

ARTICLES

Spectroscopy of Single CdSe Nanocrystallites

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Nanocrystallite quantum dots synthesized as colloids have generated growing interest in the past few years. This interest has been fueled by the high degree of reproducibility and control that is currently available in the fabrication and manipulation of these quantum-confined structures. CdSe nanocrystallites, which are often studied as a prototypical colloidal quantum dot system, can be synthesized in macroscopic quantities with sizes that are tunable during synthesis (15–100 Å) in a narrow size distribution (<5% rms).¹ In this size range, the nanocrystallites are smaller than the diameter of the bulk Bohr exciton (112 Å for CdSe). As a result, the electronic structure is dominated by quantum confinement effects in all three dimensions,² making these nanocrystallites truly zero-dimensional structures.

Once fabricated, nanocrystallite quantum dots can be dissolved in a number of polar and nonpolar solvents, embedded into a variety of polymers, and even incorporated into thin films of bulk semiconductors.³ They can also be manipulated into close-packed glassy thin films⁴ or ordered three-dimensional superlattices⁵ (colloidal crystals) or linked to form quantum dot molecules.⁶ Such a high degree of flexibility and control makes nanocrystallite quantum dots ideally suited for the study of zero-dimensional physics.

An inherent complication in the study of ensembles of nanocrystallites is the loss of spectral information resulting from structural and environmental inhomoge-

neities.⁷ For instance, theory predicts that nanocrystallites should have a spectrum of discrete, atomic-like energy states.² As a result, they are often referred to as “artificial atoms”. However, while the discrete nature of the excited states in these nanocrystallites has been verified,⁸ transition line widths appear significantly broader than expected. This is true even when size-selective optical techniques are used to extract homogeneous line widths.^{7–12}

To eliminate the effects of inhomogeneous broadening, it has recently become possible to image and take emission spectra from single nanocrystallites.^{13–18} Similar to single-molecule spectroscopy,¹⁹ single-quantum-dot spectroscopy has been extremely successful in extracting new microscopic information from these ensemble systems. In this Account, we discuss some recent results obtained through the spectroscopy of single CdSe nanocrystallite quantum dots at cryogenic temperatures.

Two types of nanocrystallites were studied. The first were synthesized by the method of Murray et al.,¹ as single-domain wurtzite crystallites which are slightly prolate along their unique crystal axis (aspect ratio 1.1–1.2). The second type, referred to as “overcoated nanocrystallites”, were prepared in a similar manner, with the addition of a final layer of ZnS.²⁰ The addition of a ZnS capping layer has been found to have many effects on the physical characteristics of these nanocrystallites, the most apparent of which is an increase in the fluorescence quantum yield, reported as high as 50% at room temperature.²⁰ Sizes quoted in this Account refer to the average diameter of the nanocrystallites (or CdSe cores for overcoated nanocrystallites) in each ensemble distribution.

Images and spectra were taken using a cryogenic far-field epifluorescence imaging microscope described elsewhere.¹⁴ Unless stated otherwise, all images and spectra described in this Account were taken with 514 nm excitation. A typical image of nanocrystallites in a thin polymer film at 10 K can be seen in Figure 1A. Each dark spot corresponds to the fluorescence from a single nanocrystallite. Variations in fluorescence intensity are a combination of the Gaussian profile of the excitation beam, and variations in individual nanocrystallites, resulting in differences in fluorescence intermittency (described below) and nonradiative relaxation rates. It is quite interesting to note that the measured density of nanocrystallites seen in images such as Figure 1A is very close to (<5× less than) the density estimated from the concentration of the starting solution. This suggests that what is observed in these experiments is not just a subset of anomalously bright nanocrystallites, but is likely to be a more general population, representative of the ensemble distribution.

On the time scale of a single image (<1 s), the fluorescence from individual nanocrystallites is occasionally seen to flicker on and off (fluorescence intermittency).

