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Electric Field Induced Switching of the Fluorescence of Single Semiconductor Quantum Rods

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ABSTRACT

The exceptional fluorescence properties of single CdSe quantum rods (QRs) arising from internal and external electric fields are studied. Reversible external field induced switching of the emission in single QRs is reported for the first time. This effect was correlated with local field induced emission intensity reduction and newly observed darkening mechanism. Bimodal spectral jumps under a zero field were also observed and assigned to charged exciton emission, a phenomenon that was likewise directly controlled through an external field. These phenomena point to the use of single QRs as spectrally tunable charge sensitive fluorophores with polarized emission in fluorescence tagging and optical switching applications.

Semiconductor quantum rods (QRs) manifest the transition between zero-dimensional quantum dots (QDs) and one-dimensional quantum wires.[1,2] Previous work on QRs in ensemble or as single rods has shown how the energy gap and electronic level structure evolves with size.[3−6] Applying an external electric field can reveal additional phenomena, as shown in quantum-confined Stark effect (QCSE) studies of nanostructured semiconductors. QCSE was first observed in quantum wells, where the excitonic transition peak persisted for applied fields of up to 50 times the bulk exciton ionization energy due to quantum confinement.[7] In quantum wires, QCSE revealed a change in polarization behavior and reduction of optical transitions probability under an applied field.[8] For colloidal QDs the application of an external field led to large spectral shifts and provided evidence for the role of internal electric fields due to surface charge in the spectral behavior of single QDs.[9] QCSE in QRs is of significant interest since elongation of the unique axis allows transformation from strong isotropic quantum confinement, typical in spherical QDs, to weak confinement. This has been the subject of a theoretical study of QCSE in QRs which predicted the reduction in optical transition probability with applied field due to decrease in electron−hole overlap.[10]

In this paper we report on the emission properties of single CdSe/ZnS QRs subjected to an external electric field revealing diverse behaviors due to the inhomogeneous distribution of rod dimensions, surface properties, and local environment. We observe reversibly controlled optical switching under the external field. This is associated with a unique observation at zero applied field of a correlation between emission intensity and spectral position, assigned to changing local fields due to surface charge accumulation and migration along the QR. Furthermore, we observed external field induced spectral jumps phenomena. This behavior is associated with bimodal spectral jumps detected also at zero field and assigned to charged exciton emission. Finally, we also report correlation of spectral width with position related to local field fluctuations resembling the behavior reported recently for elongated core/shell nanocrystals.[11] These phenomena reflect the important role played by local electric fields on the optical properties of QRs. The observations point to the potential for use of QRs in fluorescence investigations of biological environments,[12,13] suitable as charge sensitive fluorophores having polarized emission,[3,14,15] as well as to their implementation in optical switches.

For spectral diffusion measurements we studied four samples of CdSe/ZnS core/shell QRs that were grown using the methods of colloidal nanocrystal synthesis as detailed elsewhere.[1,16,17] The four samples were of dimensions (diameter × length) 4 × 13 nm, 4 × 24 nm, 6 × 15 nm, and 6 × 35 nm (shown in Figure 1A). Single QRs were deposited on a precleaned substrate by spin casting a dilute solution of QRs in toluene. For externally applied field measurements, we used photolithography patterned Au/Cr electrodes on quartz creating an interdigitated electrode

