Room-Temperature Exciton Storage in Elongated Semiconductor Nanocrystals

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The excited state of colloidal nanoheterostructures consisting of a spherical CdSe nanocrystal with an epitaxially attached CdS rod can be perturbed effectively by electric fields. Field-induced fluorescence quenching coincides with a conversion of the excited state species from the bright exciton to a metastable trapped state (dark exciton) characterized by a power-law luminescence decay. The conversion is reversible so that up to 10% of quenched excitons recombine radiatively post turn-off of a 1 μs field pulse, increasing the delayed luminescence by a factor of 80. Excitons can be stored for up to 10^5 times the natural lifetime, opening up applications in optical memory elements.

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Shape control in the synthesis of colloidal semiconductor nanostructures offers an unprecedented ability to tune the interaction of solid state quantum structures with the environment [1,2], opening up the possibility of performing truly nanoscale manipulations of the optical and electronic properties [3,4]. Besides enabling novel functions such as spectral modulation due to the quantum confined Stark effect (QCSE) [5] on the single particle level, nanoscale optoelectronics based on the control of the light-matter interaction on the single wave function level constitutes a powerful characterization tool to access the elementary physical nature of nanoparticles [3,4,6,7]. Semiconductor nanocrystals (NCs) constitute particularly complex and challenging nanoscale systems due to their hybrid nature combining a single crystalline nanoscale solid surrounded by organic ligands [8,9]. In contrast to large semiconductor quantum dots (QDs) epitaxially grown on the surface of a bulk and capped by a further semiconductor layer, these colloidal QDs are freely suspended in a solvent or matrix. Even for rather large colloidal structures with diameters of up to 10 nm, a significant fraction of the atoms constituting the crystal is located on the surface. Charging effects resulting from dangling bonds or strain in the crystal are therefore particularly dramatic in NCs and profoundly affect the photophysics of the system [6,10–12]. Although both the single particle and the ensemble are plagued by charging and quenching phenomena manifested in blinking and photodegradation [13], we report here the surprising observation that the electron wave function in a NC heterostructure can undergo a high level of electrostatic manipulation *without* necessarily leading to ionization of the particle anticipated from bulk photoconductivity [14]. This manipulation enables storage of excitation energy in individual QDs at room temperature, a crucial step towards realizing optical memory elements [15–20].

We recently demonstrated that elongated NCs consisting of a spherical CdSe core overgrown asymmetrically with a rodlike CdS shell provide excellent model systems to manipulate electronic wave functions in one dimension [3]. Application of electric fields to single particles at low temperatures enables tuning of the emission color via the QCSE [6], which depends on nanoscale shape [3]. Electrical quenching of the emission has been observed from single nanorods [3,4], but it is not ultimately clear whether this arises from a suppression of the radiative transition or a more complex irreversible quenching interaction. An indication of the former can be found experimentally if exciton storage occurs. It was previously assumed that these striking single particle effects should be much weaker in the ensemble, where an isotropic orientation of the NC with respect to the field prevails [3,4,6]. Here, we show that both a significant QCSE as well as suppression *and revival* of the luminescence are readily observable in the ensemble at room temperature by exploiting the temporal gating of the emission under electric fields typically present in NC-based optoelectronic devices. The ability to observe these effects is a direct consequence of the asymmetric NC shape and the resulting asymmetric QCSE of the individual particles [3].

NCs were dispersed in a polystyrene matrix and processed by spin coating. For electric field modulation experiments, films approximately 200–400 nm thick were sandwiched between indium tin oxide and Ag electrodes isolated by 10 nm layers of SiO_x. Photoluminescence (PL) was excited using a 1 kHz regeneratively pumped amplifier operating at 400 nm and 1–50 nJ pulse energy (180 fs pulse length). The PL was subsequently detected using an intensified gated spectrometer described in detail elsewhere [21]. All measurements were conducted under vacuum. The lifetime of the NC band-edge exciton in this study is of order 20 ns [3]. The prompt fluorescence decay of NCs is followed by a much slower and weaker fluorescence transient extending to hundreds of nanoseconds and originating from dark electronic states [11,22,23]. NCs typically do not exhibit monoexponential decay dynamics but a power-law decay in luminescence intensity [23]. This signifies that it is not the radiative dipole transition from excited to ground state which is rate limiting but rather the detrapping of more or less strongly localized charge carriers within the nanostructure. We note qualitative parallels to the case of delayed luminescence of organic semiconductors [21], which, however, arises from *intermolecular* charge separated state species.

