Photoluminescence Spectroscopy of Single CdSe Nanocrystallite Quantum Dots

S. A. Empedocles, D. J. Norris, and M. G. Bawendi
Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

(Received 18 July 1996)

We collect and spectrally resolve photoluminescence from single CdSe nanocrystallite quantum dots. The elimination of spectral inhomogeneities reveals resolution limited spectral linewidths ($<120\ \mu$eV at 10 K) more than 50 times narrower than expected from ensemble measurements. Light driven spectral diffusion is observed as a form of power broadening. These studies confirm the atomiclike nature of the emitting state in CdSe nanocrystallites. [S0031-9007(96)01486-X]

PACS numbers: 73.20.Dx, 61.46.+w, 78.55.Et

Nanocrystallite quantum dots (QDs) synthesized as colloids are particularly suited for the study of zero-dimensional structures [1,2]. They can be produced in macroscopic quantities with a high degree of reproducibility and control, a uniform shape, and diameters that are tunable during synthesis (~15–100 Å) in a narrow size distribution (<5% rms) [3]. In this size range, where the QD is smaller than the exciton Bohr diameter (112 Å), the confinement energy of the electron and hole is stronger than their Coulomb interaction, yielding true zero-dimensional structures [1].

Nanocrystallite QDs can be incorporated into a variety of polymers as well as thin films of bulk semiconductors [4]. They can also be manipulated into close packed glassy thin films [5], ordered three-dimensional superlattices (colloidal crystals) [6], or linked to form QD molecules [2]. Exceptional flexibility and structural control distinguish nanocrystallite QDs from the more traditional QD structures fabricated using epitaxial growth techniques. In addition, they facilitate the study of some potentially novel QD physics, which may be difficult or inaccessible with epitaxially grown dots (e.g., correlation effects in QD molecules, miniband formation in close packed QD arrays, etc.).

An inherent complication in the study of ensembles of dots is the loss of spectral information resulting from structural and environmental inhomogeneities [7]. QDs, often referred to as "artificial atoms," are predicted to have discrete, atomiclike energy levels, and a spectrum of ultranarrow transitions [8–10]. However, while the discrete nature of the spectrum has been verified for nanocrystallite QDs [9], transition linewidths appear significantly broader than expected. This is true even when size selective optical techniques such as fluorescence line narrowing (FLN) [7] are used to extract homogeneous linewidths [7,9,11]. Previous attempts to obtain luminescence spectra from single nanocrystallite QDs using two photon microscopy have also failed to reveal narrow features [12]. As a result, broad linewidths were thought to be an inherent limitation of colloidal QDs, making them inappropriate for use in zero-dimensional devices such as optical switches or modulators. These dots were thought to be inherently different than epitaxially grown dots which, individually, do show ultranarrow luminescence linewidths [13–17].

Since its introduction, single molecule spectroscopy has been successful in extracting new microscopic properties from ensemble systems [18–21]. In this Letter we use far-field microscopy to image and obtain ultranarrow single dot luminescence (SDL) spectra from single CdSe nanocrystallites at cryogenic temperatures.

Two types of CdSe nanocrystallites were studied. The first, referred to as "standard dots," were synthesized using the method of Ref. [3] as single domain wurtzite crystallites, slightly prolate along their unique crystal axis (aspect ratio 1.1–1.2). The second, referred to as "overcoated dots," were prepared in the same manner, with the addition of a final layer of ZnS [22,23]. A ZnS or ZnSe capping layer has been found to produce dots that are more robust during processing [4], and, in the case of ZnS, enhance the room temperature photoluminescence quantum yield, reported as high as 50% [22]. Both types of dots are surrounded by a passivating layer of organic ligands. Three size distributions of standard dots were used with average diameters of 39, 45, and 50 Å. A single distribution of overcoated dots was used (43 Å). Nanocrystallites were spin cast in hexane at extreme dilution on top of a 500 Å layer of poly(methylmethacrylate) on a crystalline quartz substrate. The concentration was chosen to produce a lateral dispersion <1 QD$/\mu$m^2 to facilitate spatial resolution using far-field optics.