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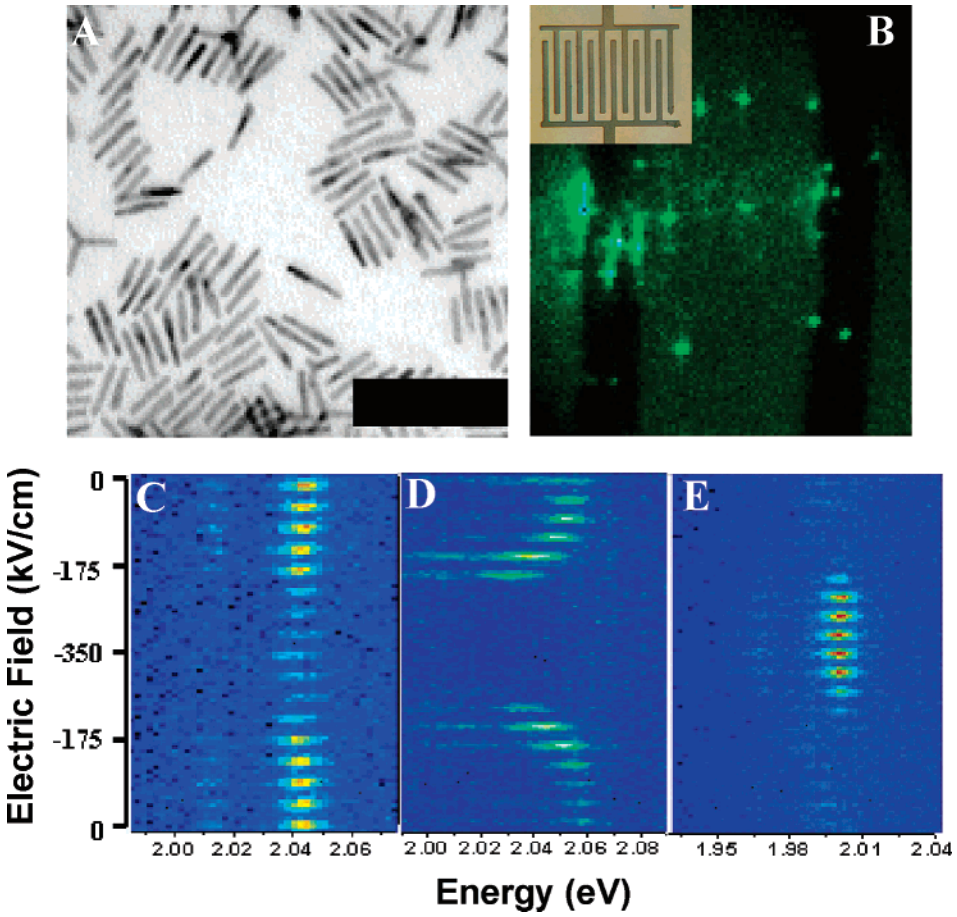

Figure 1. Electric field induced optical switching of single QRs, from the 6 × 35 nm sample. (A) TEM image of the 6 × 35 nm QR sample (scale bar 100 nm). (B) Fluorescence image of single QRs (bright spots) in between electrodes (20 μm gap). Inset: Picture of electrode architecture. (C, D) Reversible switching off. Emission is red shifted and broadens until it completely shuts off in stronger applied field and then turns on again at lower field. (E) Reversible switching on.

configuration with 20 μm electrode spacing (Figure 1B inset). The measurements were carried out on a ~10 μm region centered between the electrodes, as shown in Figure 1B, ensuring field uniformity. The field was cycled from zero stepwise to maximal field (350−400 kV/cm) and back to zero, before changing field polarity, to verify reproducible behavior. Single QR emission was measured on a locally built micro-PL setup, using an epi-illumination configuration. The emission image was split into two polarization components using a calcite plate placed in front of the monochromator, enabling orientation analysis of single QRs. Spectra were taken with 1 s (for spectral diffusion measurements) or 2 s (for electric field measurements) CCD integration time (LaVision Imager QE), and 25 W/cm^2 excitation intensity at 532 nm and at $T = 10$ K.

We monitored approximately 250 QRs from the 6 × 36 nm QR sample that showed response to the applied field. Many of the observed QRs exhibited a spectral shift in the applied field, where the majority of field induced shifts were found to be linear by nature, namely, shifting to higher (lower) energies due to an increase in the applied field and shifting to lower (higher) energies upon changing field polarity.

