

Monitoring Surface Charge Movement in Single Elongated Semiconductor Nanocrystals

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We demonstrate a universal correlation between the spectral linewidth and position of the excitonic transition in the spectral jitter observed from single elongated colloidal quantum dots. Breaking the symmetry of electron and hole confinement as well as of the spatial directions for surface charge diffusion enables us to microscopically track meandering surface charges, providing a novel probe of the particle's nanoenvironment. Spectral diffusion exhibits only a weak temperature dependence, which allows us to uncover the single particle homogeneous linewidth of 50 meV at room temperature.

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Strong spatial confinement of the electronic density of states in semiconductor nanostructures leads to a wide range of novel physical phenomena. Three-dimensional engineering of the extent of the electronic wave function gives rise to full quantization of the electronic transitions, which is readily achieved in colloidal or epitaxial quantum dot (QD) structures. Fluorescence microscopy on single particles allows a direct differentiation between homogeneous and inhomogeneous electronic properties, and has revealed atomlike transitions in epitaxial QDs [1]. Colloidal QDs, which are chemically synthesized nanocrystals (NCs) stabilized by organic ligands [2], exhibit particularly strong photoinduced spectral fluctuations in terms of both the intensity and the spectral position [3]. This has previously been attributed to a redistribution of charges within and around the NC [3–7]. A slight spectral jitter has also been observed in some epitaxial QDs [8–13]; however, as these are typically surface protrusions and are generally coupled to a large continuum of states in the bulk, fluorescence intermittency due to Auger-type processes [6,14,15] generally does not pose a major problem. Spectral diffusion has thus far been seen as a major hurdle for developing QD based quantum computing applications [10,16], as phase coherence is observable only in the time domain [17] due to the fact that single dot lines tend to be much broader than what would be expected from dephasing times measured using four-wave mixing or hole burning techniques [10,16,18]. We demonstrate here for the first time that physical information can be derived from the QD spectral linewidth through a unique correlation between the spectral position and the linewidth. Although such a correlation should not be observable for symmetrical spherical particles [5], tuning the shape of the NC from spherical to rodlike [19] allows us to define a direction of diffusion for surface charges. The location of surface charges on the elongated particle defines the electron-hole wave function overlap through the quantum confined Stark effect (QCSE) [20] and leads to a shift of the fluorescence peak position. Spatial oscillations of surface charges

give rise to spectral line broadening in strong dependence of the spatial position of charges on the NC surface, so that the linewidth provides insight into the nanoscale electrostatic environment of the NC. As this correlation, which is sensitive to photoinduced charge transfer at the single electron level [21], is also readily observed at room temperature (RT), spectral linewidth studies may become of interest for biological labeling applications of NCs employing electron rather than energy transfer.

We recently presented a novel class of colloidal NCs, which consist of a spherical CdSe core covered by an elongated CdS shell grown epitaxially on the $\{00\bar{1}\}$ facet of the hexagonal CdSe phase [19]. In contrast to conventional CdSe nanorod particles [22], our NC heterostructures exhibit substantial differences in the level of confinement of electrons and holes [19]. Whereas electrons may penetrate the elongated CdS shell, holes are confined to the CdSe core. The inset of Fig. 1 shows a typical transmission electron microscope (TEM) image of elongated NCs with a core diameter of 4 nm and an aspect ratio of 1:4. In low magnification TEM images we generally observe a contrast change towards one end of the nanorod, suggesting that shell growth occurs unidirectionally from one single facet of the CdSe core [19]. We performed photoluminescence (PL) measurements on single elongated NCs dispersed in a polystyrene matrix. The samples were mounted in a cold finger helium cryostat in an epifluorescence microscope. The PL was excited using the 457.9 nm line of an argon ion laser at typical intensities of 25 W cm^{-2} , collected with a long-distance microscope objective (NA: 0.55), dispersed in a 0.3 m monochromator with a spectral resolution of 0.1 nm and detected in time windows of 1 s using a cooled charge-coupled device camera.