Figure 1(a) shows the prompt PL emission spectra of the NC film with (solid line) and without (dashed line) an electric field of $\sim$1 MV/cm applied. The field quenches the PL by $\sim$42%. Weak field quenching of the emission of NCs by a few percent has previously been reported in NC solids and related to ionization and photocurrent generation [14]. In the present case, however, our ligand-stabilized NCs are suspended in an insulating matrix inhibiting photocurrent. Clearly, most of the particles are not ionized by application of an electric field as the fluorescence returns once the field is turned off. Figure 1(b) shows the difference in delayed emission after removal of the electric field 1.03 μs after excitation. In this example, the emission recorded under field modulation *exceeds* the unmodulated recombination by a factor of 80 in intensity. We are therefore able to store optical excitation energy in the semiconductor nanostructure for at least 50 times the $1/e$ time of the PL decay [3].

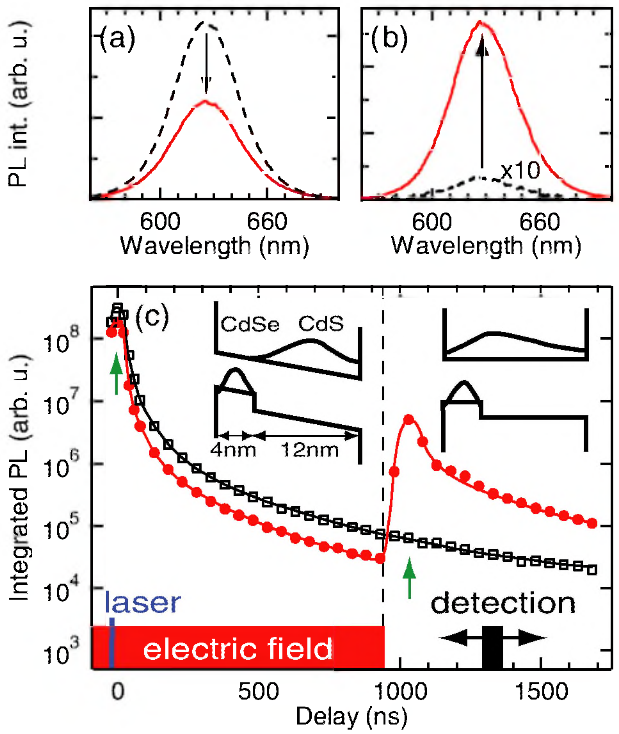

FIG. 1 (color online). Electrical exciton storage in semiconductor NCs at room temperature. (a) Prompt emission spectrum recorded in a 50 ns window overlaying excitation with (solid line) and without (dashed line) an electric field pulse. (b) As in (a) but with the detection placed 1.03 μs after excitation following the 1 μs field pulse. In this case the stored excitons result in a luminescence flash. (c) Time resolved PL decay with (●) and without (□) an electric field pulse of 1 μs duration. The arrows show the times of recording the spectra in (a) and (b). The sketches indicate the separation of electron and hole wave functions during and after the field.

Figure 1(c) summarizes the evolution of the spectrally integrated fluorescence with (circles) and without (squares) a field of 1 μs duration applied. Under the influence of the field the fluorescence is quenched at all times after excitation, while removal of the field leads to a rapid release of the stored optical energy in a fluorescence burst. The inset shows a schematic of the electron and hole wave functions of the semiconductor nanostructure. Whereas the hole is localized on the CdSe core, the electron is moveable within the CdS shell [2,3,10]. This band structure combined with the intrinsic asymmetry of the NCs allows an electric field to separate electron and hole. Control measurements using similar spherical particles [3] showed exciton storage over 20 times less efficient, thereby confirming the role of NC shape in exciton storage.

