may be compared with theoretical results from the literature. In particular, Delerue *et al.*,[6] using a tight-binding approximation for strong-confinement regime oxide-shell Si-NCs, report an average E-k curve that is well described by $k=A\exp(E/E_0)$ for constants $A=20.55$ s and $E_0=0.31$ eV. This theoretical result is plotted in Fig. 3(b) as a continuous gray line.

The pseudorate values k_{st}, obtained from the stretched-exponential fit for the same experimental decay curves [Fig. 1(b)] are shown in Fig. 3(d). Evidently, though theoretical recombination rates and rates obtained using the blinking form are both on the same order of magnitude [both shown in Fig. 3(b)], the stretched-exponential rate k_{st} is consistently an order of magnitude higher [Fig. 3(d)]. However, as shown in Fig. 3(b), the intrinsic recombination rates obtained from the PL decay curves using the blinking form (symbols) still remain somewhat higher than radiative recombination rates determined through simulation[6] (gray line).

As shown in Fig. 3(a), the characteristic exponent values α obtained from the blinking decay model exhibit an obvious evolution toward higher values with increasing confinement energy. This can be compared with the behavioral variation in β_{st} with energy, as shown in Fig. 3(c), which appears to be more random in nature with only a slight rising trend.

Significantly, for emission energies within the range $1.2<E<1.45$ eV, the blinking parameter α remains stable at approximately 1.5, corresponding to the ideal power-law exponent predicted by simple blinking models.[47,49,53,54] At higher values of emission energy ($E>1.45$ eV), α steadily increases until it exceeds 2 at approximately 1.8 eV. These values are in excellent agreement with the unusually high range of power-law exponents reported for porous Si by Cichos *et al.*[37]

V. DISCUSSION AND SUMMARY

By considering the simple case of a population of emitters decaying with a shared characteristic recombination rate and exhibiting identically distributed statistical power-law blinking durations, we have demonstrated that single lumiphore intermittency may naturally lead to multiexponential or stretched-exponential luminescence decay for carrier-confined materials. Using a number of approximations, we have furthermore derived a simple fitting form for the analysis of multiexponential time-resolved PL for nanostructured materials, which permits the extraction of intrinsic recombination rates, effectively deconvolving the curve elongation attributed to intensity intermittence from intrinsic confined-state recombination.

We have applied this technique to a series of Si-NCs embedded in Si oxide and obtained some useful agreement between extracted recombination rates and average theoretical radiative rates reported in the literature.[6] For a range of emission energies, the power-law exponents thus obtained are approximately equal to the "ideal" value of 1.5 (Refs. 53 and 54) and subsequently tend upward to surpass 2.

We suggest, therefore, that the multiexponential nature of PL decay for quantum confined systems is strongly related to the blinking phenomenon, an assertion for which there is some prior evidence. In general, the time-average PL relaxation of single NCs is observed to be multiexponential.[67,68] However, by simultaneously monitoring the emission intensity fluctuations of single NCs, and photons emitted following pulse stimulation, Fisher *et al.*[68] observe that where decay curves are reconstructed using only photons emitted during maximal intensity periods, PL relaxation is found to be characterized by a single exponential. The implication here is that intrinsic recombination for a single NC in the absence of off blinking events is characterized by a single recombination rate, indicating that the decay curve elongation is indeed a result of the blinking process.