To demonstrate spectral diffusion in the elongated NCs we compare PL spectra measured on the same single particle at different times. Figure 1 shows two spectra measured at 5 K in 1 s windows 885 s apart. The spectra exhibit a strong transition around 2.05 eV, followed by a phonon replica set off by 27 meV to the red. This phonon

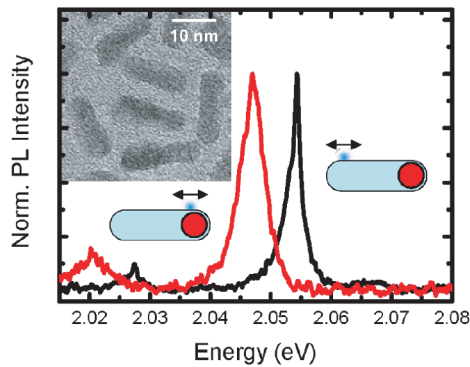


FIG. 1 (color online). Two PL spectra measured from a single elongated CdSe/CdS NC at 5 K at different times. The presence of surface charge results in spectral shifts through the QCSE, and spatial charge oscillations lead to line broadening. The sketch illustrates the influence of surface charge: depending on the proximity to the emitting CdSe core, which determines the peak position, the same spatial amplitude of oscillations (arrows) results in different spectral linewidths. The inset shows a TEM image of elongated NCs.

energy corresponds to that of bulk CdSe (cf. bulk CdS phonon at 38 meV), demonstrating that recombination occurs within the core and implying strong confinement of the hole wave function. The redshifted spectrum of the two, which peaks at 2.046 eV, is twice as broad as the blueshifted spectrum at 2.055 eV. Such spectral drifts and jumps of the emission maximum of single QDs during photoexcitation have previously been attributed to the generation of surface charges [3–6,23], whose electric field gives rise to a QCSE-induced shift of the exciton resonance. As these reorganizations of surface charges occur on all time scales, the linewidth of the single particle PL is believed to be limited by rapid oscillations of surface charges [5] rather than being a measure of the dephasing time of the excited state [16]. This results in time and intensity dependent line broadening on the single particle level [4], and explains why the narrowest single particle spectra reported thus far for CdSe NCs are over an order of magnitude broader than linewidths measured by spectral hole burning in the ensemble [18]. It was previously proposed that the spectral linewidth of a single particle should not correlate with the spectral position, as the linewidth is limited by small *fluctuations* in the local field of the particle embedded in the matrix rather than being controlled by the *overall* local field [5]. This appears to be true for spherical NCs [5]. However, our elongated NCs allow symmetry breaking in one direction and therefore enable significant changes in both the *fluctuation* in and the *overall strength* of the local field experienced by the CdSe core. It is reasonable to assume a constant spatial noise on the surface charge density, which can also be thought of in terms of charge oscillations [4,5]. Surface charges most likely arise due to trapping of electrons in shallow traps on the surface of the

CdS shell [24], which should exhibit a spatially invariant energetic density of states. In this picture, surface charge movement can be thought of in terms of dispersive transport within an energetic distribution of trapping sites, leading to a direct increase in migration distance with time, where the driving force is photoinduced electron transfer between the shallow trapping sites. Incomplete saturation of dangling bonds by ligands, which may be particularly relevant under high vacuum conditions [25], can pose a direct source for surface charge accumulation. Considering constant spatial noise in the charge density, the overall effect on the linewidth must depend on the distance of the oscillating charges to the core. In a symmetrical spherical particle this distance will always remain the same, so that a spatial relocation of charges has no effect on the line shape. In our elongated NCs, however, rapid spatial fluctuations in the charge density will have a larger effect on the linewidth, the closer the charges are situated to the core. This process is sketched in Fig. 1. The redshift of the red (grey) curve in Fig. 1 thus originates from surface charges in close proximity to the core, giving rise to a large QCSE, whereas the linewidth is controlled by spatial charge oscillations. Redistribution of the charge density to the opposite end of the NC reduces the shift and also the effect that spatial oscillations of the charge have on the linewidth.

We observe a continuous correlation between the linewidth and the peak position of single particle PL spectra. Figure 2(a) shows the spectral jitter with time of a single particle at 5 K. The intensity is virtually constant over long periods and exhibits only brief phases of intermittency. By fitting a Lorentzian to each spectrum, the peak position and full width at half maximum (FWHM) are extracted in Fig. 2(b). An increase in peak energy appears to result in a decrease in linewidth, with no noticeable dependence of the PL intensity. The effect is fully reversible during the time trace, demonstrating that the spectral shifts are random in nature and are not due to, e.g.,

