Emission from single CdSe nanocrystals in PMMA was investigated. A fraction of the nanocrystals exhibiting switching between two energy states, which have similar total intensities, but distinctly different spectra were observed. We found that the spectral shift characteristic frequency increases 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 numbers:

I. INTRODUCTION

Semiconductor quantum dots (QDs) have attracted much interest due to their properties of nanoscale quantum confinement that posses great promise for numerous optoelectronics and photonics applications including displays [1], and biology [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, 4, 5]. In colloidal solutions, however, NC’s are suspended in a solvent, making them less practical for fabrication and integration of photonic and optoelectronic devices. The introduction of such NC’s into a solid-state matrix, therefore, is of great interest for numerous applications. We have succeeded in incorporating the NC’s 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 article, we particularly studied the spectra of a single NC in PMMA. It’s useful for the future application of a single NC in PMMA photonics devices.

Novel information, concealed by the inhomogeneously-broadened photoluminescence (PL) lines, has been revealed by a single QD spectroscopy. Two of the observations include fluctuations in PL intensity and peak energy with time referred to as fluorescence intermittency and spectrum diffusion, respectively. Both phenomena have been observed in colloidal NC and self-assembled QD’s.

Fluorescence intermittency has been well studied in colloidal NC’s [8, 9, 10], silicon nanocrystals [11], and some of the self-assembled QD’s, including CdSe/ZnSe [12], and Ga0.6In0.4As quantum dots in GaAs [13]. The intermittency is reported to display a telegraph signal [13, 14, 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 [9], while for expitaxially grown dots, a model involving a mobile photoactivated defect has been proposed [14].

Spectrum diffusion, especially random switching between discrete levels, has been observed and well studied in some self-assembled systems: InAs/GaAs QD’s [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 explicitly quantify the dependence on excitation power. Also a jitter of the emission energies of the NC’s was observed. The jitter is characteristic for each NC and allow us to identify phonon replicas for single NC’s.

II. EXPERIMENT

The sample was prepared by using the colloidal CdSe/ZnS core shell NC’s (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 of about 200 nm thick was spin coated on a quartz substrate, followed by a spin coat of NC’s in toluene, leading to CdSe/ZnS NC’s distributed in a PMMA matrix. The final density was chosen to be less than one dot per µm².

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 1-20 kW/cm$^2$, and was varied using neutral density filters. The luminescence from the sample was collected through an optical microscope objective (50x, numerical aperture 0.55) with a long working distance. This collected light passed through a notch filter, dispersed in a monochromator, and was detected using a liquid-nitrogen-cooled charge-coupled device (CCD) camera. The spectral resolution of the setup was 200 µeV. Spectra from a single NC were monitored continuously with an integration time varied between 500 ms and 30 s depending on the excitation power density and NC brightness.

The density of NC’s was made so dilute that we typically observed only a single NC in the interrogated spatial and spectral range. We found and investigated several NC’s switching between two states. Spectra from a typical switching NC, recorded at six different excitation powers, are shown in order in (a)-(f). These spectra are recorded continuously with an integration time of 2 s each. The grey scale plot represents intensity, while the horizontal axis is time, and the vertical axis is emission energy. Fig. 1(g) shows the typical spectrum for 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. Fig. 1(h) is a plot of intensity vs. time for data taken from Fig. 1(a)-1(f). Again, the red line (bold line) is state 2 and the blue line (thin line) is state 1. Fig. 1(i) is the plot of the characteristic switching frequency vs excitation power.

III. RESULTS
FIG. 2: (color online) (a) Spectra from another NC were recorded continuously with an integration time of 0.5 s. The emission peak randomly shifts with small freq. changes between 2.099 eV and 2.108 eV. (b) Energy shift from one measurement to the next measurement is compared with a Lorentz distribution.

FIG. 3: (Color online) Spectra from a third NC were recorded continuously with an integration time of 2 s each. Figure 3(a-c) shows in some NC’s, higher laser intensity not only increases the switching frequency, but also makes the states moving randomly. In addition, the figures show there is an additional peak in lower energy side. The energy difference with the exciton peak is 22.7 meV.

age time) vs excitation power. From Fig. 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 QD’s [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 from the two states are light induced.

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

We also observed some NC’s exhibiting random energy shifts, similar to behavior seen for those NC’s without PMMA [9]. 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. The energy change for the two neighbor spectrum can be approximated by a Lorentz[see Figs. 2(b)]

Some NC’s can be permanently quenched after a period of time. These NC’s suddenly become dark after continuous illumination and do not recover in the measurement time (the longest time we monitored was 2 hours).

