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Radiative recombination dynamics in tetrapod-shaped CdTe nanocrystals: Evidence for a photoinduced screening of the internal electric field

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We study the radiative recombination processes in CdTe tetrapod nanocrystals at 10 K. Two intrinsic emission bands, namely the ground state (GS) and the excited state (EX), decay with three time constants, due to a power dependent Auger-like recombination process (tens of picoseconds), to the intrinsic emission of the two states (hundreds of picoseconds) and to emission from defect states (a few nanoseconds). The existence of an internal electric field originating from the e - h separation induced by the peculiar symmetry of the GS is demonstrated by a dynamical shift of the GS emission energy that is correlated to the EX population. © 2008 American Institute of Physics. [DOI: 10.1063/1.2924306]

In the last years, research on colloidal nanocrystals has undergone a rapid development triggered by the great potential of this class of materials for applications to different fields,¹ such as biology, medicine,^{2,3} energy conversion,^{4,5} and optoelectronics.⁶ Spheres, cubes, rods, and multi-branched architectures (i.e., multipods and dendrites) can be synthesized for many materials with excellent control over the various geometrical parameters, leading to a fine tuning of their physical properties.^{7,8}

The unique features of semiconductor tetrapod-shaped nanocrystals make them suitable for several applications, such as active elements in single nanocrystal transistors⁹ or for thin-film photovoltaics (once incorporated in a conductive polymer)¹⁰ and eventually for nanoelectromechanical devices. Some of the optical and electronic properties of CdTe tetrapods have been discussed in a series of works, mainly dedicated to the assessment of their crystallographic¹¹ and electronic structure.^{12,13} So far, only a few works have focused on the study of the ultrafast carrier dynamics. Recently, Malkmus *et al.*¹⁴ have investigated the e - h dynamics in tetrapod-shaped CdTe nanocrystals by transient absorption.

In this letter, we study the photoluminescence (PL) of tetrapod-shaped CdTe nanocrystals by means of time resolved PL (TRPL) spectroscopy. The radiative recombination mechanisms of the ground (GS) and excited state (EX) of the tetrapods are assessed in detail.

The preparation of CdTe tetrapod nanocrystals was described elsewhere.¹¹ A structural analysis of the sample was performed by transmission electron microscopy (TEM). For room temperature measurements, the sample was excited by a diode laser ($\lambda=405$ nm). The PL signal was collected by a 0.32 m monochromator and detected by a Si charge-coupled device camera. TRPL measurements were performed at low temperature (10 K) by exciting the tetrapods with the second harmonic (399 nm) of a Ti:sapphire laser (80 fs pulses at 80 MHz repetition rate). The signal was collected by a spectrograph (0.35 m focal length) and detected by a streak camera (temporal resolution of about 12 ps).

Figure 1 shows a low magnification TEM image of the sample and the relative PL spectrum at room temperature. The average diameter of 12 ± 3 nm and length of 90 ± 20 nm were estimated by averaging over more than 100 tetrapods. The diameter of the arms and that of tetrapod core were assumed to be equal. Unlike the tetrapods studied in our previous works,^{12,13} the average morphology of the sample investigated here is rather peculiar as the tetrapod arms have an elongated pyramidal shape due to specific synthesis conditions. In the present case and in analogy with several reported cases,¹⁵ a significantly large concentration of monomer species promoted a fast anisotropic growth, which translated in both tetrapod/hyperbranched structures with long and pointed branches with a pyramidal shape instead of the more frequently observed uniform prismatic ones.¹⁶ The PL spectrum (see inset of Fig. 1) exhibits the typical double peak structure of CdTe tetrapod nanocrystals.¹² We attribute the two peaks to emission from the GS (1.746 eV) and from the EX (1.825 eV), respectively. A small band tail at lower energy is also noticeable, ascribable to radiative recombination from surface defect states. The PL quantum yield (QY) at room temperature was lower than 1%.

Figure 2 shows the TRPL spectra of the GS and the EX recorded at $T=10$ K for an excitation density of 4 W/cm². The rise time was practically the same for the two emission

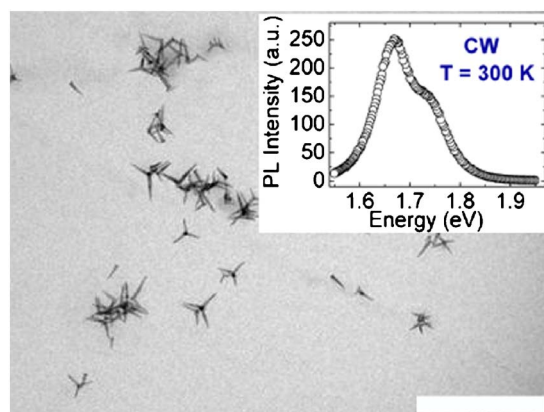


FIG. 1. (Color online) Low magnification TEM image of tetrapod-shaped CdTe nanocrystals. The scale bar is 500 nm long. Inset: PL recorded at room temperature.