Single QD images and spectra were obtained using a far-field, epifluorescence imaging microscope. The excitation light (514.5 nm) was transmitted through a 95% reflecting mirror (at an angle of 45°) and focused by a long working distance microscope objective (NA $= 0.7$) to a $\sim 32\ \mu$m spot on the sample surface. The sample was mounted on the cold finger of a liquid helium cryostat and cooled to 10 K. The luminescent image was collected by the same objective lens, reflected off the mirror, and passed through a notch filter to remove excitation light. The image was then focused onto the entrance slit of a spectrometer and detected with a liquid nitrogen cooled charge coupled device (CCD) camera. For imaging purposes, the diffraction grating was replaced

0031-9007/96/77(18)/3873(4)$10.00

with a mirror, and the image was projected directly onto the CCD. Spatial isolation of a single QD along the horizontal axis was achieved using the entrance slit of the spectrometer [see Fig. 1(a)]. It was usually possible to align several QDs at different vertical positions within the closed slit. The diffraction grating was then reinstalled, and light from each vertical position was dispersed onto the CCD [Fig. 1(b)]. In this way, it was possible to simultaneously obtain separate SDL spectra from several different nanocrystallites.

A typical image of standard dots can be seen in Fig. 1(a). Each bright spot corresponds to the luminescence from a single nanocrystallite. As can be seen, QDs within the same image fluoresce with different intensities at 10 K (average ~500 counts/sec ≈ 10^5 photons/sec emitted, assuming an isotropic source). Differences in luminescence intensity (LI) are attributed to variations in the quality of the organic surface layer surrounding individual nanocrystallites [3]. Images of individual QDs taken with an integration time of 0.5 sec appear to flicker on and off over consecutive scans, some staying "dark" for as long as 10 min before resuming emission. They do not show a gradual dimming but rather an "all on/all off" behavior consistent with the fact that we are seeing single nanocrystallites rather than aggregates of dots. This on/off behavior is thought to be the result of QD photoionization [24]. While there was no noticeable difference in the behavior of the images between the three sizes of standard dots, there was a dramatic increase in the luminescence signal of the overcoated sample (~5×). This difference is attributed to the increased resistance to surface degradation of overcoated dots [4]. These QDs appear to be robust, allowing us to monitor the luminescence from some dots for >1 h.