A. Short-time behavior

In this work we have approached investigations based on the supposition that blinking durations of single particulates follow inverse power-law statistics over a large range of time values and deviate from this behavior at some short time ξ_{min} in comparison with the excitation-pulse length. Although it is widely accepted that single emitters of various materials exhibit this behavior, including direct-gap NCs and some organic molecules,[49] the situation is somewhat less established for indirect-gap Si particulates, possibly due to their low radiative recombination rates. Indeed, of the two main works that examine the blinking durations of single Si emitters (porous Si particulates and Si-NCs, respectively), only one study[37] reports power-law behavior (within the limited observation time of 10 ms to 60 s), while the other[38] reports purely random (exponential) behavior, which is interpreted in terms of early blinking models.[69] Interestingly, the observations for porous Si (Refs. 37 and 70) appear to be in contradiction with those of Si-NCs.[38]

There is currently some evidence to suggest that power-law durations may persist in direct-gap NCs even down to excited carrier lifetimes or below,[49,53,54] however, similar methods are yet to be applied to their indirect-gap counterparts. It may be useful, therefore, to additionally consider the case in which the restrictions on short-time cutoff ξ_{min} are lessened.

For example, simplistically, if it is assumed that ξ_{min} is comparable to, but shorter than the excitation-pulse duration, the proportion of NCs that remain in a *single* on-state for the entire pulse duration should be significant (equivalent to the case in which $j=1$ for Fig. 2), on the condition that $P(\xi_{on}<\xi_{min})\approx 0$ [where an intervening mechanism causes $f_{\xi_{on}}(t)$ to tend to zero for $t<\xi_{min}$], at which point, the blinking contribution to decay [$\bar{F}_{T_c}(t)$ as appears in Eq. (2)] can be approximated by the probability that a NC, having already spent the duration of the pulse excitation T_p in an on-state, is still on at some subsequent time t. This is given by the conditional probability[71] $P(\xi_{on}>t+T_p|\xi_{on}>T_p)=(1+t/T_p)^{-(\alpha_{on}-1)}$. It is worth noting that this expression is in agreement with the general form of $\bar{F}_{T_c}(t)$ derived for $\xi_{min}\ll T_p$ given by Eq. (3), except that where T_p is instead comparable to ξ_{min}, the fitting parameter α may yield the unique value of the on-state exponent α_{on}. It is apparent, therefore, that for a specific system, in this case Si-NCs, the exact form of $\bar{F}_{T_c}(t)$ may well be dependent on the short-time behavior of the blinking mechanism, however, further experimental evidence is required in order to make progress on the specifics.

B. Dependence on pulse duration

An interesting consequence of the power-law blinking model of luminescence decay is the prediction that the form of luminescence decay is explicitly dependent on the duration of pulse excitation (T_p), as appears in Eq. (4). Unfortunately, however, there is comparatively little attention paid to such a relationship (or lack thereof) in the literature. With particular reference to confined Si, only two systematic investigations into the effect of pulse duration on the form of relaxation have been reported but with opposing conclusions.[21,72]

The first, by Pavesi,[21] reports that the form of luminescence decay of porous Si is indeed a function of excitation-pulse length independent of the excitation energy per pulse. They observe, that for increasing pulse durations within the range $20\ \text{ns}\leq T_p\leq 2.15\ \text{ms}$, stretched-exponential fits of decay curves yield increasing values of carrier lifetime and marginally increasing values of β_{st}. Kanemitsu[10] and Chen *et al.*[20,73] note simply a strong dependence on excitation conditions such as "laser-pulse width and laser intensity," however, the effects of individual parameters are not elucidated. On the other hand, Finkbeiner *et al.*[72] report no variation in decay form for pulse durations within the range $15\leq T_p\leq 200\ \mu\text{s}$. In the same vein, Pacifici *et al.*[74] report that carrier lifetimes in embedded Si-NCs are invariant with pulse duration for the range $100\ \mu\text{s}\leq T_p\leq 0.1$ s, however, they do not discuss the decay form.