The exciton storage efficiency, i.e., the percentage of quenched fluorescence returned in the PL burst for an electric field of 1 μs duration, amounts to almost 10%, i.e., roughly 4% of the overall PL intensity. This value is a lower estimate as NCs most strongly affected by the field (i.e., nanorod parallel to field, transition dipole oriented along the c axis [1]) should not emit in the forward direction detected in this setup. This remarkable figure immediately illustrates that a change in excited state species occurs without introducing significant additional nonradiative decay such as ionization [14]. We would expect the interaction of the electron wave function in the CdS shell with NC surface states [6,10,12] to increase as the electron is electrically separated from the hole. This is apparently not detrimental to the overall luminescence of the nanosystem. Excitation energy can be transferred to a dark exciton by charge trapping in local potential minima associated with surface states [23]. Recombination is then not limited by the radiative rate but by detrapping, giving a characteristic power-law signature [23]. The PL both with and without field decays roughly as t^{-2}. The exponent is not significantly affected by the field as the PL during the pulse is dominated by unquenched emission from NCs which are not suitably aligned with respect to the field [3]. The t^{-2} decay is consistent with independent measurements on NCs in solution [3].

The optical storage capability is characterized further by extending the duration of the electric pulse and recording the integrated magnitude of the fluorescence burst in a 500 ns window following the pulse. Figure 2(a) shows the evolution of the unperturbed emission and the time-delayed fluorescence burst for a $\sim$1 MV/cm field pulse of variable duration. The power-law decay of the luminescence evidently extends over orders of magnitude in time. As we now detect the decay post turn-off, the exponent is strongly affected by electric field, dropping from -1.8 without field to -0.8 with field. The origin of exciton

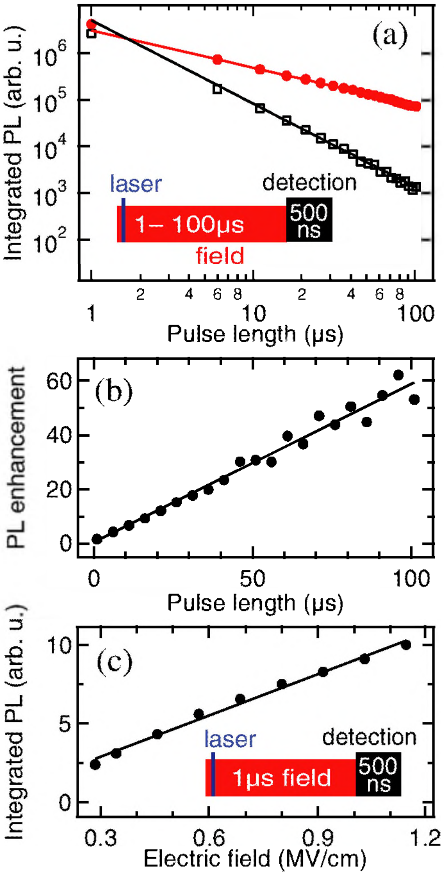

FIG. 2 (color online). (a) Dependence of the delayed fluorescence burst on the electrical pulse length detected in a 500 ns window following the pulse (●) compared to the unperturbed decay (□). (b) PL enhancement measured at the end of the field pulse. (c) Dependence of the fluorescence burst intensity on field strength for a 1 μs pulse.

storage appears to lie in the electric field impeding detrapping of charge carriers required for the conversion of dark to bright excitons. This results in a slower decay of luminescence. While a discussion in terms of rates is not meaningful in a dispersive, detrapping-limited recombination process, it is helpful to realize that the dark exciton is remarkably stable to dissociation or nonradiative recombination, for else bright exciton retrieval could not occur. Figure 2(b) illustrates this suppression of decay by plotting the increase in delayed luminescence induced by the field. This increase follows a linear relationship with time. By extrapolation, we infer that the intensity of the fluorescence burst should still be above the noise level after 0.5 ms. The storage time of optical energy is thus $\sim 10^5$ times longer than the initial lifetime of the unperturbed NCs [3]. Interestingly, both PL quenching (not shown) and overshoot appear to follow an approximately linear dependence on electric field as depicted in Fig. 2(c). This behavior is in contrast to the quadratic dependence expected from a simple picture of Coulombic electron-hole binding in solids observed, e.g., in conjugated polymers [24], and may be a signature of the NC asymmetry allowing only electrons and not holes to respond to the field [3]. In the present situation, electron-hole separation occurs *within* the nanostructure isolated from the environment, and not between molecular entities as in the case of semiconducting polymers [21,24] or from the QD to the bulk semiconductor as in epitaxial QDs [18]. In contrast, exciton quenching (and thus storage) is generally not observed in single *molecular* entities [25] characterized by a large exciton binding energy whereas it is readily observed in single semiconductor nanorods [3,4]. Exciton storage within a single QD is remarkable due to the limited volume available for charge separation. Note that a prior report on exciton storage in QDs required two coupled units for charge separation to occur *between* sites [16].