About 25% of the observed QRs showed a remarkable controlled switching behavior. Figure 1C−E shows the emission spectra of three single QRs undergoing a reversible optical switching controlled by an externally applied electric field. Panels C and D of Figure 1 shows a reversible switching *off* due to an applied field. The emission red shifts and decreases with the increase in the applied field, until at stronger applied field the emission is shut off. Decreasing again the external field the emission turns on. Although both QRs spectra, as shown in panels C and D of Figure 1, exemplify switching *off* behavior, their field-dependent behaviors diverge greatly. For instance, the QR emission in Figure 1C shifts a little to the red and its intensity decreases gradually until switching off, whereas the emission of the QR shown in Figure 1D undergoes some increase in emission intensity, while a large spectral broadening and red shift are also observed, before the emission is switched off. These diverse behaviors are related to local conditions that govern single QR specific behavior. Figure 1E shows the opposite effect, namely, a reversible field induced switching *on* of the emission. This inverted switching behavior could likewise be understood through local conditions that govern QRs behavior and shall be discussed in detail in the following paragraphs. Orientation analysis based on the depolarization ratio showed preference of field induced switching for rods aligned parallel to the field (see Supporting Information).

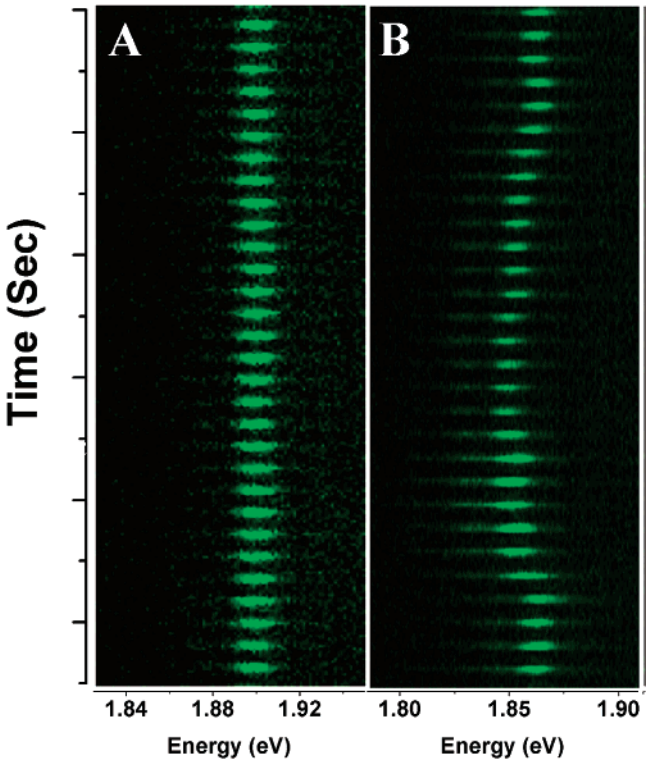

Figure 2. Spectral behavior of two different QRs from the 6 × 35 nm sample: (A) steady behavior in time; (B) shifty behavior in time.

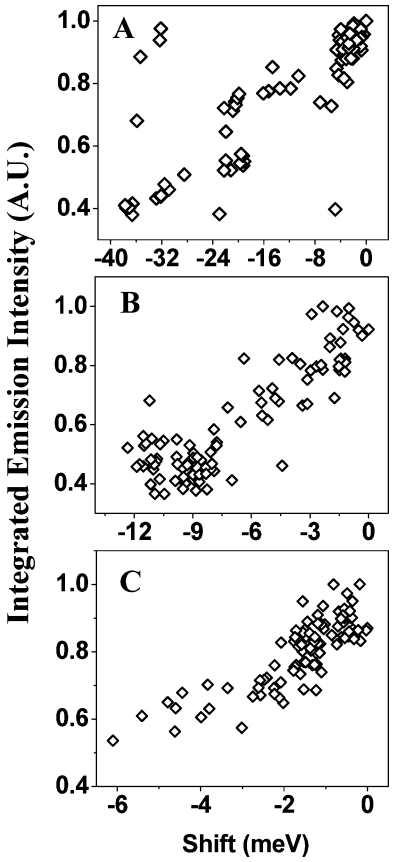

Figure 3. Effects fo local electric field on single rod spectra. Correlated intensity reduction with spectral red shift for three QRs taken from three samples: (A) 6 × 35 nm; (B) 4 × 24 nm; (C) 4 × 13 nm.

