

Blinking of CdSe/Cd_{0.33}Zn_{0.67}S semiconductor nanoplatelets

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Unstable photoluminescence quantum yield is important because it indicates changes in the transition rates between excited states. We synthesized 4.5 monolayer CdSe core, Cd_{0.33}Zn_{0.67}S gradient shell semiconductor nanoplatelets. The platelets exhibit a variety of blinking behaviors. Change points in the brightness of the platelets were investigated with frequentist and Bayesian techniques. We measured blinking power law constants ranging from 1.4 to 2.3. The brightness levels of blinking quantum particles are important because they are an accessible, if ambiguous, way to study surface photochemistry. Using histograms and a clustering algorithm, we determined that the number of brightness levels in the nanoplatelets is in the range of two to nine, with the lower end of that range appearing most likely and common. We conclude that the thickness and ensemble spectra are insufficient information to understand the evolving coupling between the excited states of platelets. Models of the interplay of excited state localization and reaction kinetics that span 10⁻¹⁰ m to 10⁻⁸ m and 10⁻¹⁰ s to 10² s are needed. © 2023 Optica Publishing Group

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1. INTRODUCTION

Quantum confined systems can exhibit blinking, which is intermittent photoluminescence. Examples include organic molecular dyes [1,2] and inorganic semiconductor quantum dots [3–5]. For semiconductor systems, blinking is interesting because it is correlated with electronic and chemical transitions that are not detectable with current imaging or analytical chemistry technology. Blinking is also important for applications of quantum dots because it reduces quantum yield, which is critical to lighting [6,7] and biomedical imaging [5,8–10].

A core-shell quantum dot consists of a nanoscale semiconductor crystal. The crystal size is chosen to be comparable to or less than the size of an exciton in a bulk crystal. The central crystal is surrounded by a coating of semiconductor material with a larger bandgap. In principle, this shell prevents excited electrons from exiting the central crystal because the shell conduction band is a potential energy barrier for electrons [11,12]. The shell valance band is a potential energy barrier for holes. The shell is further coated in an organic surfactant/ligand [13–15] that also inhibits charge transfer. The goal of the core-shell architecture is to arrange an electron and a hole so they are bound together as an exciton confined in a potential well. The electron and hole should then decay into a useful photon. Blinking indicates the system has entered into some other quantum state that does not decay into a visible photon or return to the ground state [4].

Conventional quantum dots confine the exciton in three dimensions. Nanoplatelets [16] confine the exciton in only one dimension. The mobility of the exciton in the plane of the platelet substantially increases the potential for interesting interfacial interactions. Platelet dynamics are “qualitatively different” [17]. Synthesis techniques allow atomic-level control of the platelet thickness [17–19]. The narrow luminescence line of nanoplatelets is considered a practical advantage for applications exploiting pure colors [7,20]. Thickness-dependent optical spectra [18–20], photoluminescence antibunching [21], and blinking [21–29] are conspicuous quantum features of semiconductor nanoplatelets.

In platelets, transient absorption indicates that defects can be hole traps [30]. In some cases, trap states have associated luminescence [24], including trapping of holes at unpassivated chalcogen sites [18]. The importance of Auger recombination to the transition between states has been disputed [17,25,31,32]. Trion [28,29,32,33] decay can access higher energy electron states [27]. Exciton trapping may be associated with shorter blinks, while longer blinks are related to trion capture [29], presumably in deeper traps. Transitions to nonluminescent states can be thermally activated [22]. These mechanisms potentially contribute to the platelet blinking phenomena we investigate. A few of them are illustrated in Fig. 1. The objective of this work is to provide experimental evidence that can constrain future

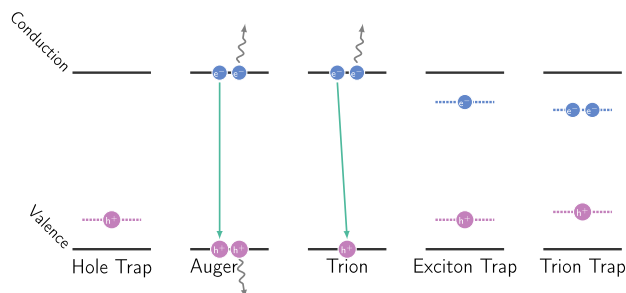


Fig. 1. This energy level diagram illustrates a few mechanisms that may contribute to blinking. Left to right: trapping of a hole, Auger biexciton decay, trion decay, trapping of an exciton, and trapping of a trion.

models of blinking mechanisms in platelets when those models become more quantitative.

2. MATERIALS

Cadmium acetate dihydrate (98%), zinc acetate dihydrate (98%), cadmium nitrate tetrahydrate (98%), zinc nitrate hexahydrate (98%), selenium powder (99.99%), oleic acid (90%), oleylamine (70%), 1-octadecene (90%), sodium myristate (>99%), polymethylmethacrylate, M_w 350 kg mol⁻¹, 1-octanethiol (98.5%), methyl acetate (99.5%) and toluene (chromatography grade) were obtained from Sigma Aldrich. *n*-Hexane (95%) was purchased from Chem-Supply. Sodium oleate (97%) was purchased from TCI chemicals.