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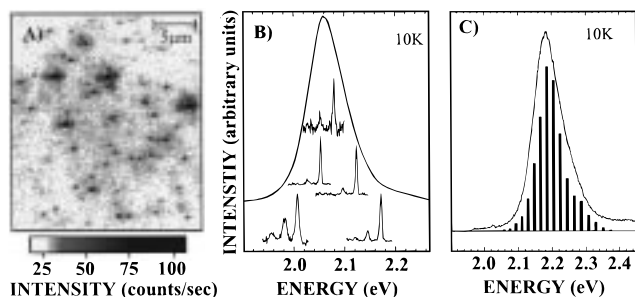


FIGURE 1. (A) Typical image of a dilute solution of 50 Å non-overcoated nanocrystallites in a 200 Å poly(methyl methacrylate) film at 10 K. This image was taken with a 1 s integration time and excitation intensity of 150 W/cm². (B) Representative sample of single-nanocrystallite emission spectra from (A) taken with a 1 min integration time. Also shown is the corresponding ensemble spectrum from that sample. (C) Ensemble spectrum of 43 Å nanocrystallites with histogram of energies of 513 single-nanocrystallite spectra obtained from that sample. The histogram includes the scaled contribution of zero, one, and two phonon lines from each nanocrystallite. Data for parts B and C are from ref 14.

The pattern of on/off behavior is strongly dependent on the particular nanocrystallite as well as the excitation intensity and is thought to result from ionization of the nanocrystallite.¹⁵ This binary fluorescent blinking, rather than a stepwise or continuous dimming of the emission from a single point, is strong evidence that the spots seen in Figure 1A originate from single nanocrystallites. The related Account in this issue by Nirmal and Brus discusses fluorescence intermittency in more detail.²¹

Figure 1B shows a comparison between a representative sample of single-nanocrystallite spectra and the corresponding ensemble spectrum from that sample. All single-nanocrystallite spectra show qualitatively similar spectral characteristics including narrow peaks and a longitudinal-optical (LO) phonon progression with peak spacing comparable to the bulk LO phonon frequency. Differences in phonon coupling are observed between different nanocrystallites with an average value equal to the ensemble-measured value.¹⁴ As expected, the ensemble emission spectrum can be reproduced by a convolution of the average single-nanocrystallite line shape with the distribution of zero-phonon energies measured within the sample [Figure 1C]. The fact that the ensemble-measured spectrum is so accurately reproduced by the distribution of observed single-nanocrystallite spectra is good evidence that what is measured on the single-nanocrystallite level is representative of the ensemble distribution.

Examination of many single-nanocrystallite spectra reveals a wide range of line widths and non-Lorentzian line shapes between different nanocrystallites. In addition, the line shape of individual nanocrystallites is found to be extremely sensitive to experimental parameters such as excitation intensity [Figure 2A–D]. This is true even though excitation occurs far from the emitting state (>200 meV) so that traditional power or saturation broadening should be insignificant. There is also a strong line shape dependence on integration time [Figure 2E]. This is similar to what is seen in single-molecule spectroscopy where line

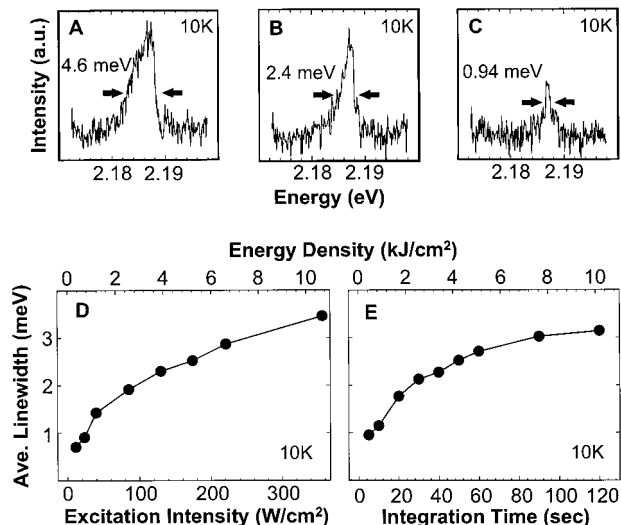


FIGURE 2. (A–C) Three spectra of the same single 45 Å nonovercoated nanocrystallite with 314, 150, and 65 W/cm² excitation intensity, respectively, and 1 min integration time. (D) Average single-nanocrystallite line width as a function of excitation intensity for a sample of 34 overcoated nanocrystallites (56.5 Å) with an integration time of 30 s. (E) Average single-nanocrystallite line width as a function of integration time for 40 nanocrystallites from the same sample as in (d) with 85 W/cm² excitation intensity. The top axes of (D) and (E) indicate the excitation energy density (time × intensity) at each point to allow a direct comparison of the effects of time and intensity on the average single-nanocrystallite line width. Data in parts A–C are from ref 14. Data in parts D and E are from ref 18.