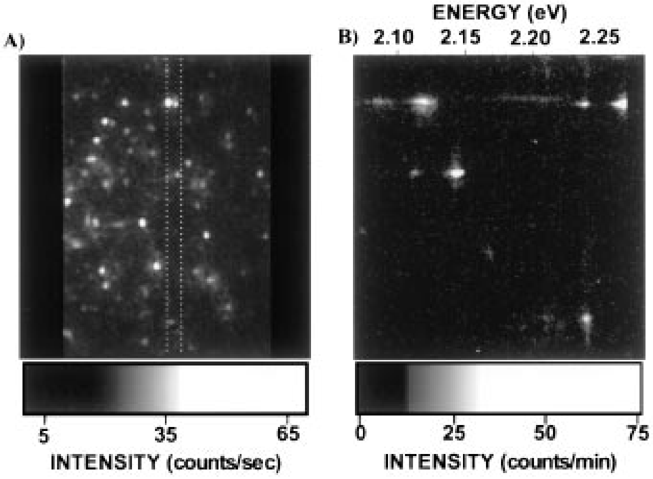

FIG. 1. (a) Typical image of standard dots at 10 K with a 0.5 sec integration time and 150 W/cm^2 excitation intensity. We detect ~5% of the total photons emitted (assuming an isotropic source) with a spatial resolution of ~0.5 μm. The wide black border represents the edges of the entrance slit of the monochromator. The white dotted lines indicate the narrowed position of the entrance slit during spectrum acquisition. Note that there are several vertically separated luminescent spots contained within the narrowed slit. Each of these spots corresponds to luminescence from a single nanocrystallite. Also note that there are two spots that are not vertically separated, located near the top of the image, one bright spot near the left edge of the slit and one less intense spot on the right edge. (b) Spectrally dispersed image of the sample shown in (a) with slits narrowed and a 60 sec integration time. Each individual spectrum appears as a sequence of spots separated by ~25 meV along the horizontal axis. These spots correspond to the expected LO phonon progression. The appropriate rows of pixels are binned to produce SDL spectra. Note that there is a SDL spectrum for each of the spots within the narrowed slit in (a). At the position where there are two spots of different intensity at the same vertical location, there are two spectra of different intensity dispersed along the same horizontal stripe.

Figure 2(a) compares spectra taken using SDL and FLN spectroscopy. As can be seen, the spectrum from an individual standard dot at 10 K shows a greatly reduced linewidth over what is obtained using FLN [25]. We clearly resolve the longitudinal-optical (LO) phonon structure of the SDL spectrum with a peak spacing comparable to that of the bulk LO phonon frequency. In addition, we do not observe emission from higher excited states, suggesting the absence of a phonon blockade.

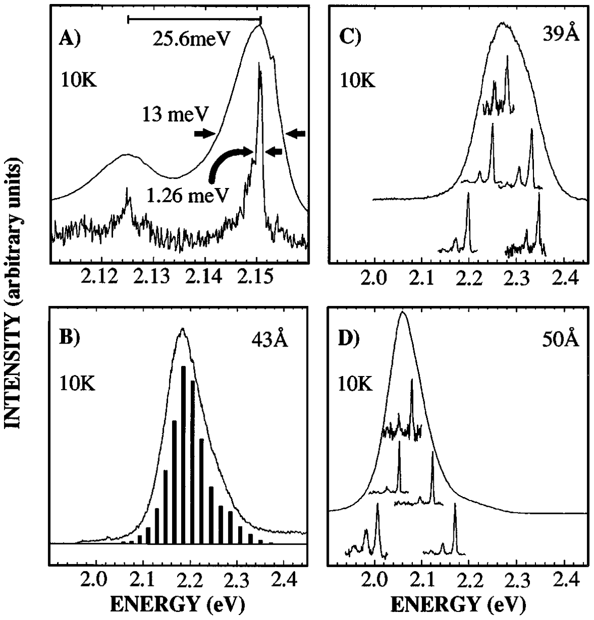

FIG. 2. (a) Comparison of a SDL spectrum from the 45 Å standard dot sample taken at 2.5 kW/cm^2 (bottom) vs FLN spectrum of a sample of comparable size (top). The small peak on the blue edge of the FLN spectrum is scattered excitation light. (b)–(d) Ensemble spectra from three different size distributions (43 Å overcoated dots and 39 Å and 50 Å standard dots, respectively) with corresponding SDL spectral information. (b) Ensemble spectrum with histogram of energies of 513 SDL spectra obtained from that sample. The histogram includes the scaled contribution of zero, one, and two phonon lines from each dot. (c),(d) Ensemble spectra with a representative set of SDL spectra obtained from these samples. All SDL spectra were taken with a 60 sec integration time.

Several observations can be used as evidence that the SDL spectra result from single nanocrystallites. First, the on/off behavior described above suggests that each spot corresponds to a single QD. We can verify this behavior in a particular QD prior to obtaining its spectrum. Second, the SDL lines are so narrow that multiple QDs within the same spectrum are easily resolved. Finally, the total emission rate measured for the brightest dots ($\sim 5 \times 10^5$ photons/sec at 375 W/cm^2 peak intensity) is within (less than) a factor of 3 of the estimated value (assuming isotropic radiation, 100% quantum yield, and an absorption cross section of 10^{-15} cm^2).