3. SYNTHESIS

The synthesis method was adapted from [34] with minor modification. Cadmium myristate was prepared by dropwise addition of cadmium nitrate tetrahydrate solution (1.5 g in 100 mL methanol) into a solution of sodium myristate (2.5 g in 250 mL methanol). The precipitate was filtered, washed thrice with methanol, and dried overnight in a vacuum oven. Cadmium oleate stock solution was prepared by reacting cadmium acetate dihydrate (6.7 g) and oleic acid (17 mL) in 100 mL of 1-octadecene and heating under vacuum at 120°C for 1 h. Zinc oleate solution was prepared by substituting an equimolar amount of zinc acetate dihydrate for the cadmium salt. Stock solutions were stored in a glovebox and heated prior to use.

To make the nanoplatelets, a mixture of cadmium myristate (340 mg), selenium powder (24 mg), and 1-octadecene (30 mL) was stirred under vacuum at room temperature for 19 min. The reaction vessel was filled with nitrogen and heated to 240°C. At 200°C, cadmium acetate dihydrate (128 mg) was quickly added; 9 min after reaching 240°C, the reaction was removed from the heat and rapidly cooled. Oleic acid (2 mL) was added to the mixture at 160°C, and hexane (5 mL) was added at room temperature. The reaction mixture was centrifuged at 9 kRCF for 10 min and redispersed in 20 mL of hexane. After 1 h, it was centrifuged at 6.5 kRCF for 7 min to give 4.5 monolayer CdSe nanoplatelets in the supernatant. It was found that a longer waiting time before the second centrifugation led to better separation of 4.5 monolayer and 3.5 monolayer CdSe nanoplatelets.

The 4.5 monolayer CdSe nanoplatelets were kept as-is in the supernatant and precipitated once more with acetone before application of the CdZnS shell.

Zn oleate (534 μL, 0.25 M), cadmium oleate (266 μL, 0.25 M), 3 mL of 4.5 layer CdSe nanoplatelets in hexane (optical density 20 at first exciton absorption peak), 5 mL of 1-octadecene, and 200 μL of oleic acid were degassed at room temperature for 30 min and at 80°C for 20 min. The vessel was filled with nitrogen, and 1 mL of oleylamine was added to the reaction. The mixture was heated to 300°C over 15 to 20 min. A solution consisting of 41.5 μL of octanethiol, 1 mL of oleic acid, and 3.5 mL of 1-octadecene was injected at 2.25 mL h⁻¹, starting at 170°C. The reaction was kept at 300°C for another 40 min after the injection finished and cooled rapidly to room temperature. At room temperature, 2.5 mL of hexane was added, and the reaction mixture was centrifuged at 9 kRCF for 6 min. The nanoplatelets were washed (2.5 mL hexane, 2.5 mL of methyl acetate at 6 kRCF, 10 min) and finally redispersed in 2 mL of hexane and purified by centrifuging at 10 kRCF for 1 min. The supernatant was passed through a 0.2 μm syringe filter.

For blinking measurements, a glass coverslip was rinsed in chloroform, ultrasonically cleaned in acetone, rinsed with deionized water, ultrasonically cleaned in 10 wt% NaOH aqueous solution, rinsed with deionized water, ultrasonically cleaned in deionized water, dried with flowing gas, and UV ozone cleaned.

The solution of nanoplatelets with shells (25 μL) was diluted in 500 μL of polymethylmethacrylate (1 wt%), oleylamine (1 μM), and toluene; 50 μL of diluted nanoplatelet solution was promptly spincoated at 5000 rotations per minute for 30 s onto a coverslip.

4. CHARACTERIZATION

Transmission electron micrographs were recorded using a Tecnai F20 at 200 kV.

Platelets were dispersed in hexane in a 1 cm cuvette such that the lowest energy absorption peak had an optical density of 0.02. The luminescence quantum yield was measured with an integrating sphere and a fluorimeter (Horiba Jobin-Yvon Fluorolog-3, F-3029) using an excitation wavelength of 400 nm.

An absorption spectrum was recorded using an Agilent Cary 60 spectrophotometer. The fluorescence spectrum was recorded using an Agilent Cary Eclipse fluorimeter with 400 nm excitation.

5. BLINKING OPTICS

A 532 nm laser (Changchun New Industries Optoelectronics Technology Co., Ltd., MGL-III-532-300mW) was passed through a bandpass dielectric filter, expanded with a telescope, and reflected off a 560 nm dichroic filter. The laser light was focused onto the sample by a 100X 1.49 numerical aperture objective. The laser power transmitted through the objective was 0.44 mW. The image of the luminescence collected by the objective and transmitted through the dichroic filter was

recorded with a camera (Andor iXon Ultra DU-897U-C50-#BV) cooled to -80°C . In each video, 16,000 frames were recorded at 24 frames per second [35] using frame transfer. The sample was exposed to air at room temperature.