widths are also found to be dependent on acquisition time.^{22–24} In single-molecule spectroscopy, line shapes are thought to arise from rapid shifting of the emission energy (spectral diffusion) on a time scale that is fast relative to the acquisition time of the experiment. These spectral shifts result from changes in the local environment which interact with single molecules through short-range strain fields.²⁴

Figure 3 demonstrates that single-nanocrystallite line shapes are also dominated by spectral diffusion. Figure 3A shows a high-resolution spectrum of the zero LO phonon line (ZPL) of a single nanocrystallite with a 10 s integration time. Figure 3B shows several spectra of the same nanocrystallite with a 0.1 s integration time. At such short integration times, a single resolution-limited peak is seen shifting in energy across the full spectral range occupied by the 10 s spectrum. A histogram of peak positions from 150 consecutive 0.1 s spectra reproduces the general shape of the longer integration time spectrum [Figure 3C].

The observation of spectral diffusion in these nanocrystallites is somewhat unexpected. While single molecules are exquisitely sensitive to changes in their surrounding environment,¹⁹ this was not expected to be true for nanocrystallites. The energies of the delocalized exciton in CdSe nanocrystallites do not appear to be sensitive to the chemical nature of the nanocrystallite surface²⁵ and should be relatively unaffected by small changes in the surrounding environment. As such, the perturbing force required to produce the observed spectral shifts must be quite large.

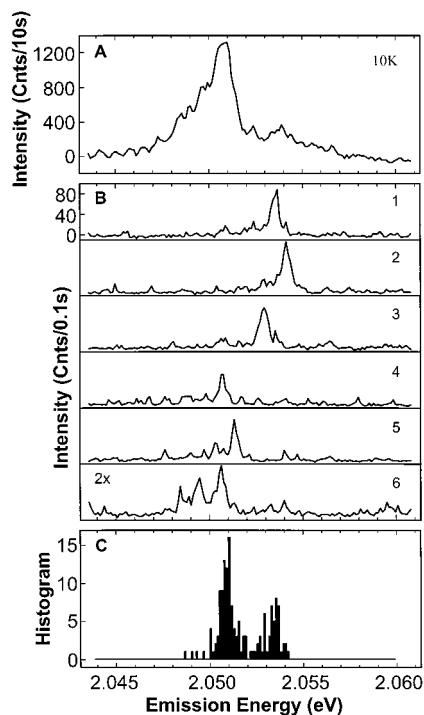


FIGURE 3. (A) Spectrum of a single 56.5 Å overcoated nanocrystallite with a 10 s integration time at 10 K. (B) A representative sample of six spectra from the same nanocrystallite as in (A), with a 0.1 s integration time. Of the 150 spectra taken in rapid succession, frames 1–6 indicate spectrum numbers 1, 16, 35, 59, 84, and 150, respectively. (C) Histogram of peak positions from each of the 150 spectra described in (B). The excitation intensity for all spectra in Figure 3 was 200 W/cm². All data in Figure 3 are from ref 18.

There are two main implications of the data in Figure 3. First, it is clear that the line shape of a single nanocrystallite contains information about changes in the surrounding environment and not the intrinsic physics of the nanocrystallite. Second, changes in the line shape of a single-nanocrystallite spectrum resulting from different experimental conditions (Figure 2) are likely to be the result of changes in spectral diffusion. In the case of broadening as a function of excitation intensity, this has been observed directly (the magnitude and frequency of small spectral shifts is found to increase with increasing excitation intensity¹⁴). In addition, the line width of a single-nanocrystallite spectrum is actually dependent on the wavelength of excitation, with excitation closer to the band edge resulting in narrower emission spectra.¹⁸ This suggests that the contribution of excitation intensity is in the form of energy released as the exciton relaxes to its emitting state. This is further supported by the close overlap of the time and intensity curves in Figure 2D,E when plotted against excitation energy density (top axis). A direct comparison reveals that changing the excitation intensity has the same effect on the average single-nanocrystallite line width as changing the integration time by the same relative amount. This overlap suggests that the observed broadening is related to the number of excitations (and therefore the amount of excess excitation energy released) during the acquisition of a single spectrum.