Examination of a large number of SDL spectra shows a distribution of emission energies that reproduces the ensemble spectrum for each size sample [Figs. 2(b)– 2(d)]. Figures 2(c) and 2(d) show a representative sample of SDL spectra. All spectra (including those for overcoated dots) show qualitatively similar characteristics. Within a sample, we observe differences in LO phonon coupling between QDs. Coupling constants range from 0.06 to 1.3 with an average of 0.488 (measured from the overcoated sample). This number is consistent with those previously reported using FLN [9].

While narrower than FLN spectra, SDL spectra appear to be broadened as a result of spectral diffusion. Observation of SDL spectra reveals a shifting of the emission energy with time, which is reversible and varies from dot to dot. A similar, though smaller, effect is seen in single molecule spectroscopy [18,19,26]. This similarity is unexpected as the exciton in QDs should have little interaction with the surrounding matrix. Spectral diffusion provides further evidence that we are collecting spectra from single nanocrystallites. Spectra collected simultaneously over many minutes shift independently of each other. If the SDL spectra were from multiple dots, they should split into multiple peaks over time. This is not observed.

The rate and extent of spectral diffusion is highly power dependent with a small number of QDs at higher intensities (2.5 kW/cm^2) shifting as much as 60 meV over several minutes [26]. Figure 3(a) shows the zero LO phonon line (ZPL) of a single overcoated dot over 5 min at 65 W/cm^2 excitation intensity. A narrow peak can be seen abruptly shifting in energy over a range of ~2 meV, usually appearing at several discrete positions within a single minute. If the excitation intensity is reduced to 25 W/cm^2, the extent of spectral shifting decreases [Fig. 3(b)]. At lower resolution and/or longer integration times, this shifting appears as a form of power broadening [Figs. 3(c)–3(e)]. Similar to single molecule spectroscopy and spectral hole burning, the linewidth of a SDL spectrum depends on the time over which the measurement is made [19,27].

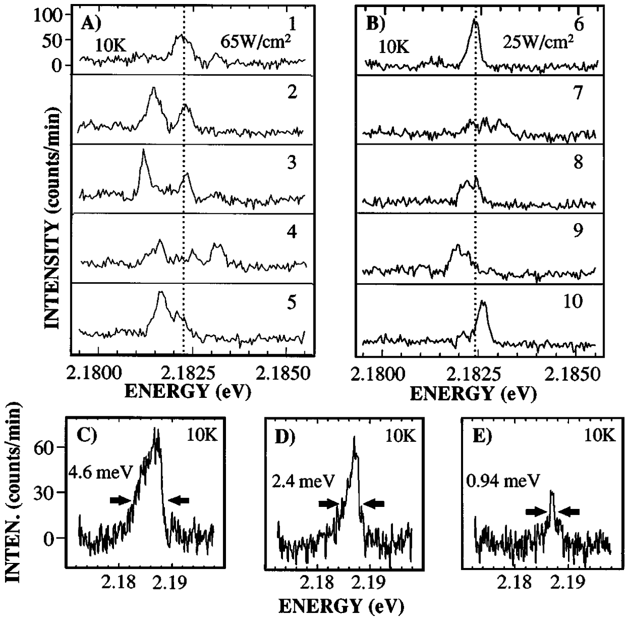

FIG. 3. (a) Five consecutive 1 min spectra of a single overcoated dot at 65 W/cm^2 excitation intensity. (b) The next five consecutive 1 min scans of the same dot at 25 W/cm^2 . (c)–(e) Lower resolution 1 min spectra of a single standard dot from the 45 Å sample at 314, 150, and 65 W/cm^2, respectively.