6. DATA REDUCTION

To reduce spatial variation in the background, a 5 pixel short pass Fourier transform filter was applied to each frame in the video. Particles that blinked were identified. Rectangular regions with 2 to 4 pixels on a side containing a particle were selected, and the mean brightness of the region as a function of time was extracted. The data were further filtered to remove particles that did not have distinct brightness levels, many sudden changes in brightness, or substantial signal-to-noise ratio. As a consequence, the results are not relevant to any particles undergoing gradual changes that might exist. Nanoplatelet brightness is presented as a signal-to-background ratio, where background was the average brightness of the corresponding entire Fourier transform filtered video frame.

For each particle, a threshold was selected [35] to distinguish the frames where the nanoplatelet was in a dark state from the frames where it was in a bright state. The number of consecutive detections of a dark or bright state was computed and converted to a logarithmically binned histogram. The histogram bins containing data were modeled with a Poisson-weighted power law regression [36–39]. The unweighted mean of the power law exponents across particles was computed.

For each time point and nanoplatelet, the posterior probability of a brightness change was computed with bcp [40] using 5000 iterations after burnin. The time series was partitioned at brightness changes using energy divisive [41] with a 0.05 significance level, $\alpha = 1$, and a minimum partition length of two measurements. The distance d between two partitions U and V with $|U|$ and $|V|$ elements, respectively, was computed using

$$d(U, V) = \frac{1}{|U||V|} \sum_{u_i \in U, v_j \in V} |u_i - v_j|. \quad (1)$$

The partitions were clustered using the Density-Based Spatial Clustering of Applications with Noise (DBSCAN) algorithm [42–44] with a minimum cluster size of two. The distance d was used as the clustering metric. A brute force search was used to adjust the value of the DBSCAN parameter ϵ to meet two criteria. Primarily, the number of clusters was maximized. Secondly, the number of partitions included in any cluster was minimized.

7. SIMULATED BLINKING

To illustrate the way the distance Eq. (1) identifies brightness levels of nanoplatelets, a theoretical particle was simulated using the algorithm of [45]. The parameters chosen to generate an easily interpretable data set were: time bin size of 10^8 units, time between laser pulses of 10^{-7} units, power law constants of 1.5 for all transitions, noise rate of 10^2 per time unit, luminescence decay rates of 10^9 per time unit for all brightness levels, and brightness levels of 10^2 , 10^3 , and 2×10^3 per unit.

This produces a blinking behavior with three highly separated brightness levels. This algorithm is intended to simulate pulsed experiments. This paper reports continuous wave experiments. This distinction is not important to the use of the algorithm to illustrate the interpretation of Eq. (1).

8. LIMITATIONS

The analysis has several intrinsic limitations. Nanoplatelets that did not emit any light during the experiment were not detected. Identification of particles with distinct brightness levels [45], sudden changes in brightness [46,47], and adequate signal-to-noise ratio had an element of subjectivity. The choice of threshold [35] for distinguishing dark and bright states is not based on a rigorous model because the probability of transitions between states within a time bin does not have a known upper bound. The brightness and power law associated with each state is uncertain. Both parameters impact the optimal threshold. Change point identification algorithms may be unreliable if their assumptions are violated. In particular, bcp may counterintuitively return a posterior probability of zero at a sudden change if that event is preceded by a small gradual change. Such gradual changes can, as an example, be induced by fluctuations in the instrument temperature. Since the underlying chemical and electronic states associated with blinking are unknown, it is not possible to determine which definition of distance and clustering algorithm best reflect those states.

9. PLATELET PROPERTIES

Figure 2 is a transmission electron micrograph of platelets viewed nearly perpendicular to the large face. The two long axes of the platelets are of the order of 20 nm long, which is larger than the exciton Bohr radius in CdSe. It has been theoretically [48] and experimentally [21] demonstrated that, even at scales smaller than 20 nm, the area of the large face is not related to the spectral properties. This image suggests that the excitons are confined in only one dimension. The shape of the platelets is not a complete Wulff construction, but each platelet has at least four facets. The facets suggest that the platelet geometry is a low energy configuration, but the surface energy has not been fully minimized. Previous x-ray diffraction experiments show nanoplatelets are at least partially crystalline [34,49].

Figure 3 shows the steady state spectra of the platelets. The narrow luminescence and defined absorption peaks reproduce

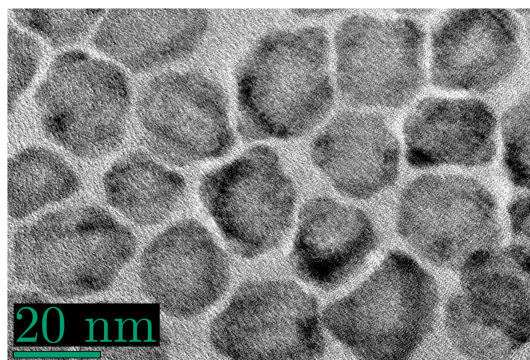


Fig. 2. Transmission electron micrograph of platelets.