It is clear, therefore, that the possibility of a relationship between excitation-pulse duration and the form of the luminescence decay for NC ensembles merits further investigation. There is no shortage of candidate effects to account for such behavior. In addition to the relationship that results from power-law blinking behavior, as suggested by Eq. (4), other dependencies have previously been predicted, particularly where pulse duration is comparable to carrier lifetimes. These have been deemed to be caused by, for example, the gradual diffusion of carriers between localized states during excitation for materials with restricted geometries,[75] the filling of nonradiative centers and increased exciton thermalization,[21] or simply the probabilistic excitation and relaxation of a distribution of states.[76]

C. Interpretation of the parameters

Despite an agreement on the order of magnitude, recombination rates obtained using the derived blinking form fit remain noticeably higher than theoretical radiative values. Such discrepancies may be indicative of nonradiative recombination processes, perhaps owing to the incomplete passivation of nonradiative defect centers. However, it is also difficult to discount the possibility that the discrepancy is related to differences in structure between embedded NC samples and the simulated oxide-shell NCs.

Extracted characteristic exponents α exhibit a good agreement with the range of values $(1<\alpha<2)$ expected for power-law exponents in blinking statistics for a variety of NC materials.[41,49,53,54] With particular reference to Si, Cichos *et al.*[37] report unusually high values for the on-state exponent $(\alpha_{on}=2.2\pm 0.1)$. Though this appears to be congruent with our results, one should bear in mind that the derivation of the blinking fit is only valid for the range of characteristic exponents $1<\alpha_{on/off}<2$. It is possible, therefore, that where α is determined to be much larger than 2, extracted parameters may be erroneous. An illustration of this is provided in Fig. 3(b); where $\alpha>2$, the $E-k$ curve begins to deviate from the exponential tendency.

The interpretation of the fitting parameter α is, however, somewhat complicated as its precise relationship to the

blinking parameters α_{on} and α_{on} remains unclear. The extracted parameter α is the result of the convolution of two stable distributions (SDs) with characteristic exponents "$\alpha_{on}-1$" and "$\alpha_{off}-1$." However, as relationships between arbitrary SD parameters and parameters of SD convolutions have not been defined, the problem must consequently be examined computationally.

It is, nevertheless, illustrative to consider the situation in which $\alpha_{on} \approx \alpha_{off}$. In this case, the fitting parameter α is equivalent to the single-NC characteristic exponent $\alpha_{on/off}$. The observation that $\alpha \approx 1.5$ for emission energy $1.2 < E < 1.5$ eV is then particularly exciting as it corresponds to the value predicted by the ideal diffusion-controlled electron-transfer model of the blinking phenomenon.[41] Considering this encouraging result, and the obvious tendency observed for α with emission energy, it is foreseeable that time-resolved PL decay analysis of large ensembles may in fact provide an extremely simple and effective alternative for the extraction of blinking data, where a greater range of excitation conditions (e.g., lower fluences) or fabrication procedures may be used. Further work is, however, required in order to understand the possible causes of the increase in α with emission energy.

D. Conclusions

We have shown that blinking statistics represent an important consideration in the analysis of time-resolved PL data for nanostructured materials. We have developed a method for the extraction of both single-NC blinking parameters and intrinsic radiative rates for recombination in quantum confined systems. We further suggest that due to the large range of systems exhibiting blinking phenomena and the prevalence of inverse power-law blinking statistics,[28] a similar approach may be used for a wide range of nanoscale systems including, for example, direct-gap nanostructures,[37,38] indirect-gap nanostructures,[36,46–48] and some organic molecules.[40]

We nevertheless caution the reader that while the blinking model does provide an excellent fit to decay data and yields useful values for recombination rate k and characteristic exponent α, one cannot yet exclude the effects of other models in contributing to multiexponential behavior. There is a clear need for further experimentation to settle this aspect.

