Photoluminescence spectral switching of single CdSe/ZnS colloidal nanocrystals in poly(methyl methacrylate)

Yaoming Shen,[*] Lin Pang, and Y. Fainman

Electrical and Computer Science Engineering Department, University of California, San Diego, La Jolla, California 92037, USA

Martin Griswold, Sen Yang, L. V. Butov, and L. J. Sham

Department of Physics, University of California, San Diego, La Jolla, California 92037, USA

We investigated emission from single CdSe nanocrystals in poly(methyl methacrylate). A fraction of the nanocrystals exhibited switching between two energy states which had similar total intensities but distinctly different spectra. We found that the characteristic frequency of this spectral shift increased with the pump power. By using the dynamic shift in the spectral position of emission peaks, we were able to correlate peaks from the same nanocrystal. The measured correlation is consistent with assignment of low energy lines to phonon replicas.

PACS number(s): 78.55.Et, 78.67.Bf

I. INTRODUCTION

Semiconductor quantum dots (QDs) have attracted much interest due to their properties of nanoscale quantum confinement. They hold great promise for numerous optoelectronics and photonics applications such as in displays[1] and as biological labels.[2] While there are many possible fabrication methods, semiconductor QDs formed in colloidal solution, called nanocrystal (NC), via chemical synthesis have been shown to be a promising route to QD realization.[3–5] In colloidal solutions, however, NCs are suspended in a solvent, making them less practical for use in the fabrication and integration of photonic and optoelectronic devices. The introduction of such NCs into a solid-state matrix, therefore, is of great interest for numerous applications. We have succeeded in incorporating the NCs into poly(methyl methacrylate) (PMMA) matrix.[6,7] The sensitivity of this composite to electron beams makes it attractive in the fabrication of photonic devices. In this paper, we study the spectra of a single NC in PMMA.

Information concealed by the inhomogeneously broadened photoluminescence (PL) lines has been revealed by the single QD spectroscopy. Two of the observations include fluctuations in PL intensity and peak energy with time—referred to as fluorescence intermittency and spectral diffusion, respectively. Both phenomena have been observed in colloidal NCs and self-assembled QDs.

Fluorescence intermittency has been well studied in colloidal NCs,[8–10] silicon nanocrystals,[11] and some of the self-assembled QDs, including CdSe/ZnSe (Ref. 12) and $Ga_{0.6}In_{0.4}As$ quantum dots in GaAs.[13] The intermittency is reported to display a telegraph signal[10,13–15] where the switching rate can be very slow, with typical time scales of seconds or even minutes. A model based on photoionization has been used to explain the switching for colloidal dots,[8] while for epitaxially grown dots, a model involving a mobile photoactivated defect has been proposed.[14]

Spectral diffusion, especially random switching between discrete levels, has been observed and studied in strain-induced GaAs QDs.[16] It has also been found when colloidal nanocrystals were deposited on gold substrates.[17] In this paper, we show that colloidal CdSe nanocrystals in PMMA also exhibit similar behavior, and we quantify the dependence on excitation power. Also, we observe a jitter of the emission energies of the NCs. Each NC has a characteristic jitter that allows us to identify phonon replicas for single NCs.

II. EXPERIMENT

The sample was prepared by using the colloidal CdSe/ZnS core shell NCs (from Evident Technologies). The CdSe core is about 5 nm in diameter capped by a few-monolayer ZnS shell to increase the quantum yield. A PMMA layer about 200 nm thick was spin coated on a quartz substrate, followed by a spin coat of NCs in toluene, leading to CdSe/ZnS NCs distributed in a PMMA matrix. The final density was chosen to be less than one dot per μm^2.

For PL measurements, the sample was placed into a continuous flow cryostat, and the temperature was kept constant at 7 K by controlling the flow of liquid helium. A diode pumped solid-state laser operating at 532 nm was used for excitation, with power densities typically between 1 and 20 kW/cm^2, and was varied using neutral density filters. The luminescence from the sample was collected through an optical microscope objective (50×, numerical aperture of 0.55) with a long working distance. The collected light was passed through a notch filter, dispersed in a monochromator, and was detected using a liquid-nitrogen-cooled charge-coupled device camera. The spectral resolution of the setup was 200 μeV. Spectra from a single NC were monitored continuously with an integration time that we varied between 500 ms and 30 s depending on the excitation power density and NC brightness.