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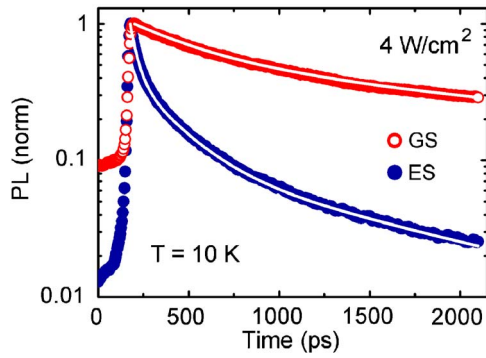


FIG. 2. (Color online) Typical normalized time resolved PL traces of GS (open symbols) and EX (full symbols) for CdTe tetrapods, recorded at 10 K and at excitation density of 4 W/cm². The white lines represent the best fit to Eq. (1).

bands (~ 26 ps), which suggests the occurrence of independent population paths for the two states, ruling out carrier relaxation from the EX to the GS. This is due to the different symmetry of GS and EX, as established by previous theoretical predictions.¹²

The PL relaxation dynamics (taken for a narrow wavelength window of 1 nm around the peaks) clearly shows a nonexponential decay for both transitions, suggesting a mixing of relaxation processes involved in the PL decay. The best fit of the PL time traces is obtained by a multi-exponential decay function,

$$\sum_{i=1}^n A_i e^{-(t-t_0)/\tau_i}, \quad (1)$$

where A_i and τ_i are the weight and the time constant of the i th decay mechanism, while t_0 represents the temporal instant at which the PL signal is maximum. We found that the decays can be well fitted by a biexponential [Eq. (1) with $n=2$] or a triexponential [Eq. (1) with $n=3$] function. The time analysis of the two emitting bands, performed at different excitation densities, is summarized in Table I, where the best fit values of the τ_i and A_i parameters are quoted.

At high excitation power, both states follow a triexponential decay. With decreasing power, the fastest component disappears in the GS emission, whereas it becomes longer and less intense in the EX emission, consistently with an Auger-like process. The second component (of the order of a few hundreds of picoseconds) is power independent and it can be attributed to radiative excitonic recombination of the two states. We note that the lifetimes measured here are much shorter than those typically reported for colloidal nanocrystals (several nanoseconds),^{17,18} thus this component cannot be attributed to purely radiative decay. Since the measurements were performed at low temperature (where exciton-phonon coupling is weak), we ascribe the possible cause of the short lifetime to carrier relaxation at nonradiative

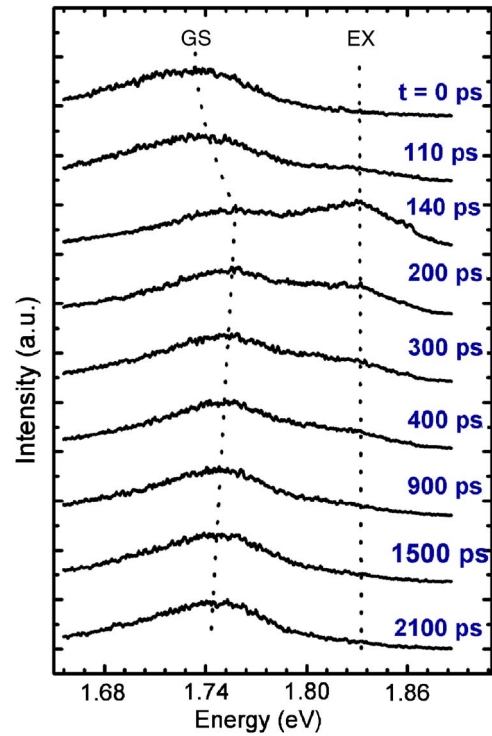


FIG. 3. (Color online) Temporal evolution of the PL spectrum at excitation density of 33 W/cm². The data were taken in a 4 ps wide window. Dotted line is a guide for eyes evidencing the remarkable dynamical shift of the GS.

centers, as also suggested by the remarkably low PL QY. The different oscillator strengths of the two transitions¹² give rise to different excitonic decay times for GS and EX. Finally, for what concerns the longest component, the time constant value (some nanoseconds) and its relatively small contribution to the whole PL decay (accounting in about 30%) suggests that it is due to radiative recombination from defects, most likely surface states.^{17,19} It should be noted that the different weights found in the GS and EX decay times account for the different partial overlap of surface emission to the two intrinsic emission bands in the 1 nm wide window studied, while the different time constants reflect a possible lifetime distribution inside the same surface band.

Figure 3 shows the temporal evolution of the PL spectra taken at different delay times after the pump pulse. In the early 140 ps, the PL intensity from both states reaches its maximum. With increasing delay, we observe a dramatic change in the relative intensity of the GS and EX bands. The EX emission disappears in about 1.5 ns, whereas the GS emission persists for a much longer time (up to 12 ns). We have fitted the transient spectra of Fig. 3 by two Gaussian curves and extrapolated the energetic positions of the two main peaks. Within 140 ps, the GS emission quickly blue-shifts by about 24 meV, whereas for longer delays, it red-shifts [see Fig. 4(b)]. The EX shows, on the other hand, a

TABLE I. Best fit values of the lifetimes τ_i and the relative weights A_i for the GS and for the EX as a function of the excitation density.