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APPENDIX: DERIVATION OF BLINKING FORM

To understand the influence of the blinking phenomenon on group intensity decay, it is important to determine the nature of the CDF $\bar{F}_{T_c}(t)$ considering the conceptual model detailed in Sec. III. We begin by recognizing that the PDF $f_{T_c}(t)$ can be represented as a sum of joint probabilities, for an integer j number of on-periods,

$$f_{T_c}(t) = \sum_{j=1}^{T_p/2\xi_{min}} f_{T_c,j}(t). \tag{A1}$$

Each of the joint PDFs $f_{T_c,j}(t)$ describes the probability that T_c (the last cutoff) is equal to t *and* occurs at the completion of the jth on-duration ξ_{on_j}. These summands $f_{T_c,j}(t)$ are therefore defined according to the relation

$$f_{T_c,j}(t) = P(T_{dis_j} = t \cap T_{en_j} < T_p \cap T_{dis_j} > T_p), \tag{A2}$$

for a given known constant pulse duration T_p. This somewhat complicated expression simply means that the probability is given here for all cases with the following three conditions in order (from left to right): (i) the last disabling jth blink occurred at $t = T_{dis_j}$, (ii) this jth PL-on event occurred before the end of the pulse at T_p, *and* (iii) this jth PL-off event (at time T_{dis_j}) happened after T_p.

If we construct a time sum S_j consisting of $j-1$ on-periods and $j-1$ off-periods, terminating in the last (jth) on-period, we have the total time from the start of the pulse to the end of the last turn-off as follows:

$$S_j = \sum_{j=0}^{j-1} (\xi_{on_i} + \xi_{off_i}) + \xi_{on_j}.$$

If we apply the relation $P(A \cap C) = P(A|C)P(C)$ to Eq. (A2), each summand $f_{T_c,j}(t)$ can then be rewritten partly in terms of the negated CDF $\bar{F}_{on}(t)$ according to the following form:

$$f_{T_c,j}(t) = H(t - T_p)\bar{F}_{\xi_{on}}(t - T_p) f_{T_{S_j}}(t), \tag{A3}$$

where $\bar{F}_{on}(t) = 1 - F_{\xi_{on}}$ and $F_{\xi_{on}}$ is given by Eq. (1). This manipulation can be understood as

$$P(T_{dis_j} = t \cap T_{en,j} < T_p) = P(T_{en,j} < T_p | T_{dis_j} = t) P(T_{dis_j} = t),$$

where the notation $P(A|C)$ reads, the probability that A is true, given C is known to be true. The conditional probability $P(T_{en_j} < T_p | T_{dis_j} = t)$ is then equal to the probability that an on-period is longer than the interval between t and T_p, i.e., $P(T_{en,j} < T_p | T_{dis,j} = t) = \bar{F}_{\xi_{on}}(t - T_p)$. Note that $f_{T_c}(t)$ is defined on the interval $T_p < t < \infty$ and is thus appropriately normalized according to $\int_{T_p}^{\infty} f_{T_c}(t)dt = 1$.

Now, the term $\bar{F}_{\xi_{on}}$ decreases rapidly to approach the horizontal asymptote at zero. (Note that for $\xi_{min} < 0.1$ μs and $\alpha_{on} \approx 1.5$, $F'_{\xi_{on}}(t)$ falls to below 0.1% μs^{-1} at 5 μs.) If we consider the minimum resolution of the recording instrument ($\approx \mu$s), it is apparent that the term $\bar{F}_{\xi_{on}}$ is effectively equal to some small constant within the region of interest. It can therefore be assumed that for $t \geq T_p$, $F_{T_c,j}(t)$ is approximately proportional to $F_{T_{Sj}}(t)$. Using the fact that the CDF of a sum of any two random variables X_1 and X_2 (which here will be ξ_{on} and ξ_{off}) is given by the convolution of their respective CDFs,[77] $F_{T_c,j}(t)$ can be decomposed according to

$$F_{T_c,j}(t) \propto F^{(j)*}_{\xi_{on}}(t) * F^{(j-1)*}_{\xi_{off}}(t), \tag{A4}$$

where $F^{(n)}(x)$ represents the n-fold convolution of the CDF $F(x)$.