III. RESULTS

The density of NCs was made so dilute that we typically observed only a single NC in the interrogated spatial and spectral range. We found and investigated several NCs switching between two states. Spectra from a typical switch-
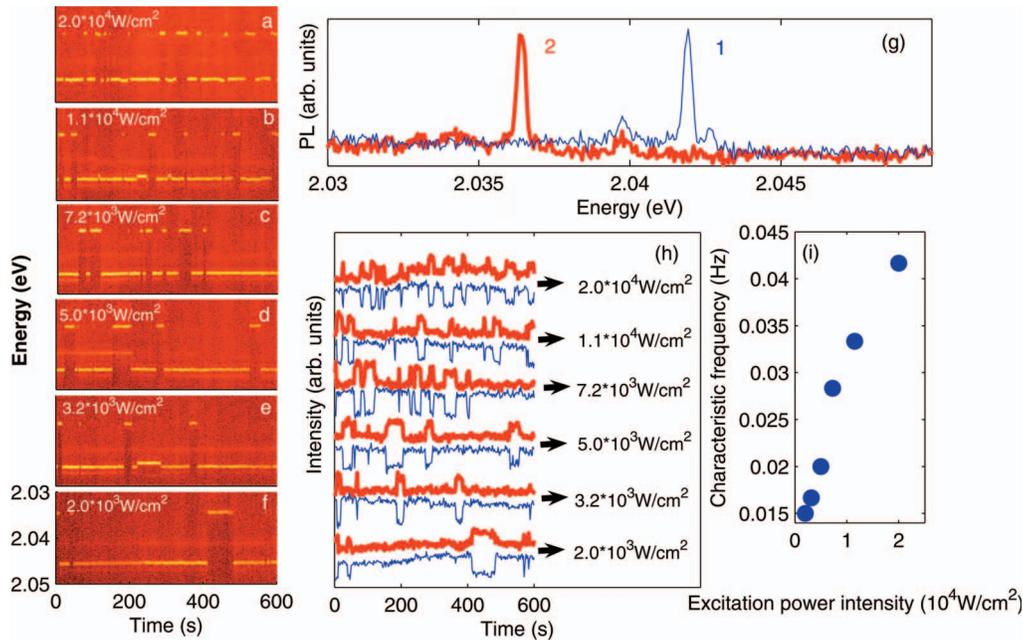
FIG. 1. (Color online) Spectra from a typical switching NC, recorded at six different excitation powers $[(2.0, 3.2, 5.0, 7.2, 11, 20)$ $\times 10^3$ W/cm^2], are shown in order in (a)–(f). The integration time of 2 s is used for this measurement. The brightness represents the intensity, the horizontal axis is time, and the vertical axis is emission energy. (g) The integration for 26 measurements (each measurement having a 2 s integration time) when the NC stays in the same state. The energy difference between the two states is 5.6 meV. (h) The intensity vs time plots for (a)–(f). The (blue) thin line is for the high energy state and the red (bold) line is for the low energy state. (i) The characteristic switching frequency vs excitation power.

ing NC, recorded at six different excitation powers, are shown in Figs. 1(a)–1(f). These spectra were recorded continuously with an integration time of 2 s each. Figure 1(g) shows the typical spectrum of each of the two states. The red line (bold line) is for the lower energy state which we will call state 2, while the blue line (thin line) is for the higher energy state, which we call state 1. The energy difference between the two states is 5.6 meV. Figure 1(h) contains plots of intensity vs time for the data taken from Figs. 1(a)–1(f). Again, the red line (bold line) is state 2 and the blue line (thin line) is state 1. Figure 1(i) is the plot of the characteristic switching frequency (the inverse of the average interval time between switching) vs the excitation power. From Figs. 1(g) and 1(h), we see that there is no sizable change in the integrated PL intensity for the two states. The excitation power density is of the order of 10 kW/cm^2, which is similar to that used for measurements with InP QDs.[18]

Figure 1 shows that the switching frequency increases with increasing excitation power density. Since the widths of both state plateaus decrease with increasing excitation power, we can conclude that the transitions between the two states are light induced.

