Surface-Enhanced Emission from Single Semiconductor Nanocrystals

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The fluorescence behavior of single CdSe(ZnS) core-shell nanocrystal (NC) quantum dots is dramatically affected by electromagnetic interactions with a rough metal film. Observed changes include a fivefold increase in the observed fluorescence intensity of single NCs, a striking reduction in their fluorescence blinking behavior, complete conversion of the emission polarization to linear, and single NC exciton lifetimes that are $> 10^3$ times faster. The enhanced excited state decay process for NCs coupled to rough metal substrates effectively competes with the Auger relaxation process, allowing us to observe both charged and neutral exciton emission from these NC quantum dots.

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Metallic interfaces play a complex role in the basic interactions of an electromagnetic field with optically active materials. For example, smooth metallic surfaces reduce the radiation from nearby organic dyes through nonradiative energy transfer [1], while molecules adsorbed onto metallic electrodes [2] show orders of magnitude increase in surface-enhanced Raman signals. Colloidal semiconductor nanocrystal (NC) quantum dots are generating increasing interest because of their nature as "customizable" chromophores that can be tailored to absorb or emit light anywhere in the visible spectrum and beyond [3]. Yet, there is little known about chromophore-metal surface interactions for colloidal semiconductor NCs. Recent advances in single molecule detection offer an opportunity to probe and understand the details of optical quenching or enhancement, details that are hidden in ensemble experiments by sample inhomogeneity [4,5]. Furthermore, there is continued interest in increasing the maximum rate of photons emitted as well as in understanding the sensitivity of NC chromophore properties to their immediate environment. Such advances would help to better implement NCs in biological and solid-state device applications. In this Letter, we combine a study of NC-metal surface interactions with single molecule detection methods to show that novel photophysics emerges from having a NC next to a rough metal surface. We find that radiative and nonradiative relaxation rates are strongly affected and that the usually dominant Auger nonradiative relaxation channel is no longer competitive. We focus on single CdSe(ZnS) NC investigations that reveal surface-enhanced exciton fluorescence via an electromagnetic interaction with the gold surface plasmon. This intensity enhancement can reach fivefold and is accompanied by dramatic changes in the dynamic optical behavior (blinking [6,7] and spectral diffusion [8]), the emission polarization, and the fluorescence lifetime. Surface-enhanced fluorescence experiments at cryogenic temperatures on single NCs show that (i) blinking effects are dramatically diminished and (ii) emission energy jumps now follow the same statistical behavior as the blinking behavior of NCs on nonmetallic substrates. These results suggest that the ionization mechanism usually responsible for blinking remains, but emission from both charged and neutral excitons in individual nanocrystals is now observed.

We used far-field photoluminescence microscopy to investigate the surface enhancement properties of the fluorescence in single CdSe(ZnS) NCs on rough gold surfaces. The substrates were fabricated by thermal evaporation of titanium/gold (20 nm/120 nm) on silicon wafers followed by electrochemical etching. Atomic force microscopy studies confirmed the formation of rough valleys and peaks with 10–50 nm size features. CdSe(ZnS) core-shell nanocrystals were synthesized following the methods in Refs. [9,10]. Single NCs were dispersed by spin-coating dilute samples directly onto the gold substrates, and the 514 nm line of an Ar ion cw laser was used for sample excitation. Further instrumental details are described elsewhere [8].

Initial experiments of CdSe(ZnS) NCs on *smooth* gold substrates showed an immediate quenching of the luminescence, a behavior that has been well documented with various organic dye molecules. We observed an increase in the number of emitting individual NCs as we increased the surface roughness while keeping the (dilute) concentration of NCs constant. Of the detectable NCs, we typically measured a threefold to fivefold increase in the fluorescence intensity [Fig. 1(a)], as compared to the same NCs placed on crystalline quartz substrates under identical conditions. Furthermore, the duration of "on" times increases to a point where the frequency of blinking events appreciably diminishes. A large distribution of NC/gold coupling strengths exists as some NCs show as much as a fivefold increase in fluorescence intensity, while other NCs show diminished fluorescence.