It is now apparent (according to Eq. (A4) and assumption 1) that the cutoff distribution $F_{T_c}(t)$ is likely to be dominated by CDFs of sums with a great number of random variable summands (large j). However, as the variance of Eq. (1) is infinite for $\alpha_{on/off}<3$, the classical central limit theorem, so often applied in similar cases, is not valid here. Contrary to intuition, the distribution of a sum of period durations ξ_{on,off_i} will, therefore, *not* tend toward a Gaussian limit irrespective of the number of summands. It is for this reason that the lesser-known generalized central limit theorem (GCLT) that must be applied here as required, where random variable summands are distributed with either infinite first or second moments.[78,79] This is indeed the case for power-law blinking durations.

The GCLT states that the distribution $F_{S_n}(x)$ of a normalized sum of identically distributed variables

$$S_n = \frac{1}{b_n}\sum_{i=1}^{n} X_i - a_n$$

does converge to some SD, $G(x;\alpha_G,\beta_G)$, which in general is not a Gaussian distribution. These SDs are members of a family of functions providing solutions to the expression $G(x-h)=G(x/c_1)*G(x/c_2)$. Each SD is parameterized by two variables, namely, the characteristic exponent α_G and the skew factor β_G.[78,79]

Application of the GCLT to Eq. (1) yields the parameters $\alpha_G=\alpha_{on/off}-1$ and $\beta_G=1$ for $\alpha_{on/off}\leq 3$ on the assumption that $F_{T_c,j}=0$ for $t<0$. The displacement constant a_n is then defined according to the range of the characteristic exponent $\alpha_G=\alpha_{on/off}-1$,

$$a_n = \begin{cases} n\mathbf{E}T, & 2<\alpha_{on/off}<3 \\ n\ \ln(n)\beta_G, & \alpha_{on/off}=2 \\ 0, & 1<\alpha_{on/off}<2 \end{cases}.$$

Assuming the range $1<\alpha_{on/off}<2$,[28] the displacement constant a_n is equal to zero. The normalization constant b_n is defined in terms of a function of n and ξ_{min} which is given for example in Ref. 79. Rewriting Eq. (A4) in terms of SDs, we obtain

$$F_{T_c,j}(t) \propto G[b_{j-1}(t_d+T_p);\alpha_{off}-1,1],$$

$$*G[(b_j)(t_d+T_p);\alpha_{on}-1,1]. \tag{A5}$$

As the convolution of two maximally skewed SDs is also a maximally skewed SD,[79] Eq. (A5) can be represented by a single SD parameterized by some exponent α and normalization constant B_j. The determination of $F_{T_c,j}(t)$ then reduces to the search for a suitable representation of maximally skewed SDs with arbitrary characteristic exponents. This, however, poses a problem as only a single maximally skewed SD can be represented in terms of fundamental functions (Levy distribution, $\alpha_G=0.5$). It is preferable, therefore, to search for a simple and general asymptotic approximation. It can be shown[78,79] that the long tail of any SD $1-G(x;\alpha_G,1)$ is asymptotic to $x^{-\alpha_G}$. Assuming this approximation and rewriting Eq. (A1) in terms of a summation over j of CDFs $F_{T_c,j}(t)$, where $F_X(x)=\int_{-\infty}^{x} f_X(u)du$, we arrive at the following simple expression for $\bar{F}_{T_c}$:

$$\bar{F}_{T_c} \propto \sum_{j=1}^{T_p/2\xi_{min}} (B_j)^{-(\alpha-1)}(t_d+T_p)^{-(\alpha-1)} \propto \left(1+\frac{t_d}{T_p}\right)^{-(\alpha-1)}. \tag{A6}$$

The substitution of Eq. (A6) into Eq. (2) for some theoretically determined intrinsic recombination rate distribution $\sigma(k)$ provides the complete intensity decay curve for confined ensembles, where all carrier populations are exposed to blinking phenomena. More importantly, in addition to this, Eq. (2) can also be used in the construction of fitting forms for experimentally obtained decay curves, where some small number of confined and/or bulk recombination mechanisms are assumed.

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