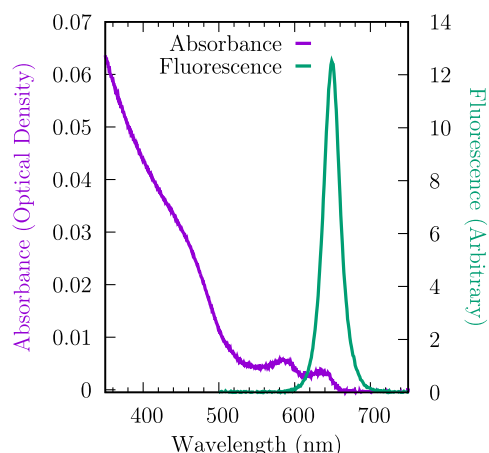


Fig. 3. Absorbance and photoluminescence spectra of platelets. Well-defined peaks demonstrate the platelets have monodisperse thickness.

the well-known features of relatively monodisperse platelets. The spectra bear a strong resemblance to the green curve in Fig. 4 of [34]. The peaks reported here are shifted a few nanometers towards higher energy. The shift may be caused by a slight increase in quantum confinement, a slightly higher zinc-to-cadmium ratio, or a slightly thinner shell.

Figure 4 is a sample from one raw video recording of platelets. The left portion of the graphic shows part of the first frame of the video. Many light-emitting particles are observed. The rest of the graphic is the brightness of a single column of pixels as a function of time. Some of the particles exhibit sudden changes in brightness. In this study, we have disregarded particles that do not have sudden brightness changes. These particles might be multiple nanoplatelets, nonblinking nanoplatelets, or blinking platelets that happened to stay in one state for the duration of the experiment. As a consequence, for those researchers seeking optimized quantum yields, these results are relevant only to the particles that need improvement.

10. BLINKING STATISTICS

Figure 5(a) is the brightness of a single platelet recorded as a function of time. This example exhibits sudden changes in brightness with at least two brightness levels. There is an off state with relative brightness near one, and an on state with relative

brightness near five. Figure 5(c) is a histogram showing the number of video frames with each relative brightness. There is a sharp peak for the off state and broader peak for the on state. The histograms are similar to Refs. [21,23]. Under the assumptions of the Poisson distribution, the greater the brightness, the broader a peak in the histogram should be. Between the two peaks, there are additional measurements that could be explained by the platelet changing states within the time the measurement was taken. The vertical line in Fig. 5(c) illustrates how the two brightness states were divided to categorize on and off states. Figure 5(a) is color coded to indicate the categorization.

Figure 5(d) is a log-log histogram of the density of blink durations. The error bars in the histogram are Poisson standard errors. As previously reported in a variety of different quantum dot types, the blink durations are accurately modeled by a power law. The power law constants are 1.6(1) for on and 1.56(5) for off. A summary of the measured power law exponents is shown in Fig. 6. The error bars for the power law constants are the standard error of the slope of a Poisson-weighted linear regression performed on log-transformed data. The details of the data are included in Supplement 1. The nanoplatelets are heterogeneous.

We identified previous measurements of platelet blink durations for a combined total of five platelets synthesized by three methods in Ref. [21] and Ref. [22]. The power law exponents previously reported are similar to our measurements. However, the previous reports show substantial discrepancies of around a factor of five between the power law models and data. Those discrepancies are mostly present for longer blink durations. Based on our data set, which includes more nanoplatelets measured to longer blink durations and complete error estimates, we conclude that those discrepancies are due to random chance. To detect a difference d [50] between the power law exponents associated with two different synthesis conditions, we estimate that $0.6/d^2$ particles of each type need to be measured.

Categorization of brightness measurements into on and off groups is useful for determining blink durations. However, it does not account for the fact that the number of categories and their brightness boundaries cannot be predicted. Therefore, we use two statistical methods that investigate brightness change points [46,47,51] without assuming or determining the number of brightness levels.

The bcp method [40], being Bayesian, answers the question: given sequential data, what is the probability a particular data

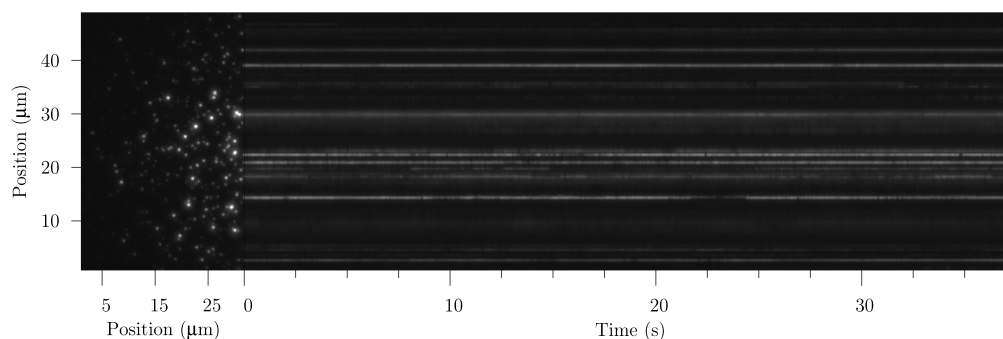


Fig. 4. Sample raw platelet photoluminescence video data. The left portion is an image. The right portion is the right edge of the image as a function of time. The platelet particles show a range of behaviors as a function of time.