Figure 1(b) shows the dynamic behavior observed for single CdSe(ZnS) NCs at 10 K on quartz substrates [11]. The optical fluctuations include the *on-off* blinking of the emission intensity as well as large and small continuous spectral shifts. In Fig. 1(c), the low temperature emission

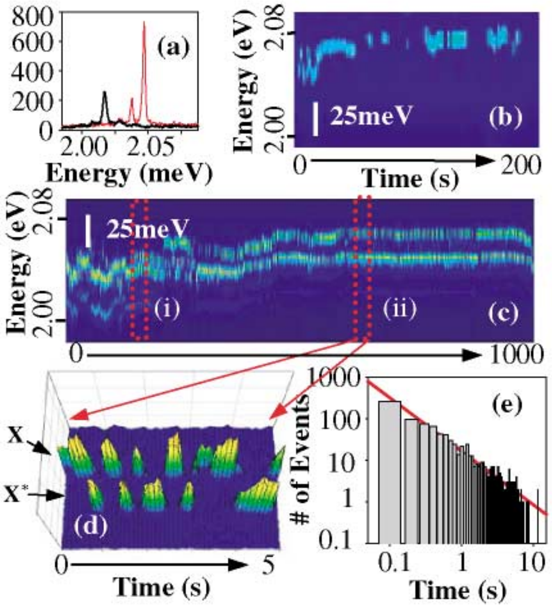

FIG. 1 (color). (a) shows the relative intensity of the emission peaks between normal (black line) and enhanced (red line) NCs. A spectral diffusion trajectory of a single CdSe/ZnS nanocrystal (b) in poly(methyl-methacrylate) polymer on quartz substrate and (c) on a roughened gold surface with no polymer matrix. (a)–(c) taken with 100 ms integration time and 514 nm cw laser excitation (200 W/cm^2). The magnified spectrum in (d) shows the clear binary shifts with the proposed charged and neutral exciton peaks labeled in (c). Statistical distribution of the time intervals in between discrete spectral shifts. (e) shows histograms of the "wait" time distribution plotted on a log-log scale. The straight line is a best-fit curve to a power law ($P = t^{\alpha}$) where $\alpha = -1.4$.

from a single NC interacting with the rough gold surface is shown. The spectral shifts occur more frequently as discrete shifts and there is no "off" behavior during the entire scan. We can identify two categories of spectral shifts that are present: the first type is *binary* with energies ranging from 10–22 meV and the second type is a more continuous, small shift that appears random in direction and magnitude. This behavior was observed over many (> 50) NCs on many similarly prepared substrates. Previous work analyzing the statistics of the fluorescence intermittency (blinking) showed that the *on* and *off* times follow a universal power-law distribution: every single CdSe(ZnS) NC blinks *on* and *off* and follows a power-law distribution in the histogram of on- and off-time durations [12,13]. This power law was attributed to the statistics of the tunneling kinetics of an extra charge between localized and delocalized states of the NC. Similarly, we measure the time intervals between spectral jumps for the NCs coupled to the gold substrates. We plot a histogram of these wait times in Fig. 1(c). Apparent in the log-log plot, we see that the distribution of wait times also shows a power-law distribution. Moreover, the exponent of the power is -1.4, similar to the results seen in previous blinking studies (-1.5 exponent).

To verify the NC/surface interaction, we also probed the emission polarization. The symmetry of the CdSe NC shape and crystal structure gives rise to a doubly degenerate emitting state with a two-dimensional emission polarization [14]. Figure 2 shows RT NC images monitoring the emission polarization of the NC/gold system. The surface interaction results in a conversion of the NC emission from a degenerate to a nondegenerate linear dipole. All of the NCs show emission polarization consistent with a linear dipole at 10 K and at room temperature; the emission polarization is easily measured at room temperature due to the decrease in blinking that would normally result in large intensity fluctuations [15]. The polarization change is not an artifact of the experimental setup as the phase from individual NCs differs from that of the laser and from that of nearby NCs.

Finally, we measured the exciton lifetime for NCs interacting with the gold surface. Figure 3(a) shows 40 single CdSe(ZnS) NC exciton lifetimes at 10 K simultaneously. These individual NCs were easily imaged and fluorescence lifetimes as fast as 130 ps were measured. The black trace in Fig. 3(b) shows the lifetime of an ensemble CdSe(ZnS) NC film at 10 K; although multiexponential, the lifetime is roughly on the order of 200 ns. Previous fluorescence lifetimes have been reported as ~150 ns at 10 K [16].