Figure 4 shows sixteen consecutive 1 min SDL spectra at 2.5 kW/cm^2, demonstrating a reversible redshift over time. As the spectrum shifts red, there is a corresponding decrease in total LI and an increase in phonon coupling. This behavior is consistent with a Stark effect. Low temperature Stark studies show a redshift in emission with an increase in phonon coupling and a decrease in band edge emission as electric field strength is increased [28]. It is possible that we are observing a self-induced Stark effect resulting from changing local electric fields,

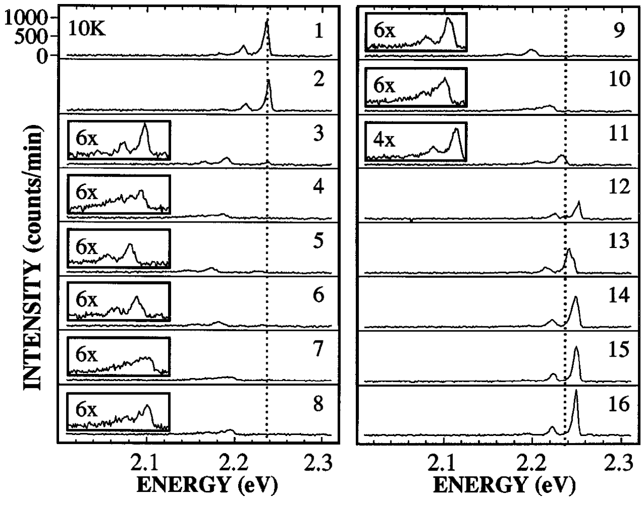

FIG. 4. Sixteen consecutive 1 min spectra of a single standard dot from the 39 Å sample at 2.5 kW/cm^2. Insets show magnification of the y axis by the indicated amounts. The progression shows a large, reversible redshift over time accompanied by a decrease in LI and an increase in phonon coupling. As the spectrum begins to shift back to higher energies, there is a corresponding increase in emission with a complete recovery of LI and phonon coupling.

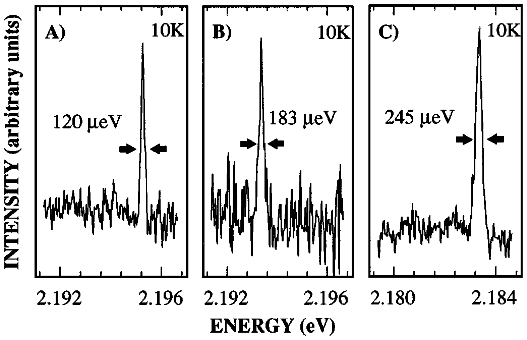

FIG. 5. (a)–(c) Three 1 min spectra of single overcoated dots showing ultranarrow ZPLs at 25 $\mathrm{W/cm^2}$ excitation intensity. At this intensity, the dots are in their excited state ~5% of the time, assuming a 500 ns excited state lifetime.

possibly the result of QD photoionization and trapping of charges in the surrounding matrix.

Integrated over time, the redshift, with its corresponding decrease in LI, results in broadened asymmetric peaks with a red tail as in Fig. 2(a). This is not the result of acoustic phonons but rather the integration of several spectral positions for the same nanocrystallite during a 1 min spectrum [note asymmetric broadening in Figs. 3(c)–3(e)].

At low intensity, it was possible to reduce spectral diffusion and obtain resolution limited linewidths as narrow as 120 μeV full width at half maximum (FWHM) at 10 K [29]. Figure 5 shows a representative sample of ultranarrow luminescence peaks. These lines are ~50× narrower than the linewidths extracted from FLN and are significantly narrower than for single quantum wells. As the narrowest lines are resolution limited, we can only report an upper bound for the homogeneous luminescence linewidth of these QDs. Even at current resolution, these linewidths are small compare to kT at 10 K, indicating a lack of coupling to low energy acoustic phonons.

In conclusion, we have demonstrated the atomiclike nature of the emitting state in CdSe nanocrystallite QDs. We observe light driven spectral diffusion appearing as a form of power broadening, analogous to what is seen in single molecule spectroscopy. This study reinforces the description of these structures as artificial atoms and demonstrates the similarities between colloidal nanocrystallite QDs and those fabricated using epitaxial growth techniques.