W/cm ²	GS			EX			GS			EX		
	τ_{1G} (ps)	τ_{2G} (ps)	τ_{3G} (ns)	A_{1G}	A_{2G}	A_{3G}	τ_{1E} (ps)	τ_{2E} (ps)	τ_{3E} (ns)	A_{1E}	A_{2E}	A_{3E}
0.3		417 ± 15	3.5 ± 0.2		67%	33%	45 ± 1	262 ± 30	1.3 ± 0.2	40%	51%	9%
4		410 ± 63	3.3 ± 0.3		65%	35%	38 ± 1	228 ± 8	1.3 ± 0.7	58%	33%	9%
33	85 ± 2	420 ± 10	3.1 ± 1.0	9%	57%	34%	29 ± 1	194 ± 18	1.4 ± 0.5	66%	27%	7%

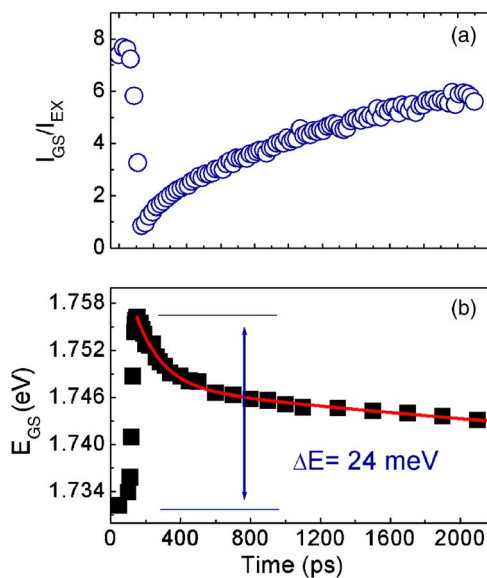


FIG. 4. (Color online) (a) Temporal evolution of the GS and EX PL intensity ratio. (b) Plot of the dynamical shift of the GS emission energy (symbols) and relative best fit (continuous line) to a biexponential function. The data refer to the transient spectra reported in Fig. 3.

negligible shift with respect to the GS, most probably due to its faster decay. The observed rapid blueshift of the GS band is not consistent with biexciton emission, since in this case a typical spectral broadening, accompanied by the appearance of the biexciton peak, should be observed at short delay times. In addition, the shift does not show any dependence on the excitation density, since it occurs even at the lowest excitation power, though a complete power dependent analysis is hindered by the photodarkening suffered by such tetrapods. Since both the nanocrystals in solution and those drop casted on a substrate exhibit a shift of just a few meV, we rule out energy transfer as cause of the redshift. Instead, in Fig. 4(a) a clear correlation between the intensity ratio of the GS/EX PL and the shift of the GS emission is observed. Initially, the intensity of the EX increases with respect the GS, until I_{GS}/I_{EX} reaches a minimum value (~ 1). This is accompanied by the rapid blueshift of the lowest energy peak. Later on, a dynamical redshift of the GS band is observed, accompanied by an increase in the I_{GS}/I_{EX} ratio. A shift of the PL energy in time is typically attributed to the dynamical screening of an internal electric field.²⁰ Likewise, we assume that the shift of the lowest energy level can be explained with the presence of excess carriers in the EX, which substantially changes the electronic configuration of GS by screening the internal polarization field. To assess the origin of this field, we refer to the structural features of the CdTe tetrapods investigated here, which can be thought as formed by a sphalerite core with four wurtzite arms protruding from such core.¹⁰ Besides the spontaneous polarization typical of the wurtzite crystal structure,²¹ we can consider another contribution to the internal electric field arising from the different crystallographic phases of the core (sphalerite) and of the arms (wurtzite), which leads to a type-II band alignment (hence to an offset of the bands) at each of the four core-arm interfaces.²² Such offsets should lead to a spatial separation of the GS $e-h$ wave functions,¹² and a larger dipole moment should be present due to both localization of the electrons in the core²² and the delocalization of the holes

in the four arms of the tetrapod. According to this interpretation, upon rapid population of the EX (within 140 ps), the photoexcited carriers produce an amount of charge that partly screens this electric field, and therefore induces a blueshift of the lower energy transitions. As the photoexcited carriers relax and the emission of the EX decays, the strength of the screening is reduced, and the GS emission dynamically redshifts and returns to the initial energy. The time constant of the GS emission shift was found to be equal to 154 ± 14 ps, very close to the EX lifetime, suggesting that the PL shift is actually induced by the EX population. Since the strength of the field follows the population of the ground level, i.e., the GS decay, the screening should be observable only if the EX PL decays with an average lifetime (referred as the time at which the PL signal is reduced of a $1/e$ factor) much shorter than the GS. In our samples, the EX average lifetime is indeed about 100 ps, whereas the GS decays in about 1 ns, allowing for a measurable dynamical shift of the PL.

In conclusion, we found that the PL emission in colloidal CdTe tetrapods is mainly due to radiative recombination from the two intrinsic states, controlled by rapid localization at nonradiative centres. In addition, we found evidence for an internal electric field, arising from the GS electron-hole wave function separation.

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