The blinking model suggests that fast Auger relaxation rates [6,17] are responsible for quenching the emission from charged exciton in CdSe NCs. Theoretical predictions indicate that if the emission were observable, the charged NC should emit 25 meV to the red of the neutral exciton emission [18]. In the context of our results, we propose that the observed binary emission shifts are caused by neutral (X) and charged (X^*) exciton emission from a single NC for the following reasons: First, the binary shifts in the emission energy fluctuate between two positions with a spacing of 15–25 meV. Second, these

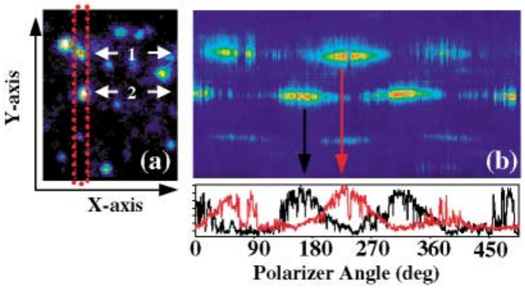

FIG. 2 (color online). RT images monitoring the emission polarization of a single NC coupled to gold substrates. (a) A single NC image averaged over ten frames. (b) Emission polarization of single NCs while the linear analyzer is rotated continuously during the scan. Data taken with 100 ms integration time and 150 W/cm^2 laser excitation.

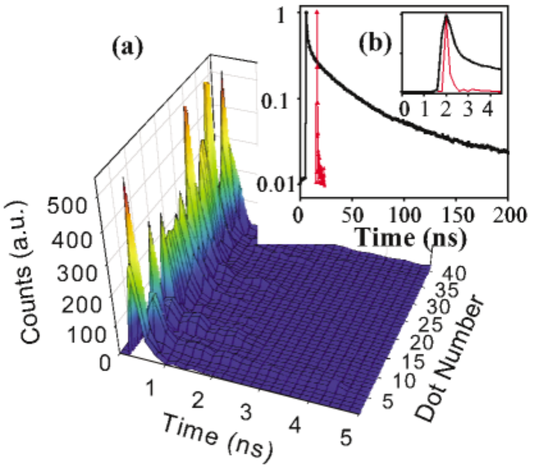

FIG. 3 (color). Photodecay scan taken with a gated, intensified CCD camera (LaVision Picostar) with 533 nm, ps-pulsed excitation, 300 W/cm^2 (Coherent Mira/OPO) at 10 K. (a) A 3D plot showing the decay of 40 individual NCs taken simultaneously. (b) Comparison of time scales between the lifetime of an ensemble film (black) and a single CdSe/ZnS NC interacting with the gold substrate (red); the two decays are offset in time for ease in comparison. The inset shows the same curves in a linear plot for the first 5 ns, now superimposed in time.

shifts are not optical phonon progressions since the two emissions seldom emit together within our integration bin time. This also excludes the possibility of biexciton emission. If a biexciton were created, we would observe both lines simultaneously within our integration time as the biexciton relaxes to the exciton radiatively, followed by exciton emission [19]. A charged exciton, on the other hand, would relax to a charged NC, which can persist for many seconds or longer. Third, and possibly the most significant, the statistics of the dynamics between the two emissive states follows a power-law distribution matching that of the kinetics observed in previous blinking studies.

When we examine the magnitudes of the binary shifts ($X \rightarrow X^*$), we observe that there is a correlation between the spectral position of the high-energy peak (label X in Fig. 1(d)) and the size of the energy jump (ΔE) from X to X^*. In Fig. 1(c), the region marked (i) has $\Delta E \approx 10$ meV with the spectral position of X at 2.04 eV, whereas the region marked (ii) has ≈ 22 meV with the spectral position of X at 2.065 eV. A change in the local electric field and the appearance of mirror changes in the metal will cause a Stark shift [20] of both X and X^*, but theses shifts need not be identical, hence the varying ΔE values.

The source of the fluorescence intensity enhancement can be explained through previous studies on surface-enhanced fluorescence and Raman scattering. Although many models persist in the literature, a leading contributor to the surface-enhanced behavior is the electromagnetic model [21]. Simply, the rough corrugation of the surface is approximated by ellipsoids that scatter the incident electromagnetic field. A dipole near the surface of this ellipsoid interacts with both the incident and the scattered field; however, the coupling of the scattered field to the dipole can become much larger than the incident field when the dipole frequency is near resonance with the metal surface plasmon. Other factors such as the shape of the rough features lead to further enhancement, i.e., the lightning rod effect [22]. In the case of radiative dipoles (i.e., organic dye molecules or semiconductor nanocrystals) two competing factors determine the overall enhancement of the luminescence intensity [23]: increased absorption and emission due to the coupling of the radiative mode of the transition dipole with the metal plasmon, and nonradiative energy transfer from the excited dipole to the metal. We examine our observed enhancement factor in the context of this model. We define the quantum yields for NCs coupled (Y) and uncoupled (Y_{free}) to the metal surface as follows:

$$Y = \frac{k_{\text{r}}}{k_{\text{r}} + k_{\text{nr}}}, \tag{1a}$$

$$Y_{\text{free}} = \frac{k_{\text{r-free}}}{k_{\text{r-free}} + k_{\text{nr-free}}}, \tag{1b}$$

where k_{r} is the radiative rate and k_{nr} is the nonradiative rate for the nanocrystal. The excited state lifetime of the NC is $\tau = (k_{\text{r}} + k_{\text{nr}})^{-1}$. To take into account the increase in absorption, we relate the change in the intensities by an enhanced intensity factor γ,

$$\gamma = \frac{Y\sigma}{Y_{\text{free}}\sigma_{\text{free}}}, \tag{2}$$

where σ is the effective absorption cross section of the NC/metal system (σ_{free} is for the uncoupled NC). Finally, we make an order of magnitude approximation following Ref. [22] that assumes similar enhancements in cross sections for both absorption and emission; $(\sigma/\sigma_{\text{free}}) = g(\omega_{\text{ex}}) \approx g(\omega_{\text{fl}}) = (k_{\text{r}}/k_{\text{r-free}})$, where $g(\omega)$ is the rate enhancement function, and ω_{ex} and ω_{fl} are the excitation and emission frequencies, respectively. By rearranging terms,

$$\frac{k_{\text{r}}}{k_{\text{r-free}}} = \sqrt{\gamma \frac{\tau_{\text{free}}}{\tau}} \tag{3}$$

and

$$\frac{k_{\text{nr}}}{k_{\text{nr-free}}} = \frac{\frac{\tau_{\text{free}}}{\tau} - Y_{\text{free}}\sqrt{\gamma \frac{\tau_{\text{free}}}{\tau}}}{1 - Y_{\text{free}}}. \tag{4}$$

By applying the measured values $\gamma = 5$, $\tau_{\text{free}} = 150$ ns [16], $\tau = 130$ ps, and $Y_{\text{free}} = 0.3$, we obtain radiative rate and absorption cross-section enhancements of $\sim$70 and a nonradiative rate enhancement of $\sim$1400. While the apparent quantum yield of the NC is lower in the surface-enhanced system, the enhancement factors are large enough that we still see an overall increase in intensity.

The linear polarization in the emission is also consistent with a surface coupled electromagnetic model tht breaks the degeneracy in the symmetry of the free NCs. The linear polarization results primarily from the electric dipole polarization of the metal that couples to the NC radiation.

How do we observe emission from charged nanocrystals? The blinking of single NCs is due to an Auger relaxation process that competitively inhibits radiative relaxation when the NC is charged [24]. However, by increasing the nonradiative decay rate, the Auger rate (~ 147 ps for 2.8 nm radius at RT) [25] is no longer the rate-determining step in the excited state relaxation process. Despite the ~1400-fold increase in the nonradiative rate, the neutral and charged NCs both show emission due to the combination of an increased radiative and absorption rate; the only distinction for the charged emission is the shifting of the emission energy by the binding energy of the extra charge. According to calculations in Ref. [18], the binary, discrete redshift in emission observed here is predicted to be similar whether it is an electron or hole that is involved in the charging process.

The observation of some room temperature blinking in NCs coupled to the gold substrate may be an indication of mobile NCs. That is, if the NC can move on the surface of the substrate, the distance and orientation of the NC on the metal substrate can change in time, leading to significant changes in the decay rates. We have previously observed mobile NCs in trioctylphosphine-rich films that diffuse a few microns within 1 sec.

Our results strongly suggest that we have observed emission from *charged* single CdSe(ZnS) NCs. The same mechanism for giant enhancements observed in surface-enhanced Raman and surface-enhanced fluorescence effects for molecular species are presented here in the context of single NC optical dynamics. By dramatically decreasing the NC lifetimes, the charged exciton relaxation has crossed over from nonemissive to emissive and allowed the identification of the charged exciton spectrum in single NCs.

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