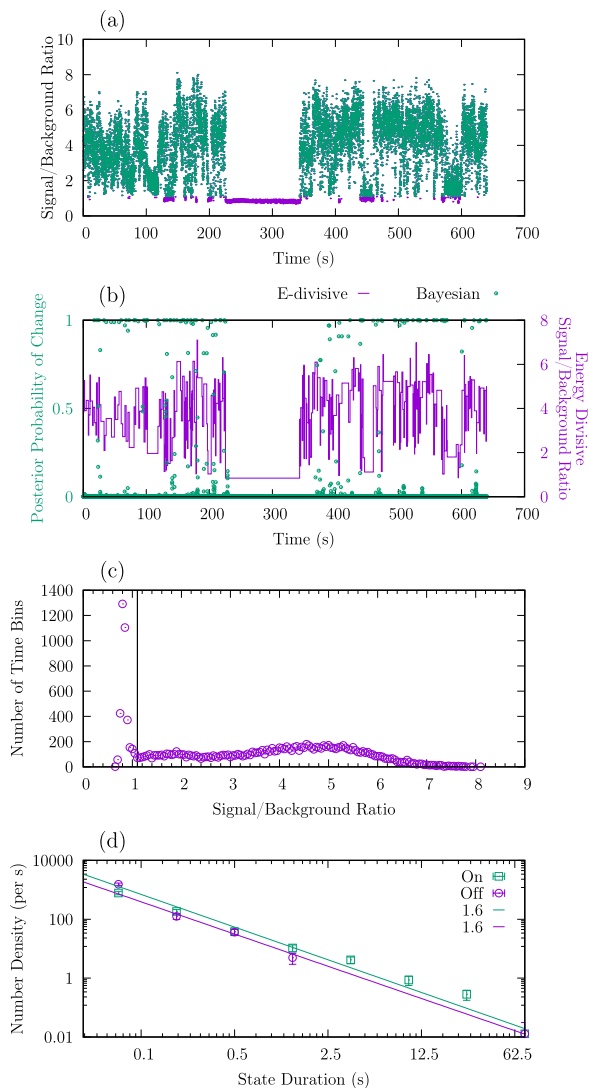


Fig. 5. (a) Single nanoplasmic photoluminescence as a function of time. Color coding indicates the assignment of data points to “off” and “on” states. (b) The energy divisive algorithm (purple lines) accurately describes the photoluminescence trajectory (a) using sudden transitions. The bcp algorithm (green dots) computes the posterior probability of a brightness change. (c) Histogram of the number of time bins (video frames) versus platelet brightness. (d) Histogram of on and off blink durations with a power law model. The legend displays the measured power law exponent.

point is at a change point? The energy divisive method [41] answers the question: assuming no change point has occurred, is the probability of these data less than 0.05?

The bcp method has several advantages. It answers an intuitive question. It provides relatively few opportunities for user bias to be introduced. It effectively captures uncertainty when it returns a probability greater than zero and less than one. The disadvantages of the Bayesian approach include the imperfect separation of the peaks in the brightness histogram in Fig. 5(c), and imperfect instrument stability implies that there is a small probability of a gradual change, but bcp cannot detect gradual changes. If the probability of a change point is near 0.5, no interpretation that is useful to us is available. The

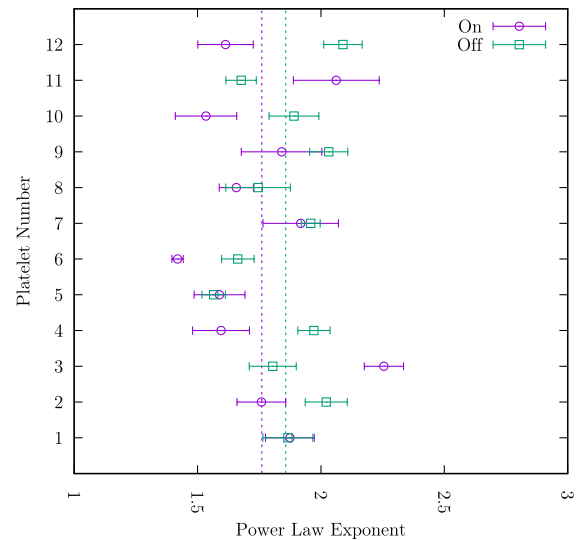


Fig. 6. Measured power law exponents for on and off blinks of nanoplasmic platelets. The power law exponents of the different platelets are not expected to be the same. Likewise, the on and off power law exponents of a single nanoplasmic platelet are expected to differ. The dashed vertical lines indicate the unweighted mean of exponents across nanoplasmic platelets.

posterior probability is zero 87% of the time, indicating that most measurements are not change points. The mean posterior probability is 0.008. Example posterior probabilities are shown as points in Fig. 5(b).