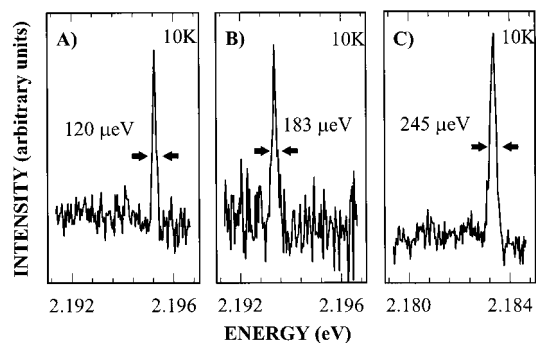


FIGURE 4. (A–C) High-resolution spectra of ultranarrow ZPLs from three different single nanocrystallites from a 43 Å overcoated sample. Spectra were taken with a 1 min integration time and an excitation intensity of 25 W/cm². Data in Figure 4 are from ref 14.

The effect of excess excitation energy is not the result of heating. Heating is expected to be insignificant in these experiments due to rapid dissipation of heat into the surrounding matrix ($\sim 10^5$ excitations/s with $\Delta T \approx 6$ K/excitation which dissipates in $< 10^{-12}$ s). Instead, phonons emitted as the exciton relaxes to its lowest excited state may couple directly to the local environmental changes that are responsible for spectral diffusion. While the nature of these environmental changes has not yet been discussed, evidence which is presented further in this Account suggests that spectral diffusion is the result of changing local electric fields around individual nanocrystallites. These fields are thought to result from charges trapped on or near the surface of the nanocrystallite. The role of the released excess excitation energy may be to facilitate movement of these charges between local trap sites, resulting in fluctuations in the local electric field which produce the observed spectral diffusion shifts.

By decreasing the excitation intensity, it is possible to reduce spectral diffusion in some nanocrystallites to the point where shifts that are observable above our resolution limit occur on a time scale of many seconds to minutes. At these intensities, resolution-limited line widths as narrow as 120 μeV have been observed at 10 K (Figure 4). These peaks are $\sim 600\times$ narrower than the full ensemble fluorescence. Such narrow line widths suggest very weak coupling to low-energy acoustic phonons. This finding is consistent with theoretical predictions and reinforces the description of these nanocrystallites as “artificial atoms”.

While the small spectral shifts described above occur on a very fast time scale, a second type of spectral shifting is also observed. These shifts result in much larger changes in the emission energy and occur on a time scale from seconds to many minutes, even under high excitation intensities. Figure 5 shows 16 consecutive low-resolution spectra of a single nanocrystallite which reversibly shifts in energy more than 80 meV over 16 min. The spectral characteristics of these shifts are found to be similar to what is observed in low-temperature ensemble Stark experiments.²⁶ In the presence of an applied electric field, ensemble emission spectra are seen to shift to lower energies with a corresponding increase in phonon coupling and a decrease in band edge fluorescence. The

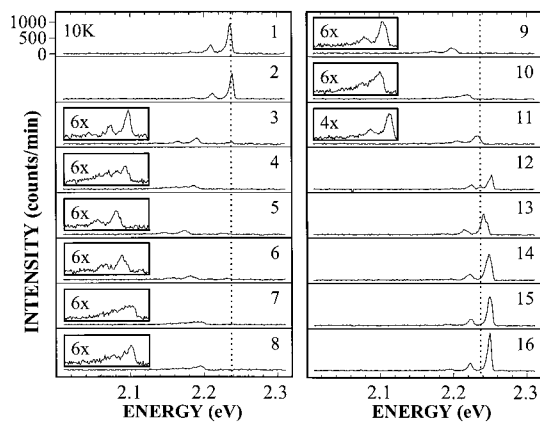


FIGURE 5. Sixteen consecutive 1 min spectra of the same single nanocrystallite (39 Å nonovercoated) with an excitation intensity of 2.5 kW/cm². Insets show magnification of the y-axis by the indicated amounts. Data for Figure 5 are from ref 14.

observed similarities suggest that changing local electric fields may play a role in spectral diffusion.