Some NCs were observed to operate outside of the two-state description. We found NC switching among three levels or more.

We also observed some NCs exhibiting random energy shifts, similar to the behavior seen for those NCs without PMMA.[8] In Fig. 2, we analyze a series of 1500 spectra taken in intervals of 0.5 s. The spectrum peak is seen to wander randomly.

Some NCs were observed to abruptly become dark after continuous illumination and did not recover in the time under measurement (where the longest time we monitored was 2 h).
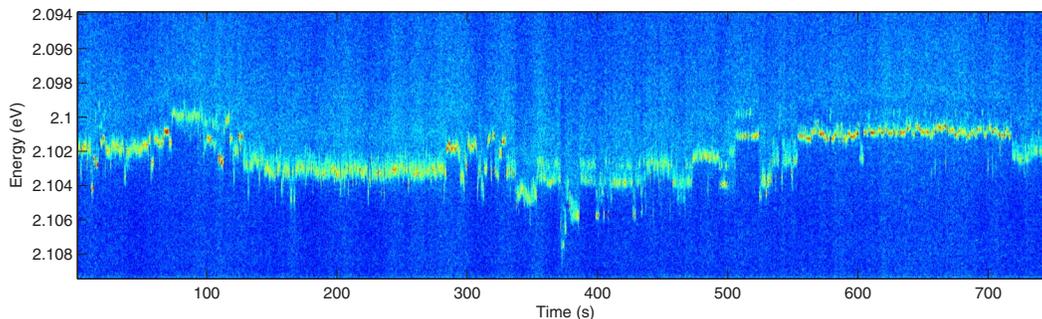

FIG. 2. (Color online) Spectra from another NC were recorded continuously with an integration time of 0.5 s. The emission peak randomly shifts with small energy changes between 2.099 and 2.108 eV.
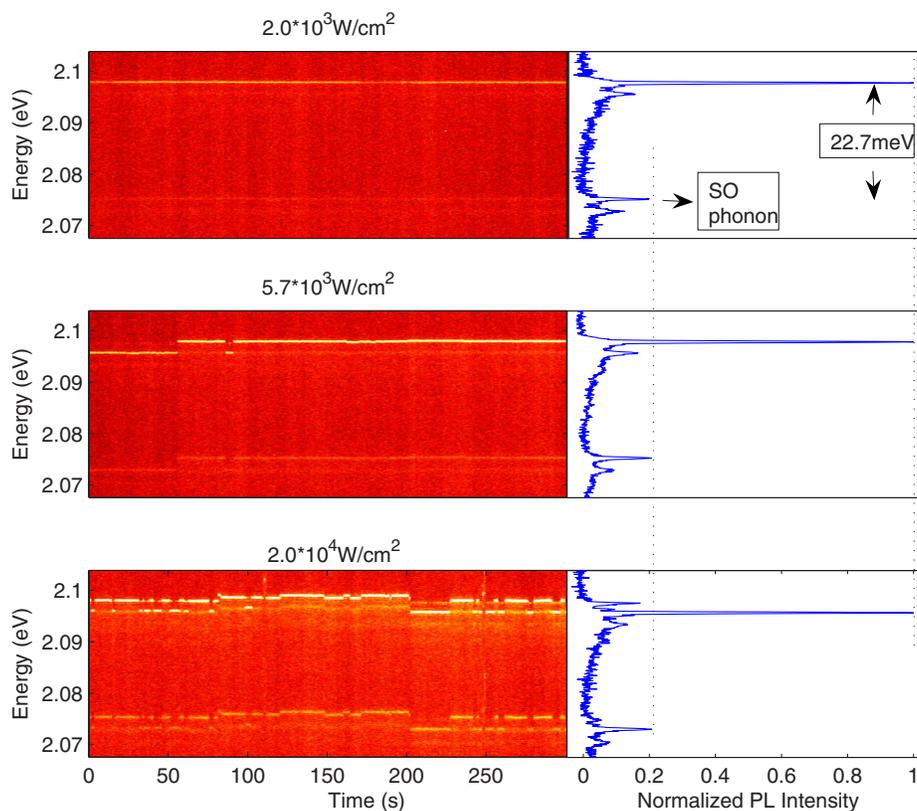
FIG. 3. (Color online) Spectra from a NC were recorded continuously with an integration time of 2 s each. (a)–(c) show that in some NCs, higher laser intensity not only increases the switching frequency but also makes the states move randomly. In addition, the figure shows that there is an additional peak in the lower energy side. The energy difference from the exciton peak is 22.7 meV.