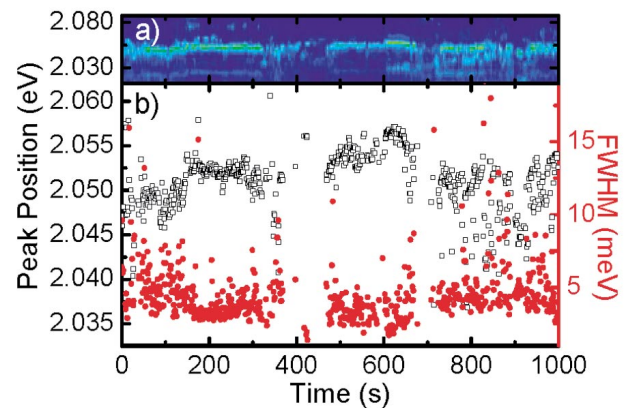


FIG. 2 (color online). (a) Spectral jitter of the single NC emission at 5 K. (b) Dependence of PL peak position (squares) and linewidth (circles) on time.

photodegradation. We plot the linewidth in dependence of peak energy in Fig. 3. The open squares indicate the raw data taken directly from Fig. 2. A clear correlation is visible, although the linewidths scatter strongly for redshifted peak energies, resulting in a conical shape of the data. This increased scatter results from the fact that the effective electric field is reciprocal to the charge motion, so that the measured QCSE shift is nonlinear in charge position. This increases the uncertainty on the PL linewidth for charge densities close to the core due to charge redistribution during the measurement. The increased scatter is in agreement with our suggestion that the spatial noise on the charge distribution be independent of position, and implies that the spatial noise cannot decrease towards the core. To minimize the effect of charge motion during the measurement, we consider only spectral shifts which occur on time scales longer than 1 s, and discard data points for which the drift in peak position between the preceding and the subsequent spectra is larger than 2 meV. The remaining 70% of the data points are shown by the solid squares in Fig. 3, and exhibit much less scatter on the FWHM axis. Averaging the data in bins of 1 meV gives the large squares, which display an excellent correlation between the width and the energetic position. We studied traces of over 50 particles, of which half exhibited a clear correlation between peak position and linewidth. A quarter exhibited data of comparable quality to Fig. 3, with a pronounced conical scatter to the red.

The inset of Fig. 3 gives a histogram of the energetic magnitude of the spectral shift $E_{\max}^i - E_{\max}^{i-1}$ between adjacent spectra with index number i , which exhibits an almost Gaussian distribution [6] and provides a measure of the random walk of charges inducing the spectral meander. We found that the width w of the distribution

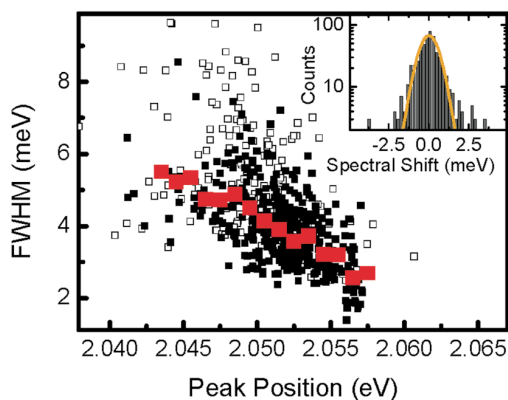


FIG. 3 (color online). Correlation between the linewidth and the PL peak position for a single NC showing the raw data from Fig. 2 (open squares). Selection of spectra that do not shift over 3 s results in the solid small squares. The large squares show the statistical average of the single particle correlation. The inset displays the histogram of spectral shifts from one spectrum to the next, with a Gaussian fit.

of spectral shifts between subsequent measurements during an “on” period increased approximately linearly with laser intensity I according to $w \cong 0.83 \text{ meV} + 0.008 \text{ meV cm}^2/W \times I$. In contrast, much larger spectral jumps occur before and after an “off” period, which were found to follow an almost Gaussian distribution [6] of width $w \cong 1.9 \text{ meV} + 0.036 \text{ meV cm}^2/W \times I$. Whereas the spectral jumps succeeding a PL intermittency have been proposed to arise from a charging of the NC [6], resulting in the NC entering a nonemissive state in which efficient Auger recombination competes with spontaneous emission [4,14,15], the drifts during the emission occur through reorientation of NC surface charges [6] and interactions with the environment. Both of these processes depend on excitation density, but only weakly on temperature. We determined an average width of the diffusion histograms as in Fig. 3 of 1 meV at both 5 and 50 K. Strong spectral diffusion was also observed at RT, but even there the average width of the universal distributions describing spectral diffusion was found to be 7 meV, much less than the overall linewidth. The fact that the spectral drift is invariant over an order of magnitude rise in temperature provides direct evidence that spectral diffusion reports on photoinduced charge transfer alone. As a consequence of the jitter, the PL width increases with integration time and intensity [4]. Although this effect is convoluted with the statistical treatment of the spectral jitter, the line broadening alone does not convey the dynamics of the photoinduced random process in the way the Gaussian histograms do.