We thank Manoj Nirmal, Jay Trautman, Louis Brus, and Alexander Efros for invaluable conversations and advice, Bashir Dabbousi for the synthesis of overcoated dots, and Masaru Kuno for providing the FLN spectrum. S. A. E. and D. J. N. benefited from DoD and NSF Fellowships, respectively. M. G. B. thanks the David and Lucille Packard Foundation and the Sloan Foundation for Fellowships. This research was funded in part by NSF Grant No. DMR-91-57491 and by the NSF-MRSEC program (DMR-94-00034). We also thank the MIT Harrison Spectroscopy Laboratory (NSF-CHE-93-04251) for support and use of its facilities.

[1] L. Brus, Appl. Phys. A **53**, 465 (1991), and references therein.

[2] A. P. Alivisatos, Science **271**, 933 (1996), and references therein.

[3] C. B. Murray, D. J. Norris, and M. G. Bawendi, J. Am. Chem. Soc. **115**, 8706 (1993).

[4] M. Danek *et al.,* J. Cryst. Growth **145**, 714 (1994); Chem. Mater. **8**, 173 (1996).

[5] C. R. Kagan *et al.,* Phys. Rev. Lett. **76**, 1517 (1996).

[6] C. B. Murray, C. R. Kagan, and M. G. Bawendi, Science **270**, 1335 (1995).

[7] A. P. Alivisatos *et al.,* J. Chem. Phys. **90**, 3463 (1989).

[8] Al. L. Efros and A. L. Efros, Sov. Phys. Semicond. **16**, 772 (1982); L. E. Brus, J. Chem. Phys. **80**, 4403 (1984).

[9] D. J. Norris and M. G. Bawendi, Phys. Rev. B **53**, 16 338 (1996); D. J. Norris *et al.,* Phys. Rev. B **53**, 16 347 (1996).

[10] Al. L. Efros *et al.,* Phys. Rev. B **54**, 1 (1996).

[11] M. Nirmal *et al.,* Phys. Rev. Lett. **75**, 3728 (1995).

[12] S. A. Blanton *et al.,* Chem. Phys. Lett. **229**, 317 (1994).

[13] R. Leon *et al.,* Science **267**, 1966 (1995).

[14] M. Grundmann *et al.,* Phys. Rev. Lett. **74**, 4043 (1995).

[15] J. Y. Marzin *et al.,* Phys. Rev. Lett. **73**, 716 (1994).

[16] K. Brunner *et al.,* Appl. Phys. Lett. **64**, 3320 (1994).

[17] Y. Nagamune *et al.,* Appl. Phys. Lett. **67**, 3257 (1995).

[18] W. E. Moerner, Science **265**, 46 (1994), and references therein; T. Basché (to be published).

[19] J. K. Trautman *et al.,* Nature (London) **369**, 40 (1994).

[20] M. Pirotta *et al.,* Chem. Phys. Lett. **250**, 576 (1996).

[21] E. Betzig and R. J. Chichester, Science **262**, 1422 (1993).

[22] M. A. Hines and P. Guyot-Sionnest, J. Phys. Chem. **100**, 468 (1996).

[23] B. O. Dabbousi *et al.* (to be published).

[24] M. Nirmal *et al.,* "Fluorescence Intermittency in Single Cadmium Selenide Nanocrystals" (to be published).

[25] The measured linewidth in FLN is actually a convolution of homogeneous absorption and emission linewidths (Ref. [9]). The extracted linewidth for this size sample is ~6 meV (FWHM).

[26] The largest shifts observed in single QDs are more than 10 times greater than what has been reported for single molecules at cryogenic temperatures [18].

[27] M. Berg *et al.,* Chem. Phys. Lett. **139**, 66 (1987).

[28] A. Sacra and M. G. Bawendi (to be published).

[29] At this power, only those QDs with the highest luminescence efficiency are visible above the background. As a result, the narrowest lines are obtained from overcoated dots. This appears to be an effect of luminescence efficiency and not the result of inherently narrower linewidths. The narrowest standard dot spectra (FWHM = 590 μeV, 39 Å sample) were obtained at 185 $\mathrm{W/cm^2}$.