

Characterizing Quantum-Dot Blinking Using Noise Power Spectra

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Fluctuations in the fluorescence from macroscopic ensembles of colloidal semiconductor quantum dots have the spectral form of $1/f$ noise. The measured power spectral density reflects the fluorescence intermittency of individual dots with power-law distributions of “on” and “off” times, and can thus serve as a simple method for characterizing such blinking behavior.

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Colloidal semiconductor nanocrystals, or quantum dots (QDs), can exhibit bright, long-lived fluorescence, with an emission wavelength that is simply tuned by changing the size of the nanocrystal. This property makes them promising, for example, as biological labels, and as the active medium in light-emitting diodes or lasers. However, such applications may be compromised by fluctuations in the intensity of the QD fluorescence. Optical microscopy of single immobilized QDs has shown a blinking behavior, where the dots alternate between “on” (fluorescing) and “off” (non-fluorescing) states,¹ with power-law distributions for on and off periods.²⁻⁴ Such measurements, though, are relatively difficult and time-consuming, making it difficult to study large numbers of different samples in different environments. This Letter shows that complementary information is provided by measuring the power spectral density of fluctuations in the fluorescence from macroscopic ensembles of QDs. The power spectrum has the form of $1/f$ noise, which can be understood as the incoherent sum of the identical noise spectra of individual QDs. The ensemble noise measurements thus provide a simple, rapid technique to obtain information about the blinking statistics of individual QDs. It can be applied to a wide range of environments, including those not previously accessible to experiment, which should simplify the task of identifying and possibly eliminating the causes of blinking.

We demonstrated the applicability of this technique by making measurements on monodisperse CdSe QDs capped with trioctyl phosphine oxide (TOPO), prepared using established methods,⁵ with a fluorescence maximum around a wavelength of 610 nm. We investigated both bare CdSe nanocrystals and nanocrystals capped with ZnS shells;⁶ our results were essentially identical for both types. The noise measurements were made at room temperature by exciting the QDs with stable laser light having a wavelength of 532 nm. The fluorescence was collected perpendicular to the excitation beam using an optical fiber bundle, sent through a dichroic mirror to eliminate scattered laser light, and detected with a silicon photodiode. The photodiode output was electronically filtered to reject frequencies below 1 Hz, amplified, and

sent to a digital signal analyzer, which collected a time series $I(t)$ and calculated the power spectral density as $S(f) = |\mathcal{F}\{i(t)\}|^2$, where \mathcal{F} represents the Fourier transform, and $i(t) = I(t) - \langle I \rangle$ is the instantaneous deviation of the intensity from the mean $\langle I \rangle$. We recorded power spectra between frequencies of 200 Hz and 3 kHz. Outside this range, fluorescence fluctuations are overwhelmed by noise in either the excitation laser (at low frequencies) or in the detection electronics (at high frequencies). By varying the incident laser power, we verified that the power spectral density is proportional to the excitation power, with no change in its form. We therefore normalized the measured QD power spectrum by the measured power spectrum of the laser, removing artifacts due to fluctuations in laser power.

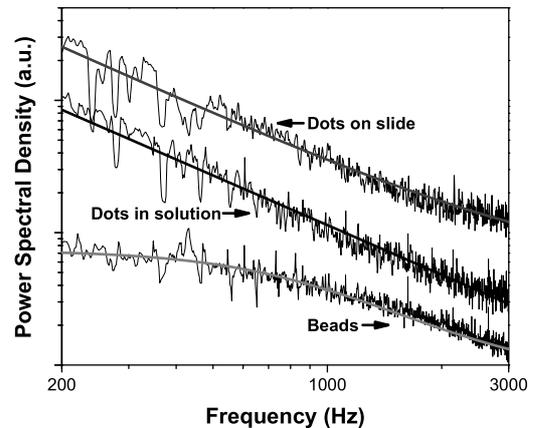


FIG. 1: Power spectral densities of fluctuations in the fluorescence from macroscopic ensembles of quantum dots, deposited on a glass slide and dissolved in chloroform, and from fluorescently dyed polystyrene beads. The spectra have been offset by arbitrary scale factors for clarity. Thick lines are fits to the power spectra: the dot spectra are fit to power laws, while the dye spectrum is fit to a Lorentzian.