Finally, we need to confirm that it is the spatial separation of electron and hole within the nanostructure which is responsible for the reversible transition between bright and dark excitons in our nanorods. Such carrier displacement reduces the confinement energy, giving rise to the QCSE [5]. Both storage and QCSE should depend strongly on the orientation of the asymmetric nanorods with respect to the field. As the delay time of the detection gate is increased,

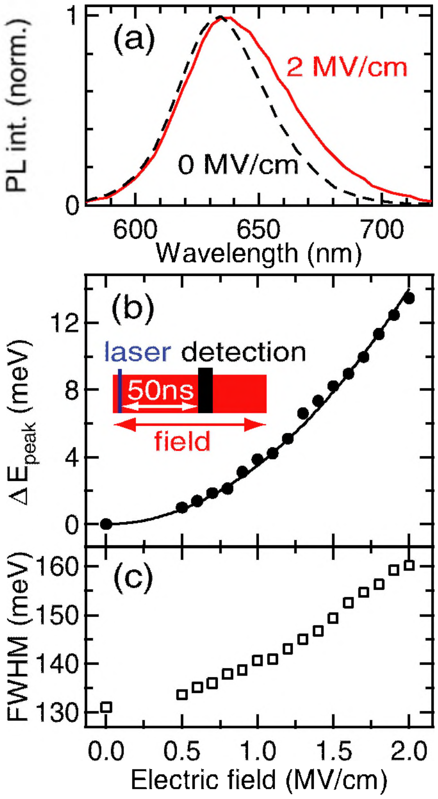

FIG. 3 (color online). Quantum confined Stark effect in the room-temperature emission of an NC ensemble. (a) Normalized PL spectra recorded 50 ns after excitation in a 50 ns detection window with (solid line) and without (dashed line) application of a 1 μs pulse of 2 MV/cm field strength. (b) Quadratic dependence of the energy shift of the PL maximum on applied field. (c) Dependence of the spectral width on field strength.

the contribution to the emission of delayed recombination from electrically stabilized carrier pairs increases, providing a route of temporally gating a specific subset within the ensemble which is most strongly influenced by the field. Single rodlike NCs exhibit QCSE spectral shifts at low temperature in excess of 20 nm [3], whereas the ensemble of energetically disordered and randomly oriented NCs typically shows no Stark effect in emission [6]. Figure 3(a) illustrates how application of an electric field of 2 MV/cm leads to an immediate red shift of the delayed emission recorded in a 50 ns detection window 50 ns after excitation. In agreement with ensemble electroabsorption [26,27], the peak of the gated emission shifts to the red with increasing field following the quadratic relationship given in Fig. 3(b). It is the largest (and thus lowest energy) particles which are most polarizable and display the most pronounced Stark shift and quenching [3]. Consequently, as the field is raised, the overall inhomogeneity of the emitting species increases by adding more lower energy NCs to the emission, leading to the spectral broadening by over 25% shown in Fig. 3(c).

The electric field allows direct control over the interaction of electron and hole. As the particles are evidently not ionized by this intervention we conclude that electron and hole remain Coulombically correlated. This prevents the anticipated electron ejection from the particle [4,6,10,12]. The delayed luminescence dynamics are dominated by the conversion of dark to bright excitons. The remarkable observation is that nonradiative decay is not increased substantially during storage of excitation energy in the dark state, or else retrieval would not be possible after the pulse. While the power-law decay does not allow us to quantify rates at present [23], the results do suggest that nonradiative decay is intrinsic to the excited state of the core (bright exciton) rather than to the dark exciton. We speculate that charge separation may even reduce nonradiative loss to enable prolonged exciton storage. Surface states in these hybrid semiconductor systems therefore actually turn out to be beneficial in terms of the overall photophysics.