Figures 3(a)–3(c) show that in some NCs, higher laser intensity not only increases the switching frequency but also makes the states move randomly. In addition, the figure shows that there is an additional peak in the lower energy side with the energy difference 22.7 meV. The energy shifts of the lines are correlated; therefore, we infer that these lines come from a single NC. The right side of Figs. 3(a)–3(c) shows the normalized spectrum at each laser intensity, respectively. The ratio of the side-peak intensity to the exciton-peak intensity remains constant when the pump intensity changes.

In order to observe more spectral lines, we integrated for over 30 s each frame in Fig. 4. We recorded 200 measurements continuously with constant temperature and excitation power. Again, the energy shifts of the lines are correlated; therefore, we conclude that these lines come from a single NC. The energy differences between the main line and the satellite lines are 22.7 and 25.8 meV, respectively. Also, we can see more lines on the lower energy side. The energy differences with the main line are 45.4 and 48.5 meV, respectively. We attributed the side peaks to phonon replicas and identified them as the lines from surface optical (SO) phonons, longitudinal optical (LO) phonons, two SO phonons, and one SO plus one LO phonons; see Sec. IV.

IV. DISCUSSION

The blinking behavior of CdSe/ZnS NCs has attracted much scientific attention.[8–10] In these papers, it was found that the statistics of fluorescence intermittency in single CdSe NCs exhibits a power-law distribution in the histogram of on and off times, i.e., the time period before the NC turns from emitting to nonemitting (bright to dark) and vice versa. Every NC shows a similar power-law behavior for the off-time distribution regardless of temperature, excitation intensity, surface morphology, or size.[19] In our observation of spectral shifts, the PL does not completely turn off (within the time resolution of the measurement), which could be caused by the surrounding PMMA matrix. The spectral shift is dominant most of the time.

Besides the normally observed random spectral shifts (Fig. 2), we have found large abrupt spectral jumps between two states. The two emission peaks in Fig. 1(g) seldom emit together within our integration time, which excludes the possibility of biexciton emission and phonon replicas. If a biexciton was created, we would observe both lines within the recombination times which are much shorter than our integration time as the biexciton relaxes to the exciton radiatively, followed by exciton emission. The same observation applies to phonon replicas.

In 2002, Shimizu et al. found a spectral shift between two positions when they put CdSe/ZnS NCs on a rough metal surface.[17] The emission energy fluctuates within 15–25 meV. The authors suggested that the observed emission shifts were caused by neutral (X) and charged (X′) exciton emissions from a single NC. Theoretical calculation indicated that the charged NC could emit 25 meV lower in
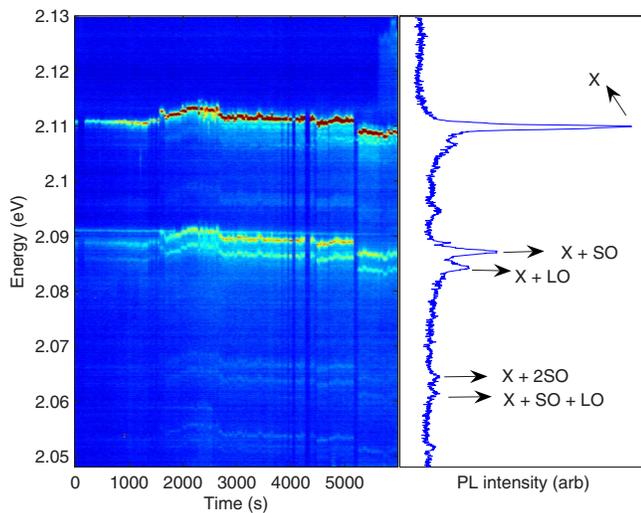
FIG. 4. (Color online) Spectra from a NC were recorded continuously with an integration time of 30 s each and constant temperature and excitation power. We used a 30 s integration time for each frame to see the lower energy peaks which are weaker than the exciton peak. Spectrum jitter allows us to group spectral transitions from individual NCs. The energy differences between the main line and the satellite lines are 22.7, 25.8, 45.4, and 48.5 meV.