For the first measurements, we deposited QDs in a dense layer on a glass slide. The measured power spectrum is shown in Fig. 1, and can be seen to have the form of $1/f$ noise over the experimentally accessible bandwidth. More specifically, it can be fitted using a rela-

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tionship of the form $S(f) = Af^{\nu-2} + B$, where A is an arbitrary proportionality constant, B is an additive offset representing the instrumental noise floor, and ν is the spectral exponent characterizing the noise. In this case, $\nu = 0.70 \pm 0.02$.

We confirmed that the $1/f$ noise spectrum is characteristic of the QDs by comparing to the power spectrum of an ensemble of polystyrene microspheres doped with a green fluorescent dye (Duke Scientific, part number G300). This noise spectrum, shown in Fig. 1, can be fit using a single Lorentzian, $S(f) = A/(f^2 + f_0^2) + B$, with a width $f_0 = 1.8$ kHz. This noise spectrum can be understood as the result of a fluctuation process with a single, characteristic time scale; in this case, it may reflect shelving in a dark triplet state.

The ability to characterize the statistics of fluorescence fluctuations in the ensemble means that immobilization of the QDs is not necessary. We therefore made a second measurement on an ensemble of QDs dissolved in chloroform. We illuminated a large volume ($\mathcal{O}(10)$ mm³), so that the variation in observed particle number due to diffusion was negligible. The measured spectrum is shown in Fig. 1, and can be seen to have the same form as the spectrum of dots on glass, with an equivalent fitted exponent of $\nu = 0.75 \pm 0.03$. The observed insensitivity of the blinking statistics to the QD environment is surprising, in the light of currently proposed blinking mechanisms.^{7,8}

The ensemble $1/f$ noise can readily be understood as the result of fluctuations in the emission from individual QDs. By the Wiener-Khinchin theorem, the power spectral density is equal to the Fourier transform of the intensity autocorrelation function. The autocorrelation function for the ensemble emission is thus

$$G^{(2)}(\tau) = \sum_n \langle i_n(t) i_n(t+\tau) \rangle + \sum_{m \neq n} \langle i_m(t) i_n(t+\tau) \rangle, \quad (1)$$

where $i_n(t)$ are the intensities emitted by the individual dots, and angle brackets indicate averages over time t . The second term describes cross-correlations of fluctuations from different QDs, and vanishes if the fluctuations are independent. In this case, the power spectrum of the total intensity is simply the sum of the single-dot spectra.

If all dots exhibit the same fluctuation statistics, then, the ensemble power spectrum will have the same form as the power spectra of the individual quantum dots. We tested this assumption by monitoring the fluorescence from single QDs, and verifying that they indeed all exhibit nearly identical power spectra. A sparse layer of dots with emission maxima around a wavelength of 535 nm was deposited on a glass microscope coverslip, and was observed using a standard epifluorescence microscope. The sample fluorescence was imaged onto a cooled CCD camera, allowing the intensities from particular QDs to be monitored over time. Time traces for two particular QDs are shown in Figs. 2(a) and (b). Power spectral densities were calculated from these time traces, after subtracting the mean values and multiplying by a

Hann window function.⁹ Resulting spectra are shown in Fig. 2(c); they can be seen to have the same $1/f$ form as the ensemble power spectra. Nearly identical spectra were obtained for all 20 QDs studied; fitting these single-dot spectra to inverse power laws yields a mean value of $\nu = 0.74 \pm 0.09$, in agreement with the exponent obtained for the QD ensembles. Further confirmation that the ensemble measurement reflects single-dot statistics is provided by adding together the measured time traces from the individual QDs point by point, and calculating the power spectrum from the time trace of the sum (shown in Fig. 2(c)); the fitted exponent in this case is $\nu = 0.69 \pm 0.03$.