To further investigate the role of electric fields in spectral diffusion, it is possible to make direct measurements of the quantum-confined Stark effect in single nanocrystallites.¹⁷ In addition to potentially contributing to the understanding of spectral diffusion, the quantum-confined Stark effect can also be used to probe the nature of the excited states in these nanocrystallites. For instance, delocalized exciton states within the nanocrystallite core should be highly polarizable, while localized surface trap states should have a strong dipole character. These two types of states should be easily distinguished by the application of an electric field. In the past, however, inhomogeneous broadening has greatly complicated the interpretation of ensemble Stark measurements. For example, while the presence of an excited-state dipole has been suggested in ensemble Stark absorption studies,²⁷ nearly identical Stark data have also been interpreted without the need for a polar state.²⁸ By eliminating the effects of ensemble averaging, single-nanocrystallite spectroscopy should allow a conclusive determination of the nature of the emitting state.

Figure 6A shows the ZPL of a single nanocrystallite under a range of electric fields. The peak can be seen shifting continuously over more than 60 meV. The slight change in zero-field energy over the series is due to spectral diffusion. Shifts of this magnitude support the potential of these nanocrystallites for use in electro-optic modulation devices. Although the first absorbing state has not yet been characterized for single CdSe nanocrystallites, even conservative estimates based on ensemble measurements suggest that these shifts are more than an order of magnitude greater than the width of this state.²⁹ Shifts observed in these experiments are even comparable to room-temperature single-nanocrystallite line widths,³⁰ suggesting the potential for use in noncryogenic devices.

Figure 6B plots Stark shift as a function of field for the nanocrystallite in Figure 6A. The Stark data can be fit with the sum of a linear and quadratic function of the applied field, indicating the presence of both polar and polarizable

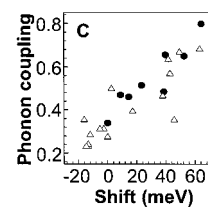
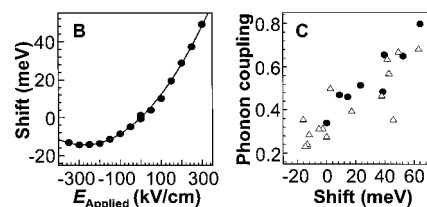
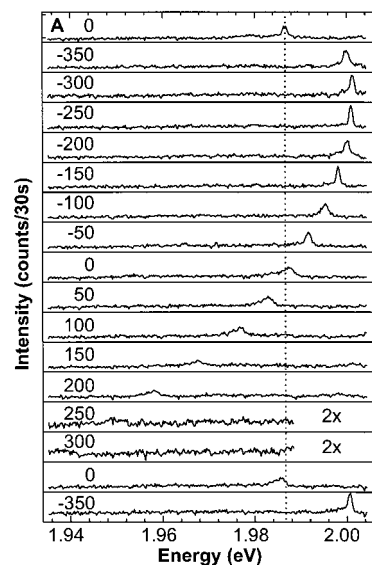


FIGURE 6. (A) Seventeen spectra of the same single nanocrystallite (75 Å overcoated) under a range of electric fields. Spectra were taken with an excitation intensity of 25 W/cm² and an integration time of 30 s. Inset numbers indicate the applied field in kV/cm and magnification of the y-axis. (B) Plot of Stark shift versus electric field for the single nanocrystallite in (A) with fit to the sum of a linear and quadratic function of the applied field. (C) Phonon coupling versus Stark shift for a single nanocrystallite in the presence of an applied electric field (closed circles) and versus spectral diffusion shift in the absence of an applied field (open triangles). Phonon coupling is measured as the ratio of the integrated intensity of the one LO phonon line to the ZPL. Stark and spectral diffusion data in (C) were taken from different nanocrystallites. Data in Figure 6 are from ref 17.