energy than the neutral exciton.[20] These values are different from our result, since the energy spacing in our experiments between two positions is 5.6 meV or smaller.

Similar spectral switching behavior has also been observed in InP quantum dots in a $Ga_xIn_{1-x}P$ matrix grown by metal-organic vapor-phase epitaxy.[18] The authors found that the quantum dot spectrum switched between two states which had the same integrated PL, similar to our result. The difference is that each state has multiple lines in the experiment.

Bawendi and co-workers proposed a model to explain the CdSe NC fluorescence intermittency.[8,21] A charged NC was taken to be a dark NC. The transition back to a bright NC occurred through recapture of the initially localized electron (or hole) in the NC core or through capture of another electron (or hole) from nearby traps. We adopt this model to explain the spectral switching and assume that there are two metastable states of the NC which are connected with the charging and discharging of a metastable trap in the host matrix close to the NC. The Stark shifts caused by the charge could explain the two spectra we observed.

The observed lower energy peaks can originate from SO phonons or LO phonons in the NCs. The energies of the SO

modes Ω_{SO} are determined by the energy of the TO phonons Ω_{TO} in CdSe NCs, the shape of the NCs, and the dielectric constants of the core and surrounding medium. For spherical NCs the classical dispersion relation for the interface phonons is given by the following equation:[22]

$$\Omega_{SO} = \Omega_{TO} \left[\frac{\varepsilon_0 l + \varepsilon_M(l+1)}{\varepsilon_\infty l + \varepsilon_M(l+1)} \right]^{1/2}, \qquad (1)$$

where ε_0 and ε_∞ are the static and high-frequency dielectric constants of the bulk CdSe and ε_M is the static dielectric constant of the surrounding medium. Only SO phonons with ℓ=even integers are allowed (SO phonons with ℓ=odd integers are forbidden). By using the bulk CdSe values of Ω_{TO} =167.5 cm^{-1}, ε_0=9.3, ε_∞=6.1,[23] and the dielectric constant of hexagonal ZnS, ε_M=8.3, we have calculated for the lowest (ℓ=2) and the infinite limit ($\ell \to \infty$) modes of spherical CdSe NC values of $\Omega_{SO}^{l=2}$=180 cm^{-1} (22.4 meV) and $\Omega_{SO}^{l=\infty}$ =185 cm^{-1} (23.0 meV), respectively. The calculated energy is close to the experimental value (22.7 meV).

LO-phonon energy of 25.8 meV is smaller than the bulk value of 26.1 meV,[24] and is in good agreement with the values expected from theory for a 2.5 nm radius CdSe NC, which are in the range 23.8–26.0 meV for the first four LO phonons.[25]

The Huang-Rhys factors (electron-phonon coupling strength) can be roughly estimated from the ratio between integrated intensities of the 2SO and SO lines. We obtained a value of $S \approx 0.2$.

V. CONCLUSIONS

We have investigated random switching between two states in the PL from CdSe/ZnS colloidal nanocrystals in PMMA. The spectral switching and spectral diffusion behaviors are similar to what has been observed in III-V quantum dots.[16,18] They may be explained within the model of Bawendi and co-workers.[8,21] The lower energy lines are identified as phonon replicas of the exciton transition involving local SO-phonon and LO-phonon modes of the NC. The Huang-Rhys factor is found to be $S \approx 0.2$.