The field induced switching *off* behavior is understood within the framework of the effective mass envelope function approximation, in which the emission intensity is proportional to the overlap of the electron and hole wave functions $I \propto \int \psi_e \psi_h$.[10] By application of an external field, the electron and hole are being pulled in opposite directions, distorting the excitonic structure and diminishing the total electron−hole overlap until switching off the emission. The switching off is obtained at applied fields of $E_{appl} \sim 150-200$ kV/cm. Taking into account the dielectric constant and aspect ratio, the effective field in the QR is in the range of $0.3E_{appl}$ to $0.7E_{appl}$, depending on the QR orientation relative to the external field.[18] Comparison with the theoretical prediction shows that at the measured effective field for switching for our QR dimensions, the band gap transition probability is significantly reduced.[19] The description for the switching phenomena therefore agrees quantitatively with the theoretical calculation in ref 10.

We next turn to monitor and analyze the spectral behavior of single QRs at zero applied field which exhibited diverse behaviors (Figure 2). Figure 2A shows a time trace of the spectrum of a QR that remained steady for a long period of time with seemingly no spectral change in intensity, width, and position, while in Figure 2B the spectrum moves to and fro and changes also in width and intensity. To analyze these spectra, we applied a Lorenzian fit extracting the spectral position, width, and integrated emission intensity. Figure 3 shows the correlation of intensity versus spectral position for QRs from three samples. A distinctive correlation where the emission intensity is reduced with spectral red shift is seen. It is important to note that this correlation is not due to photodegradation, as the intensity reduction was not correlated in time.

Moreover, a unique new darkening route of single QRs was observed, as shown in Figure 4A. Previous studies of QDs proposed two main darkening routes: an ionization route in which the QDs become charged resulting in nonradiative charge recombination[20] and a thermal route.[21] Here we present a third route: local field induced darkening, having a direct implication on QRs fluorescence properties.

Our suggested model for local field induced darkening is illustrated in Figure 4B clarifying also the phenomenon of emission intensity reduction correlated with spectral red shift. At low local electric fields the exciton distortion is minimal and thus the electron−hole overlap is large yielding higher emission intensity. As the local electric field is increased, possibly due to surface charge accumulation and migration closer to the exciton, the overlap is reduced resulting in a decrease of the emission intensity and the spectrum is red shifted, providing the correlated behavior discussed above. Finally, when the magnitude of the local field is greatest, the exciton is completely distorted, and no emission is observed, providing a new darkening route. The local electric field in QRs originates from charge residing in trap sites at the surface or at the core/shell interface, which can accumulate and change in position with time. Another possible source for a local field that varies between different QRs is

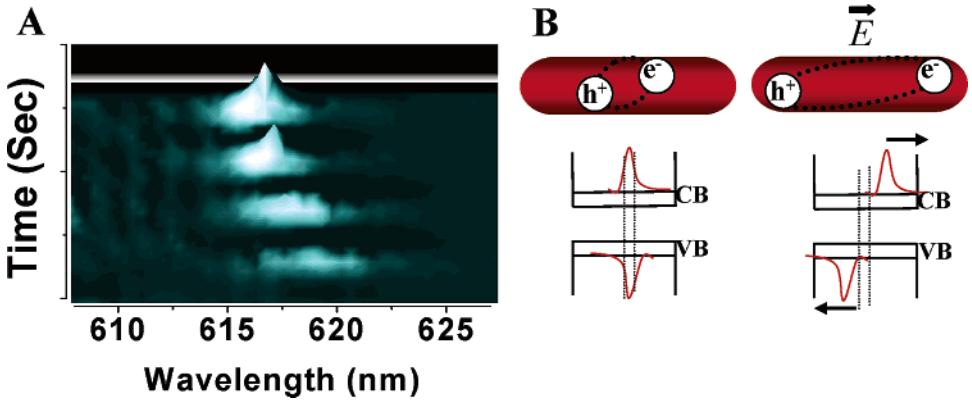

Figure 4. Darkening of a single QR from the 6 × 15 nm sample. (A) Spectral change in time. Intensity decreases while width is increased as spectra are red shifted, until no emission is observed. (B) Scheme of darkening mechanism induced by a local electric field, which leads to reduced electron−hole overlap.

due to permanent surface charge imbalance resulting from lack of cylindrical symmetry along the QR's *c*-axis.[22]