Figure 3 (a-c) shows that in some NC’s, higher laser intensity not only increases the switching frequency, but also makes the states moving randomly. In addition, the figures show that there is an additional peak in lower energy side with the energy difference 22.7 meV. The energy of the lines are shifting in step. Therefore, we infer that these lines come from a single NC. The right side of Figure 3(a-c) shows the normalized spectrum respectively. We attribute the side peaks to phonon replicas since the ratio of its intensity to the exciton intensity remains constant when the pump intensity changes.

In order to observe more spectral lines, we integrated over 30 second for each frame in figure 4. We record 200 measurements continuously with constant temperature and excitation power. Again the energy shifts of the lines are correlated, and therefore, we conclude that these lines come from a single NC. The energy difference between the main line and the satellite lines are 22.7 meV 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 meV, 48.5 meV respectively. We 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 section IV.

IV. DISCUSSION

The blinking behavior of CdSe/ZnS NC’s has attracted much scientific attention [8, 9, 10]. Through this body of work, it was found that the statistics of fluorescence intermittency in single CdSe NC’s exhibit 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 dis-
distribution regardless of temperature, excitation intensity, surface morphology or size [19]. In our experiment, the blinking behavior does not play a major role, 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. 2a), we have found large abrupt spectral jumps with more than one energy change. The two emission peaks in Fig. 1(g) seldom emit together within our integration time, which excludes the possibility of biexciton emission and optical phonon progressions. If a biexciton were created, we would observe both lines simultaneously within our integration time as the biexciton relaxes to the excitation radiatively, followed by exciton emission. The same observation applies to optical phonon replicas.

In 2002, Bawendi’s group also found a spectral shift between two positions when they put CdSe/ZnS NC on rough metal surface. The emission energy fluctuates with a spacing of 15-25 meV [17]. They suggested that the observed emission shifts were caused by neutral (X) and charged (X') exciton emission from a single NC. However, theoretical calculation indicated that the charged NC could emit 25 meV to the red of the neutral exciton emission [20]. Both are different from our result since our energy spacing between two positions is 5.6 meV or smaller.

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

We conclude that the spectral shift is a universal behavior for all quantum dots of III-V and II-IV compound self-assembled QD’s and colloidal nanocrystals. A new theory is needed to explain this behavior.

The observed peaks in lower energy can originate from surface optical (SO) phonons or longitudinal optical (LO) phonons in the NC’s. The energies of the SO modes, $\Omega_{SO}$, are determined by the energy of the TO phonons, $\Omega_{TO}$, in CdSe NC’s, the shape of the NC’s, and the dielectric constants of the core and surrounding medium. For spherical NC’s the classical dispersion relation for interface phonons can be presented by the following equation [21]:

$$\Omega_{SO} = \Omega_{TO} \left[ \epsilon_0^l + \epsilon_M^l(l+1) \right]^{1/2}$$

(1)

where $\epsilon_0$ and $\epsilon_\infty$ are the static and high-frequency dielectric constants of the bulk CdSe and $\epsilon_M$ is the static dielectric constant of the surrounding medium. Solely SO-phonons with $\ell=$even integers are allowed (SO-phonons with $\ell=$odd integers are forbidden). By using the bulk CdSe values of $\Omega_{TO} = 167.5 \text{ cm}^{-1}$, $\epsilon_0 = 9.3$, $\epsilon_\infty = 6.1$ [22] and the dielectric constant of hexagonal ZnS $\epsilon_M = 8.3$, we have calculated for the lowest ($\ell=2$) and the highest ($\ell\rightarrow \infty$) modes of spherical CdSe NC’s values of $\Omega_{SO}^{23}= 180 \text{ cm}^{-1}(22.4 \text{ meV})$ and $\Omega_{SO}^{26}= 185 \text{ cm}^{-1}(23.0 \text{ meV})$, respectively. The calculated energy is close to the experiment value (22.7 meV).

LO phonon energy 25.8 meV is smaller than the bulk value of 26.1 meV [23], and is in good agreement with the values expected from theory for a 25Å radius CdSe nano-crystal, which are in the range 23.8-26.0 meV for the first four LO phonons. [24]

The Huang-Rhys factors (electron-phonon coupling strength) can be roughly estimated from ratio between integrated intensities of the 2SO and SO lines. We have obtain 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 commonly observed blinking behavior was suppressed. The spectrum switching behaviors are dominant and some of them are similar to what has been observed in III-V quantum dots. To explain these observations new models going beyond those established in the literature need to be developed. We also found the random energy shift which follows approximately a Lorentzian distribution. Identical jitter patterns allow the unambiguous identification of the emission spectra of single NC’s. By means of excitation density dependent spectroscopy the lines are identified as phonon replica of...
the exciton transition involving local SO-phonon and LO-phonon modes of the NC. Huang-Rhys factors of $S \approx 0.2$ are observed.

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