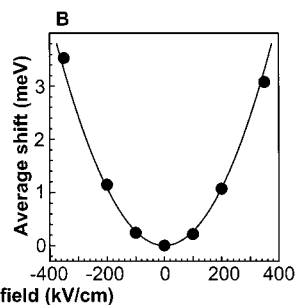
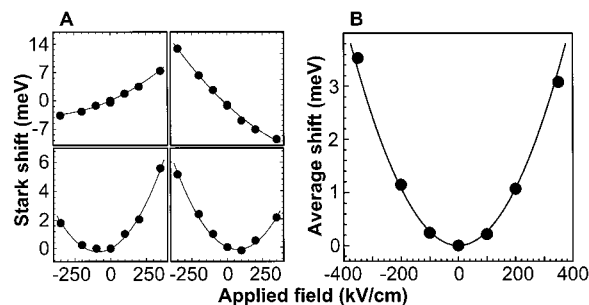


FIGURE 7. (A) Stark shift of emission versus applied electric field for four different single nanocrystallites from a 58 Å nonovercoated sample. Lines indicate fits to the sum of a linear and quadratic shift as a function of field. (B) Average shift versus field for 54 single nanocrystallites from the same sample with a fit to a pure quadratic function of field. Data in Figure 7 are from ref 17.

character in the emitting state.³¹ While a wide range of values for the excited-state dipole along the applied field axis are measured between individual nanocrystallites [Figure 7A], all nanocrystallites demonstrate this dual character.

Previous ensemble Stark fluorescence measurements of CdSe nanocrystallites revealed a purely quadratic shift of the peak emission energy as a function of applied field.²⁶ In light of the current single-nanocrystallite experiments, this result can be explained as the product of ensemble averaging. While individual nanocrystallites reveal a strong linear component in the Stark shift, the average dipole over the ensemble is zero [Figure 7B]. The result is that ensemble samples should have a quadratic shift of the peak emission as a function of field with an additional broadening due to the linear contribution of individual nanocrystallites. Consistent with this, ensemble experiments reveal a broadening of the emission with increasing electric field. These studies, however, are further complicated by additional broadening due to changes in phonon coupling. In the past, ensemble emission broadening has been attributed entirely to changes in phonon coupling.²⁶ These single-nanocrystallite results, however, indicate that a polar contribution must also be considered.

The observed excited-state dipole is consistent with a highly polarizable excited state in the presence of a strong local electric field. A comparison between the changes in phonon coupling observed in spectral diffusion and those induced by the presence of an applied electric field indicates that they are very similar.¹⁷ A plot of phonon coupling vs shift for the two effects can be seen in Figure 6C. Phonon coupling is a measure of the overlap of electron and hole wave functions and should be sensitive to changes in the local electric field. Figure 6C strongly suggests that spectral diffusion results from changes in the local electric field.

The presence of large local electric fields has several implications. First, the magnitude of the average internal electric field extracted in all samples ($\sim 10^5$ V/cm) implies extensive state mixing near the band edge. This conclusion has also been reached on the basis of ensemble nonlinear optical experiments, where state mixing has been observed directly.³² At the same time, this state mixing may help explain the anomalously large LO phonon couplings measured in these nanocrystallites.²⁹ According to current theory, emission occurs from a delocalized "dark-exciton" state³³ which should only weakly couple to optical phonons.³⁴ A strong local field breaks the inversion symmetry of the exciton wave function, creating a separation of charge within the ionic crystal. This charge asymmetry should then increase exciton-phonon coupling through a Frolich interaction. Previous theoretical calculations of LO phonon couplings have concluded that the experimentally observed ensemble values could be accounted for by the presence of a local electric field equivalent to an electron on the surface of the nanocrystallite.³⁴ This field magnitude is consistent with what is observed in these single-nanocrystallite experiments. In addition, different local electric fields around individual nanocrystallites may also explain the wide range of phonon couplings seen in these experiments [see Figure 1B and ref 14 for examples].