With accordance to this model, we could now explain the switching *on* behavior at large applied field (Figure 1E). Initially the QR is dark due to a local electric field that causes a complete deformation of the exciton. Upon exerting an external field opposite in direction to that of the local field, the local field contribution is canceled enabling overlap of the electron and hole wave functions and thus switching the emission on. The local field contribution could also account for the different trends in switching off shown in Figure 1C,D, since the total field exerted on the QR is the vector sum of the external field and the local field. These behaviors clearly prove the crucial role of the local field in the radiative emission of QRs. Switching off and intensity reduction culminating in darkening due to the reduced electron−hole overlap is uniquely associated with the presence of the elongated axis in QRs, which approaches a weak-confinement regime. In spherical QDs the reduction of electron−hole overlap due to electric field is limited by the strong confinement.

An additional ramification of the shape effect in the QR emission is given by a correlation between the spectral width (fwhm) and position, monitored during zero field spectral diffusion of single QRs from the different samples (Figure 5). This behavior was first observed for QDs with elongated shell.[11] It was attributed to the effect of surface charge density fluctuations where fluctuating charge located in the vicinity of the emitting QD core results in a broad and red shifted spectrum, while the fluctuating charge situated far from the emitting QD core has a lesser effect on the spectral width and position. A similar correlation is indeed seen here for QRs, and as further confirmation we apply a model similar to that used in ref 11 (solid lines) and described in the following. First, the spectral shift under an electric field is

$$\Delta E = \mu\epsilon + \frac{1}{2}\alpha\epsilon^2 + ...$$

where ΔE is the spectral shift, ϵ is the local field induced by fluctuating surface charge, and μ and α are the excited-state dipole moment and polarizablity, respectively. From this equation, the change in the spectral width $\delta(\Delta E)$ due to the field fluctuations $\delta\epsilon$ is $\delta(\Delta E) = (\mu + \alpha\epsilon)\delta\epsilon$. The magnitude of $\delta\epsilon$ due to the surface charge fluctuations depends on its distance from the exciton r: $\delta\epsilon \approx 1/r^2 - 1/(r + \delta r)^2$ with δr the spatial fluctuation estimated to be ~0.3 nm at $T = 10$ K, reflecting the distance between surface ligands. We used μ and α taken from external field dependent shifts of the 6 × 36 nm sample as rough values for the modeling and observe qualitative agreement with the experimental correlation. In spherical QDs such a correlation

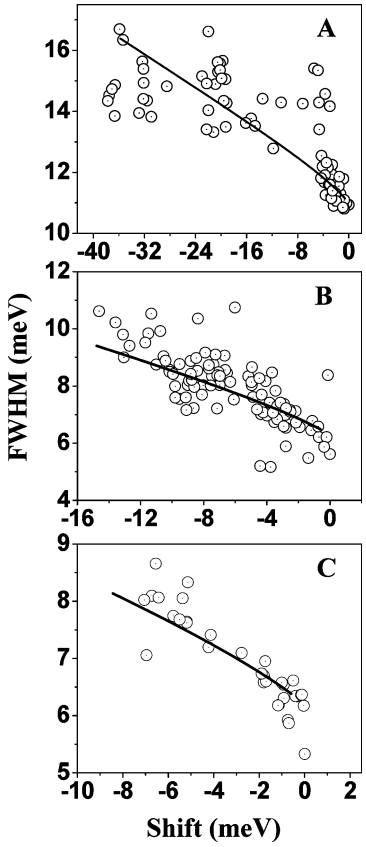

Figure 5. Correlation in spectral position and width (fwhm) of three single QRs from three different samples: (A) 6 × 35 nm; (B) 4 × 24 nm; (C) 4 × 13 nm. Solid lines are calculated using the model describes in the text.