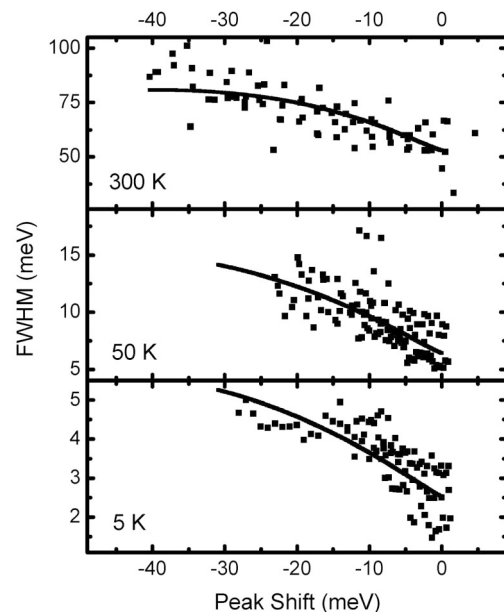


FIG. 4. Temperature dependence of linewidth-peak shift correlations. The data of five single NCs are shown for each temperature. The solid line represents the QCSE calculated for a single charge moving along the long axis of the NC.

Temperature should not perturb the surface charge induced QCSE in these elongated NCs. Figure 4 shows a plot of linewidth-peak position correlations for three different temperatures with five particles each, comprising approximately 7000 spectra. The peak shift was determined by subtracting the peak position of the bluest spectrum recorded for the particle. The spectral range of 30 ± 10 meV over which peak shifts occur is virtually independent of temperature, although the average linewidth of the spectrum increases by almost 2 orders of magnitude with increasing temperature. For all temperatures the spectral width varies by a factor of 2 during the spectral diffusion. The observation of correlated spectral diffusion at RT is surprising, yet fully consistent with our model proposed above. The spatial amplitude of surface charge oscillations, i.e., the average distance the charge distribution moves randomly in a given time, should depend on temperature, but not the effect of the local field on the spectral position via the QCSE. The larger oscillations simply imply that the spectra broaden with increasing temperature. The maximum and minimum fields that surface charges can exert on the CdSe core, however, must be independent of temperature, and therefore the overall energy range over which drifts can occur during a measurement.

Although we can only speculate on the nature of the surface charges, we can verify the consistency of our model by estimating the field effect of a single charge migrating along the long axis. Assuming a polarizability of the nanorods comparable to spherical NCs [5] and following the equations in [5], a single charge must be separated from the core by about 3 nm to induce a Stark shift of 40 meV. This is in good agreement with the diameter of the nanorods [19]. By moving the charge along the NC and considering a constant fluctuation in position we can estimate the dependence of FWHM on relative peak position, shown by the lines in Fig. 4. As the QCSE is minimal when the charge is situated at the far end of the nanorod (i.e., far from the core), yet a finite linewidth is measured, a FWHM offset has to be considered due to residual broadening at zero peak shift. The free parameter is the magnitude of spatial oscillations, which we determine as 0.2, 0.6, and 2.2 nm for 5, 50, and 300 K, respectively. We note that the 5 K value is of the order of the typical distance between ligands and surface defects, respectively [26]. The simplest conceivable model of one-dimensional charge transfer along the nanorod thus provides both qualitative and quantitative agreement with the data. As we are interested in only the overall change in field and not the actual charge distribution, the dynamics of the charge distribution can be well approximated with the dynamics of a single point charge. Also, we note that even if the spatial amplitude of charge oscillations were not constant along the rod, the experimental correlation would still provide a measure of

charge migration, although this would complicate the microscopic model.

Evidently, the RT spectra are broader than the maximal achievable spectral shift of ~ 40 meV. Even if the oscillations of surface charge were so strong that the charge were completely annihilated and created during the detection window of 1 s, it is unlikely that local field induced oscillations account for the observed widths of 100 meV. This implies a second contribution to line broadening at RT, which is due to efficient exciton scattering on optical phonons, representing a very rapid dephasing process [16,27]. Whereas the low temperature single NC lines are inhomogeneously broadened by spectral diffusion and do not provide insight into dephasing processes, the opposite is true for RT measurements. We conclude that the narrowest spectra at RT (~ 50 meV width) are predominantly homogeneously broadened. Homogeneous broadening governed by phonon scattering thus accounts for approximately 50 meV of the single particle linewidth at RT.

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