Another implication of changing local electric fields is

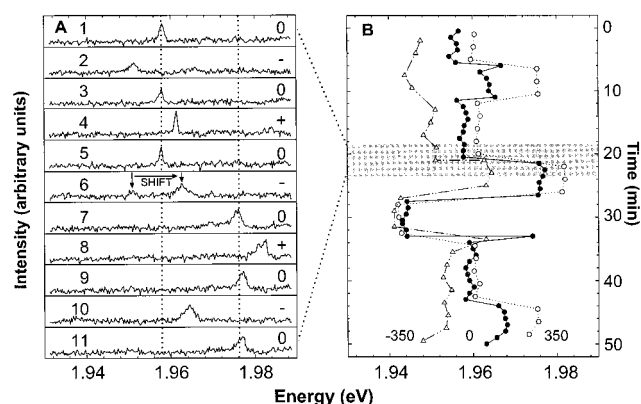


FIGURE 8. (A) Eleven consecutive 30 s emission spectra from a single nanocrystallite (75 Å overcoated) in the presence of a repeating sequence of electric fields: negative field, zero field, positive field, zero field. Inset numbers and symbols represent the frame number and applied field, respectively. (–), (0), and (+) represent –350, 0, and +350 kV/cm applied fields, respectively. A spectral diffusion shift is indicated in frame 6. (B) Summary of 100 consecutive 30 s spectra of the same nanocrystallite under the field conditions described above. Data are plotted as a function of time, peak energy, and electric field. Open triangles, closed circles, and open circles indicate fields of –350, 0, and +350 kV/cm, respectively. The excitation intensity for all spectra in Figure 8 was 25 W/cm². Data for Figure 8 are from ref 17.

that there should be a direct correlation between spectral diffusion shifts and changes in the magnitude of the induced excited-state dipole. Consistent with this prediction, distinct changes in the single-nanocrystallite Stark shift can be seen accompanying spectral diffusion shifts. Figure 8A shows 11 consecutive spectra of the same single nanocrystallite under different field conditions. Following a spectral diffusion shift in the sixth frame, there is an increase in the magnitude of subsequent Stark shifts. Over 50 min, distinct changes in the zero-field position are clearly observed [Figure 8B]. Accompanying each of these shifts is a corresponding change in the response to the applied field. During minutes 26–32, the Stark shifts become almost purely quadratic, indicating that the excited-state dipole along the applied field has become very small. Analysis of the Stark parameters between spectral diffusion shifts in Figure 8B reveals no change in the measured polarizability over the 50 min, while the dipole contribution changes by almost a factor of 50. The correlation of spectral diffusion with changes in the response to an applied electric field supports the Stark model of spectral diffusion.

It is important to note that the changes seen in Figure 8 are not the result of nanocrystallite reorientation on the substrate surface. Such movement should be extremely slow at 10 K. In addition, similar results are obtained from dots embedded in a polymer matrix which should quench any movement of the nanocrystallite at these temperatures.

Ensemble dielectric dispersion measurements have suggested the presence of a ground-state dipole in CdSe nanocrystallites.³⁵ However, while the data in Figure 8 do not preclude a contribution to the excited-state dipole from intrinsic structural or charge asymmetries in the

ground state,^{32,35} they do indicate that a large portion of this dipole arises from an extrinsic source. In fact, the changes observed in Figure 8 are on the same order of magnitude as the average dipole measured for that sample. By measuring the magnitude of the excited-state dipole along the applied field axis for many single nanocrystallites, it is possible to extract the average dipole present in each size sample. If we assume that this dipole is the result of local electric fields, either intrinsic or extrinsic, the magnitude of this average field is found to be quite large, comparable to that produced by a point charge (electron or hole) trapped on or near the surface of the nanocrystallite. Photoionization has been proposed as the source of fluorescence intermittency in single CdSe nanocrystallites at room temperature (see Account in this issue by Nirmal and Brus²¹ as well as ref 15). Photoionization leaves a charged nanocrystallite core that may not relax radiatively upon further excitation.³⁶ Emission resumes when the core is neutralized by the thermally activated return of the ejected charge. As discussed above, a similar on/off behavior is observed at liquid helium temperatures.^{14,16} At 10 K, however, there is little thermal energy available to promote the return of an external charge. Instead, neutralization may also occur through an additional ionization event, resulting in an emitting nanocrystallite in the presence of a potentially large and randomly oriented local electric field. This second neutralization pathway may be relatively insignificant at higher temperatures compared to thermal neutralization. This would explain why Nirmal and Brus see no power dependence of the “off” times in their intermittency studies. Additional ionization or recombination events, as well as relocalization of external charges, could result in changes in both the zero-field energy as well as the excited-state dipole of a single nanocrystallite. This is consistent with what is observed in Figure 8.