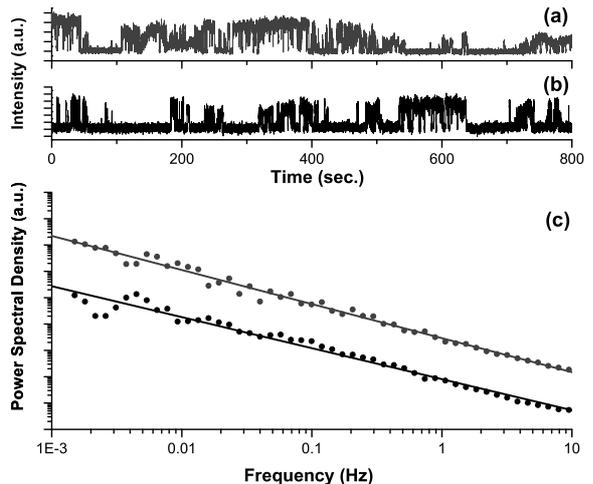


FIG. 2: (a),(b): Fluorescence intensity from two individual quantum dots as a function of time. (c): Log-log plot of the power spectral densities calculated from the above time traces (circles), together with power-law fits (solid lines). The two power spectra are offset by arbitrary scale factors for clarity. Also shown is the power spectral density calculated from the sum of 20 single-dot time series (squares). Calculated power spectral densities have been grouped in logarithmic frequency bins.

The measured power spectra are consistent with previous reports that the probability density functions of on and off blinking periods $T_{\text{on/off}}$ for individual QDs follow an inverse power law: $\Psi(T_{\text{on/off}}) \propto (T_{\text{on/off}})^{-1-\nu}$, with ν between zero and one.² In order to convert this probability distribution into a noise power spectrum, we ignore intensity fluctuations within the on and off states, and we assume that the probability density falls abruptly to zero beyond lower and upper cutoff periods T_{min} and T_{max} , respectively. Experimentally, T_{min} can be associated with the measurement time resolution, and T_{max} with the total duration of the measurement. If we also assume, for simplicity, that the same exponent ν can be used to describe on and off times, then the power spectral density is $S(f) \propto (1/\langle T \rangle) f^{\nu-2}$, where $\langle T \rangle$ is the mean on/off duration.¹⁰ The cutoff times T_{min} and T_{max}

enter only through a proportionality constant, so the form of the power spectrum is independent of the details of the measurement. Similar results are obtained if the on and off durations follow different probability distributions; for example, if they follow power laws with different exponents, the larger value of ν dominates the power spectrum.¹¹ The value of ν that we have obtained from the power spectrum is consistent with the exponents previously obtained by different researchers from probability distributions of bright and dark times.²⁻⁴

Other ensemble measurement techniques can also provide information on fluorescence fluctuations. For example, the reversible decay in the fluorescence signal from an ensemble of QDs has been shown to have a purely statistical origin.⁴ It has been proposed that the variance in the number of photons emitted by an ensemble of QDs should diverge over time.¹² Measurement of the autocorrelation of emitted photons allows fluctuations dynamics to be characterized over a wide range of time scales.¹³ Fluorescence correlation spectroscopy (FCS), the measurement of autocorrelation functions for emitters diffusing through a microscopic excitation volume, has been used to study the fluorescence of QDs in solution.¹⁴ The authors of Ref. 12 were able to fit their results with a model based only on single-particle diffusion, with no systematic deviation that would need to be explained by blinking. Their results can be reconciled with ours by considering that the power-law blinking statistics result in an autocorrelation function that is weakly dependent on delay time for short delays, and abruptly drops to zero as the delay time approaches the total measurement time

T_{\max} .^{7,13} This means that autocorrelation functions from blinking and diffusing QDs will be nearly indistinguishable from ones that result only from diffusion.

We have found that it is particularly practical to study the dynamics of QD blinking by measuring the power spectral density of fluorescence fluctuations. Representative power spectra can be measured on ensembles of dots, contrary to the popular wisdom that blinking studies require isolation of single emitters. This means that blinking can be observed in cases where microscopy is impractical, such as when QDs are in solution. Using lower-noise components, it should be straightforward to extend the measurement bandwidth beyond that obtained in this first experiment. Since the ensemble power spectrum can be measured very quickly, it will be possible to rapidly characterize the blinking behavior of different samples in different environments, eventually leading to a better understanding of and control over the blinking mechanism. Finally, we have used the same measurement technique to observe the fluorescence dynamics of dye-doped microspheres; indeed, the method we have introduced should be applicable to any fluorophore that exhibits blinking within the observable bandwidth.

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