The observation of exciton storage is important for developing an understanding of the fundamental interaction of semiconductor nanostructures with electric fields in devices such as light-emitting diodes and solar cells. The electrostatic optical memory demonstrated here is distinct from previous implementations based on the creation of potential pockets in a quantum well [15] or the electrical tuning of the coupling between two adjunct QDs in order to spatially separate charges [16]. Our approach exploits the intrinsic property of the NC surface to trap charges allowing us to store excitation energy. Storage effectively occurs within a single nanostructure, which is much less sensitive to the environment (such as the temperature) than prior approaches [15–19]. Consequently, by careful design of semiconductor heterostructures, exciton storage becomes possible at room temperature, a feat previously identified as highly desirable yet improbable with prior methods [20]. Exciton storage in the ensemble of NCs opens up new potential applications for these fascinating material systems in optical memory elements [15], light retarders for optical communication and smart pixels [16] combining image detection, processing, and generation in one semiconductor element [20]. The ability to store excitation energy may also be directly relevant to more conventional uses of NCs such as in biolabeling [28], as it provides a facile method of removing prompt autofluorescence characteristic of most biological environments [29].

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[1] X. Peng *et al.*, Nature (London) **404**, 59 (2000).
[2] D. V. Talapin *et al.*, Nano Lett. **3**, 1677 (2003).
[3] J. Müller *et al.*, Nano Lett. **5**, 2044 (2005).
[4] E. Rothenberg *et al.*, Nano Lett. **5**, 1581 (2005).
[5] D. A. B. Miller *et al.*, Phys. Rev. Lett. **53**, 2173 (1984).
[6] S. A. Empedocles *et al.*, Science **278**, 2114 (1997).
[7] J. Seufert *et al.*, Appl. Phys. Lett. **79**, 1033 (2001).
[8] A. P. Alivisatos *et al.*, Science **271**, 933 (1996).
[9] C. B. Murray *et al.*, Science **270**, 1335 (1995).
[10] J. Müller *et al.*, Phys. Rev. Lett. **93**, 167402 (2004).
[11] M. Nirmal *et al.*, Phys. Rev. Lett. **75**, 3728 (1995).
[12] R. G. Neuhauser *et al.*, Phys. Rev. Lett. **85**, 3301 (2000).
[13] I. Chung *et al.*, Phys. Rev. B **70**, 165304 (2004).
[14] C. A. Leatherdale *et al.*, Phys. Rev. B **62**, 2669 (2000).
[15] S. Zimmermann *et al.*, Science **283**, 1292 (1999).
[16] T. Lundstrom *et al.*, Science **286**, 2312 (1999).
[17] M. Rüfenacht *et al.*, Appl. Phys. Lett. **70**, 1128 (1997).
[18] J. J. Finley *et al.*, Appl. Phys. Lett. **73**, 2618 (1998).
[19] C. Rocke *et al.*, Phys. Rev. Lett. **78**, 4099 (1997).
[20] J. P. Kotthaus, Science **286**, 2286 (1999).
[21] M. Reufer *et al.*, Nat. Mater. **4**, 340 (2005).
[22] A. L. Efros, Phys. Rev. B **54**, 4843 (1996).
[23] J. M. Smith *et al.*, cond-mat/0604292v2.
[24] B. Schweitzer *et al.*, Chem. Phys. Lett. **304**, 365 (1999).
[25] F. Schindler *et al.*, Nat. Mater. **5**, 141 (2006).
[26] V. L. Colvin *et al.*, J. Chem. Phys. **101**, 7122 (1994).
[27] A. Sacra *et al.*, J. Chem. Phys. **103**, 5236 (1995).
[28] M. Bruchez *et al.*, Science **281**, 2013 (1998).
[29] M. Dahan *et al.*, Opt. Lett. **26**, 825 (2001).