Within the framework described above, the large spectral shifts seen in Figure 5 may result from ionization and recombination of carriers, while the small shifts in Figure 3 may result from slight field modulations due to movement of charges between local trap sites on or near the nanocrystallite. For electric fields on the order of the local fields measured in these experiments, Figure 7B indicates that the dependence of the Stark shift (ΔE) on electric field (F) is in the quadratic regime ($\Delta E \propto F^2$). This implies that the magnitude of the change in energy [$\Delta(\Delta E)$], and therefore the observed line width due to a fluctuating field (ΔF), also depends on the average field present [$\Delta(\Delta E) \propto F \cdot \Delta F$]. Consistent with this prediction, Stark-shifted emission spectra like those in Figure 6A are seen to broaden as they shift to lower energies (higher total internal fields). Figure 9A plots the line width of a single nanocrystallite as a function of relative shift in the presence of an applied field. These data can be roughly fit with a function that varies as the square root of the observed shift. This is consistent with the Stark model. In addition, Stark measurements have found that overcoated nanocrystallites have a smaller average internal electric field than nonovercoated nanocrystallites due to physical

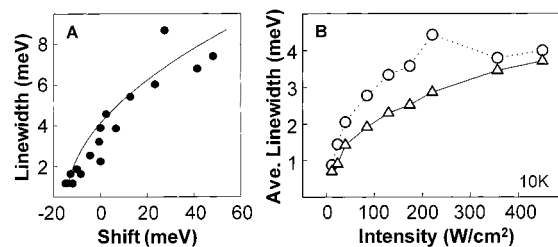


FIGURE 9. (A) Line width vs shift from the zero-field energy for a single 75 Å overcoated nanocrystallite in response to an applied electric field. (B) Average single-nanocrystallite line width as a function of excitation intensity for 34 overcoated nanocrystallites and 25 nonovercoated nanocrystallites (triangles and circles, respectively) with the same CdSe core size (56.5 Å). Data for parts A and B are from refs 17 and 18, respectively.

and electrical screening by the ZnS shell.¹⁷ As a result, overcoated nanocrystallites should have narrower average line widths resulting from the same local field fluctuations than nonovercoated nanocrystallites. This is also found to be true [Figure 9B].

As a final comment on spectral diffusion, it has been proposed here that the changes in the local electric field responsible for spectral diffusion are the result of charge carriers near individual nanocrystallites. One thing that has not been addressed, however, is the nature of the trapped charges (i.e., where are they?). To our knowledge, no evidence currently exists which can conclusively locate these charges; however, some speculation can be made. Both spectral diffusion and the Stark results shown in Figure 8 have been observed in nanocrystallites embedded in a polymer matrix as well as ones deposited onto a quartz substrate with no surrounding matrix. Since these effects are present in the absence of a matrix, this suggests that charges may reside in trap sites on the surface of the nanocrystallite. While this is just speculation, it is consistent with the experimental evidence currently available.

In conclusion, current work being performed in single quantum dot spectroscopy has greatly increased our understanding of CdSe nanocrystallites. Many new and previously unobserved or unexpected phenomena have been revealed including ultranarrow transitions, a wide range of phonon couplings between individual nanocrystallites, and spectral diffusion of the emission spectrum over a wide range of energies. Electric field studies have revealed both polar and polarizable character in the emitting state. The polar component has been attributed to an induced excited-state dipole resulting from the presence of local electric fields. These fields, which are thought to result, in part, from trapped charges on or near the surface of the nanocrystallite, are seen to change over time, resulting in spectral diffusion. Careful observation of spectral diffusion has shown that, on the time scale of a typical single-nanocrystallite spectrum, line shapes are primarily the result of spectral shifting and not the intrinsic physics of the nanocrystallite. The effects of integration time and excitation intensity on observed single-nanocrystallite line widths also demonstrate the sensitivity of single-nanocrystallite spectroscopy to ex-

perimental conditions. These and other experiments on single quantum dots should continue to provide valuable insight into the theoretical and practical issues surrounding this unique and interesting physical system.

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