The energy divisive method has the advantage that it returns a specific yes/no answer. This permits calculation of the duration of a brightness level and summary statistics of the brightness. The energy divisive method answers an unintuitive question, which is a disadvantage. It relies on an arbitrary probability threshold [51], for which we use the traditional value (0.05). In a large data set, this threshold will inevitably identify excess change points. Energy divisive is unable to return partitions with a length of less than two measurements, while our expectation is that brightness changes occur much more quickly than that. It assumes that the α th moment exists, but since we do not know what distribution we are sampling, this is not guaranteed to be satisfied. We selected $\alpha = 1$, which is the mean; 3429 significant change points were identified, excluding the first and last data points. Example energy divisive partitions are shown as lines in Fig. 5(b).

To compare the two methods, the cross-correlation of the results was computed. Figure 7 shows that the bcp and energy divisive methods have a highly significant cross-correlation. The cross-correlation is averaged over 12 platelets. The standard error depicted in the error bars is based on the small differences between platelets. The cross-correlation provides evidence that our calculations based on the energy-divisive method reflect probable change points.

11. BRIGHTNESS LEVELS

Based on brightness histograms, we believe the semiconductor nanoplasmic platelets we are analyzing have at least two brightness levels [51]. We wished to identify an upper bound on the number of brightness levels using a clustering algorithm. To illustrate the

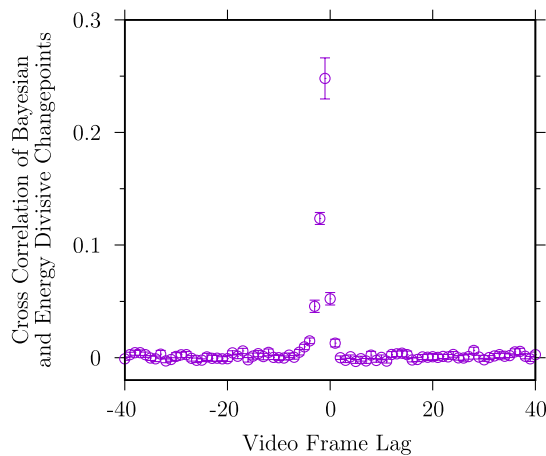


Fig. 7. Cross correlation of the Bayesian and energy divisive approaches to change points. The two calculations have a highly significant cross-correlation.

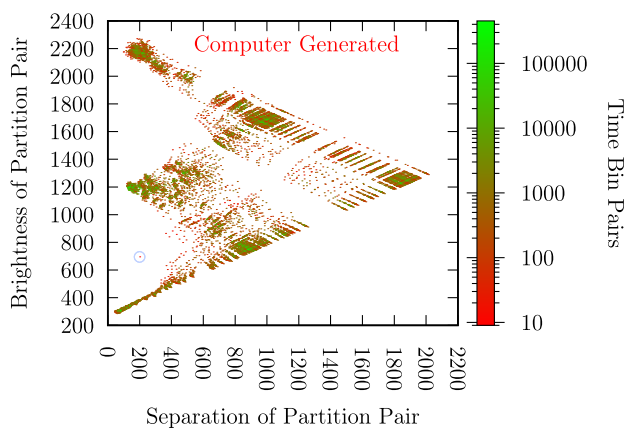


Fig. 8. Blink partition pairs obtained from a simulation. In the simulation, there are three brightness levels that are well separated. The brightness trajectory was split into partitions, where each partition is expected to be a period of constant brightness. When the separation of partition pairs is low [Eq. (1)], three brightness clusters are easily visualized. For each partition pair, the length of the two partitions was multiplied together to compute the number of time bin pairs. The number of time bin pairs indicates the sample size. Green color indicates that a partition includes greater exploration of the brightness population.

method, we started with simulated data with an exaggerated signal-to-noise ratio. The number of brightness levels in the simulation was chosen to be three. Brightness change points determined by the energy divisive method were used to split the simulation into partitions. Figure 8 shows all the pairs of partitions, along with the brightness of the pair. In this case, brightness is defined as the mean of the two partition means. Separation was defined in Eq. (1). Partition pairs that include more time bin pairs have a higher statistical validity.

In Fig. 8, three obvious clusters of partition pairs are apparent. Clusters appear when the separation of partition pairs is small. The three clusters are located at brightness 300, 1200, and 2200. Poissonian brightness noise would imply that brighter clusters exhibit higher separation. This is observed in practice.

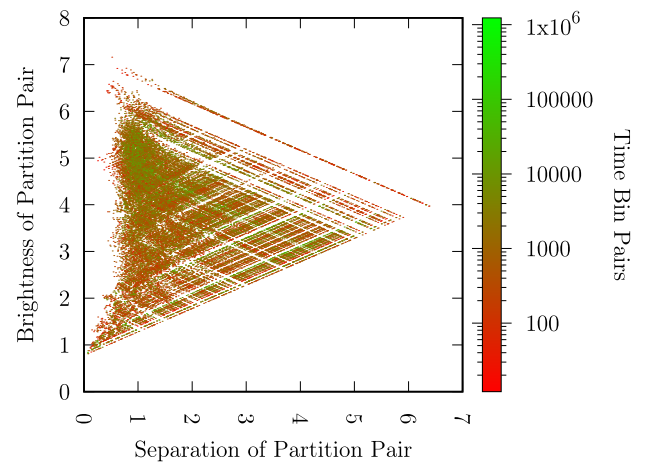


Fig. 9. Blink partition pairs obtained experimentally from the platelet data in Fig. 5(a). The brightness clusters are not as clearly defined as in the simulation. There is a cluster at very low separation and relative brightness one, exactly where an off state is expected. There is a second, looser cluster at low separation and brightness of approximately five, in agreement with Fig. 5(a). Green color indicates that a partition includes greater exploration of the brightness population.