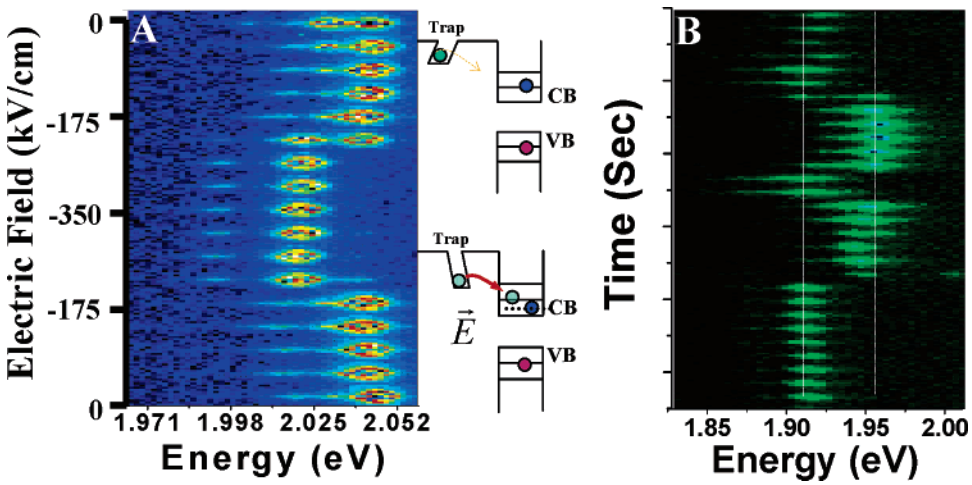

Figure 6. Charged exciton emission (6 × 35 nm sample). (A) Electric filed induced charging. Spectrum exhibits a spectral jump to the red at larger field and returns as field is lowered again. Right: drawing representing charging process due to an external field, where charge transfers from the trap into the CB (or VB for a trapped hole). (B) Correlated bimodal spectral jumps between neutral and charged exciton emission at zero field.

is not seen as the charge fluctuation occurs at a fixed distance from the exciton.

An additional observation upon applying an external field was of a distinct spectral jump of the emission shown in Figure 6A. The red-shifted emission is attributed to the charged exciton emission, where under the externally applied field we were able to reversibly control spectral bimodal jumps between the neutral/charged exciton states in single QRs. The emission at lower fields is attributed to a neutral exciton state, though the charged state is also observed, indicating of a metastable trap state. Upon increase of the external applied field, there is a jump to a red-shifted position, which is the charged exciton state, that persists as long as the field is strong enough. This could be understood by the schematic illustration in Figure 6: While no external field is present, the charge within the trap has a lower probability of tunneling into the conduction band (valence band). Under the applied field, a bending in both the level structure and the trap state may occur enabling the surface charge to tunnel into the conduction band (valance band) resulting in a charged exciton and a red-shifted emission. Upon decrease in the field, the charge returns to its metastable surface trap.

This observation can be directly associated with bimodal spectral jumps monitored in zero field emission spectra of single QRs (Figure 6B), an effect observed in 15−20% of the QRs within all four samples. This behavior is attributed to jumps between a charged and neutral exciton states,[5] resulting from a surface electron (hole) tunneling from a surface trap into the conduction band (valence band), creating a charged exciton with a red-shifted emission, while neutralization of the exciton results from the charge tunneling back to the surface. The shifts between the two spectral positions, extracted for all bimodal QRs, were found to be in the range of 10−24 meV, with a good approximation to the calculated[23] and observed[24] charged exciton energies reported for QDs. Although charged exciton emission of QDs had been reported,[25] intense emission could be favorable for the charged exciton in QRs as Auger relaxation is significantly suppressed in the larger rods.[26]

In conclusion, the optical behavior of single QRs is strongly affected by electric fields. The external field provided direct control for reversible on−off optical switching of single QRs. This was interrelated with optical phenomena observed for single QRs at zero applied field, where emission intensity reduction was correlated with spectral red shifts. Furthermore, a new field induced darkening route was observed. An additional occurrence due to applied field is the controlled charging of single QRs, resulting in charged exciton emission which is manifested in bimodal spectral jumps at zero field.

These new observations point to the 1D nature of colloidal QRs, reflecting shape evolution of confinement effects. Moreover, the unique field induced behaviors make QRs candidates for optical biosensors of electrical activity, with the added benefit of linearly polarized emission and absorption that could serve as a prominent tool for orientational analysis. Additionally, QRs could possibly be applied in wavelength-tunable optical switching devices.

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Supporting Information Available: Description of sample preparation and figure showing optical switching and relative orientation. This material is available free of charge via the Internet at http://pubs.acs.org.

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