*ymshen@ucsd.edu

[1] V. Colvin, M. Schlamp, and A. Alivisatos, Nature (London) **370**, 354 (1994).

[2] M. Bruchez, M. Morone, P. Gin, S. Weiss, and A. P. Alivisatos, Science **281**, 2013 (1998).

[3] Y. Wang, A. Suna, W. Mahler, and R. Kasowski, J. Chem. Phys. **87**, 7315 (1987).

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

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

[6] L. Pang, Y. Shen, K. Tetz, and Y. Fainman, Opt. Express **13**, 44 (2005).

[7] L. Pang, K. Tetz, Y. Shen, C. Chen, and Y. Fainman, J. Vac. Sci.

Technol. B **23**, 2413 (2005).

[8] M. Nirmal, B. O. Dabbousi, M. G. Bawendi, J. J. Macklin, J. K. Trautman, T. D. Harris, and L. E. Brus, Nature (London) **383**, 802 (1996).

[9] F. D. Stefani, W. Knoll, M. Kreiter, X. Zhong, and M. Y. Han, Phys. Rev. B **72**, 125304 (2005).

[10] A. L. Efros and M. Rosen, Phys. Rev. Lett. **78**, 1110 (1997).

[11] I. Sychugov, R. Juhasz, J. Linnros, and J. Valenta, Phys. Rev. B **71**, 115331 (2005).

[12] V. Türck, S. Rodt, O. Stier, R. Heitz, R. Engelhardt, U. W. Pohl, D. Bimberg, and R. Steingrüber, Phys. Rev. B **61**, 9944 (2000).

[13] N. Panev, M.-E. Pistol, V. Zwiller, L. Samuelson, W. Jiang, B. Xu, and Z. Wang, Phys. Rev. B **64**, 045317 (2001).

[14] M.-E. Pistol, P. Castrillo, D. Hessman, J. A. Prieto, and L. Samuelson, Phys. Rev. B **59**, 10725 (1999).

[15] M.-E. Pistol, Phys. Rev. B **63**, 113306 (2001).

[16] D. Bertram, M. C. Hanna, and A. J. Nozik, Appl. Phys. Lett. **74**, 2666 (1999).

[17] K. T. Shimizu, W. K. Woo, B. R. Fisher, H. J. Eisler, and M. G. Bawendi, Phys. Rev. Lett. **89**, 117401 (2002).

[18] N. Panev, M. E. Pistol, J. Persson, W. Seifert, and L. Samuelson, Phys. Rev. B **70**, 073309 (2004).

[19] K. T. Shimizu, R. G. Neuhauser, C. A. Leatherdale, S. A. Empedocles, W. K. Woo, and M. G. Bawendi, Phys. Rev. B **63**, 205316 (2001).

[20] A. Franceschetti and A. Zunger, Phys. Rev. B **62**, R16287 (2000).

[21] K. T. Shimizu and M. G. Bawendi, in *Semiconductor and Metal Nanocrystals: Synthesis and Electronic and Optical Properties*, edited by V. I. Klimov (Dekker, New York, 2004), p. 224.

[22] A. V. Fedorov, A. V. Baranov, and K. Inoue, Phys. Rev. B **56**, 7491 (1997).

[23] *Semiconductors*, edited by O. Madelung, W. von der Osten, and U. Rössler, Landolt-Börnstein, New Series, Group III, Vol. 22, Pt. A (Springer, Berlin, 1982).

[24] *Semiconductors. Physics of II-VI and I-VII Compounds, Semimagnetic Semiconductors*, edited by K. H. Hellwege, Landolt-Börnstein, New Series, Group III, Vol. 17, Pt. B (Springer-Verlag, Berlin, 1982).

[25] C. Trallero-Giner, A. Debernardi, M. Cardona, E. Menéndez-Proupín, and A. I. Ekimov, Phys. Rev. B **57**, 4664 (1998).