Semiconductor nanoplatelets can change brightness during a measurement. They can also change brightness multiple times in a single measurement for several consecutive measurements. As a result, small spurious clusters are expected even if the signal-to-noise ratio is excellent, the partitioning is accurate, and the clustering is precise. Indeed, the clustering algorithm DBSCAN found four clusters in the simulated data. DBSCAN is a widely used clustering algorithm that provides relatively few opportunities for experimenter bias to be introduced. Three clusters were in the expected location. The fourth is circled in Fig. 8. It consists of only two short partitions. This is why clustering only suggests an upper bound on the number of brightness levels present in the semiconductor nanoplatelets. As with all outliers, the number of spurious clusters increases with sample size.

Figure 9 was created with the same procedure, but using experimental data. The most noticeable difference is that the real data have more noise than fake data. Two clusters are visually apparent. The first is at brightness one and low separation. This cluster is consistent with partitions in which the platelets emit no light (brightness one). The second cluster is near brightness five. An interpretation of Fig. 9 is that partitions with a long time scale frequently occur around brightness five. This results in a large number of time bin pairs around five and increases the denominator of the separation distance d .

Figure 10 shows the number of clusters found by DBSCAN as a function of the clustering parameter ϵ for a platelet. Smaller values of ϵ cluster fewer partitions. Larger values of ϵ broaden the clusters to include more partitions. For this platelet, DBSCAN gives an upper bound of six clusters of partitions. Among the strengths of the DBSCAN algorithm is its ability to leave outliers unclustered. Unless all the clustered partitions are forced into a single cluster ($\epsilon > 0.6$), most of the partitions are unclustered. This is unsurprising because the signal-to-noise ratio is limited and platelets frequently change brightness during a video frame. Figure 11 is a violin plot of the clusters obtained with DBSCAN with ϵ chosen primarily so that the number of

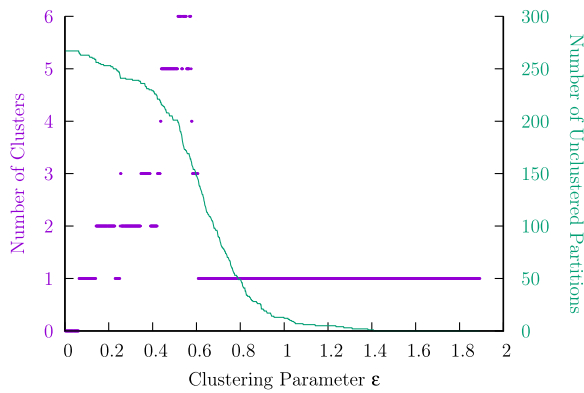


Fig. 10. Clustering results obtained from the nanoplatolet data in Fig. 5(a). DBSCAN clustering has only one parameter, ϵ . Small ϵ always results in unclustered data. Large ϵ places all data in a single cluster. Seeking an upper bound on the number of clusters in the data, we choose ϵ to maximize the number of clusters.

clusters is the maximum of six and secondarily so that as few partitions are clustered as possible. Clusters one and three match the maxima of the histogram in Fig. 5(c), as expected. Clusters consisting of partitions with identical brightnesses cannot be visualized.

Repetition of the clustering analysis is included in Supplement 1. Figure 12(a) is an overview of the clusters produced from measurements of 12 nanoplatolets. Many partitions are unclustered. Of those partitions that are clustered, low brightness partitions are the most common. None of the data sets produced more than nine clusters. This is a small number of clusters relative to the 200 to 338 partitions per particle. Every data set has at least three clusters. Most of the clusters are very small; the second largest cluster contains eight partitions on average, but the third largest cluster contains only three partitions on average. For the platelet that

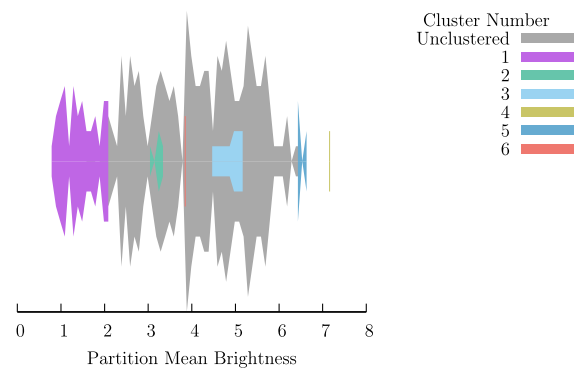


Fig. 11. Violin plot of the DBSCAN clusters obtained from the nanoplatolet data in Fig. 5(a) with ϵ chosen at the peak of Fig. 10. There is an off state cluster near relative brightness one, as expected. There is an on state cluster near brightness five, consistent with 5. Most of the partitions, including many small ones, are unclustered. There are four small clusters. Clusters four and six have so few members they cannot be visualized.

produced the most clusters, the median cluster size is just four partitions. Comparison of Figs. 12(a) and 12(b) shows that, within the limitation that the number of clusters is maximized, the parameter ϵ does not alter the results much.

12. CONCLUSION

Semiconductor nanoplatolets achieve both quantum confinement and a large surface-to-volume ratio. As a result, they are interesting for exploring interactions between excitons and interfaces. Semiconductor nanoplatolets can change brightness suddenly, indicative of a quantum transition. The nanoplatolets have several recurring brightness levels. We interpret these brightness levels as ensembles of excited quantum states. In

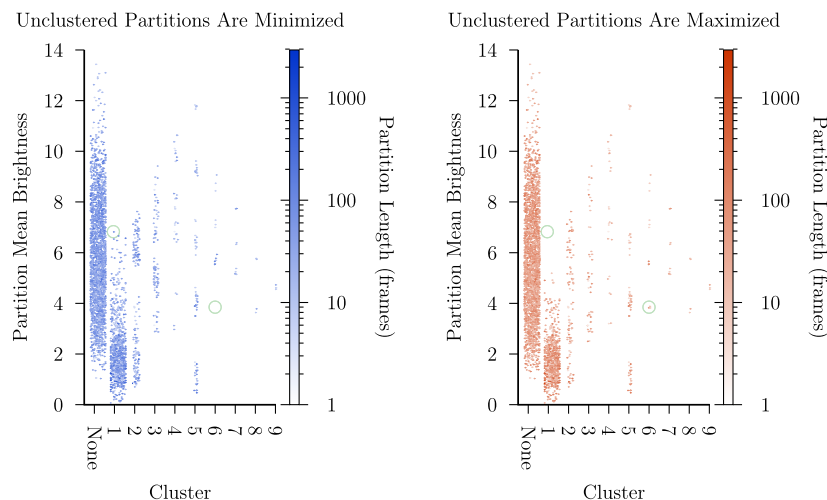


Fig. 12. DBSCAN clustering results aggregated across 12 nanoplatolets. There are always fewer than 10 clusters. A large portion of the partitions are not clustered. The clusters are ordered by the number of elements in the cluster. There are many partitions in off state clusters (cluster 1: mean relative brightness near 1). Clusters containing few data points may be formed by chance. We highlight that the mean brightness is not used to determine the cluster because it does not fully utilize the underlying information. Darker data points indicate a longer partition, which implies greater exploration of the brightness population. Within the restriction that the number of partitions was maximized, the calculation was performed with unclustered partitions minimized (left) and maximized (right). The two calculations are similar, with selected differences highlighted by green circles. To enhance visibility, data points are slightly offset in the horizontal direction.

this study, we investigated 3417 partitions exemplifying those brightness levels.

Based on brightness histograms, we conclude that the nanoplatelets in our data set have at least two brightness levels. Brightness levels were further examined with a clustering algorithm that, unlike traditional manual brightness classification, was weighted to prioritize consistency and sample size. From the results of the clustering analysis, we conclude that these platelets have less than 10 brightness levels. Overall, two to three brightness levels seem to be the most likely explanation of the data. The clustering analysis consistently produces a cluster of brightness levels near the background level.

Under the assumption that there are two brightness levels, the blink durations were consistent with a power law distribution across the time domain of the data. Previously observed inconsistency between the power law model and data is attributable to chance. Differences between power law exponents across identically prepared platelets are greater than would be expected from random error.

To discover a structural cause of blinking, it is desirable to find relationships between synthesis conditions and power law exponents. We estimate [50] that it is necessary to measure 100 platelets for each of two synthesis conditions to reliably discover such a relationship. Simply measuring a few platelets for longer is not sufficient. This presents a concrete technical barrier to understanding blinking, which is better attacked with multiplex (widefield) instruments instead of monoplex (confocal) instruments.

Extrapolation of the power law distribution to short blink durations is not physical. This leaves us with an interesting ambiguity regarding the statistical distribution being sampled by the experiment. We have attacked that ambiguity using both Bayesian and frequentist statistical techniques. The two approaches yield highly correlated results. Bayes' theorem is the only way to determine the probability that a brightness change has occurred.

Finally, ensemble optical spectra with narrow peaks indicate that the nanoplatelets are highly uniform. Single particle brightness trajectories, however, show that nanoplatelets are highly variable. We attribute this variability to changes in chemical and electronic states at crystal interfaces. This highlights the importance of these interfaces to the photoluminescent properties of quantum wells, even for nanoplatelets that ostensibly have very highly passivated surfaces.

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Data availability. The raw video data are available from Ref. [52]. Data analysis code is available from Ref. [53].

Supplemental document. See Supplement 1 for supporting content.

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