Extended storage of multiple excitons in trap states of semiconductor nanocrystals
Qinfeng Xu, Xiangnan Huang, Zheng Hua, Lian Hu, Lingxiao Du, Huizhen Wu, Chunfeng Zhang, Xiaoyong Wang, and Min Xiao

View online: http://dx.doi.org/10.1063/1.4943367
View Table of Contents: http://scitation.aip.org/content/aip/journal/apl/108/9?ver=pdfcov
Published by the AIP Publishing

Articles you may be interested in
Charged two-exciton emission from a single semiconductor nanocrystal

A microscopic picture of surface charge trapping in semiconductor nanocrystals

Photoluminescence properties of single Mn-doped CdS nanocrystals studied by scanning near-field optical microscopy
Appl. Phys. Lett. 87, 133104 (2005); 10.1063/1.2058228

Multiple temperature regimes of radiative decay in CdSe nanocrystal quantum dots: Intrinsic limits to the dark-exciton lifetime
Appl. Phys. Lett. 82, 2793 (2003); 10.1063/1.1570923

Zero-dimensional excitonic properties of self-organized quantum dots of CdTe grown by molecular beam epitaxy
Appl. Phys. Lett. 73, 3757 (1998); 10.1063/1.122885
Extended storage of multiple excitons in trap states of semiconductor nanocrystals

Qinfeng Xu,1,2 Xiangnan Huang,1 Zheng Hua,1 Lian Hu,3 Lingxiao Du,4 Huizhen Wu,4 Chunfeng Zhang,3 Xiaoyong Wang1,a) and Min Xiao1,5,b)

1 National Laboratory of Solid State Microstructures, School of Physics, and Collaborative Innovation Center of Advanced Microstructures, Nanjing University, Nanjing 210093, China
2 Department of Physics and Optoelectronic Engineering, Ludong University, Yantai 264025, China
3 School of Science, Jiangnan University, Wuxi 214122, China
4 Department of Physics and State Key Laboratory of Silicon Materials, Zhejiang University, Hangzhou 310027, China
5 Department of Physics, University of Arkansas, Fayetteville, Arkansas 72701, USA

(Received 7 December 2015; accepted 14 February 2016; published online 3 March 2016)

Owing to the Auger recombination effect, multiple excitons (MEs) in semiconductor nanocrystals (NCs) are dissipated nonradiatively at the sub-nanosecond time scale, which sets a stringent limit on the time window within which one can operate with them. Here, we show that this issue can be resolved by utilizing an intrinsic energy transfer system in CdSe NCs, where MEs created in the donor quantized states can be effectively extracted to the acceptor trap states. This was evidenced by the step-like increase in the intensity and the apparent decrease in the rise time of the trap-state photoluminescence with the elevated laser excitation power. With the radiative lifetime being tens of nanoseconds for the trap states, extended storage of MEs has been achieved and marks a crucial step towards flexible manipulations of their optoelectronic properties. © 2016 AIP Publishing LLC.

Multiple excitons (MEs) of a single semiconductor nanocrystal (NC) describe an intriguing electronic configuration with two or more electron-hole pairs being present simultaneously within its excitation volume.1–3 Due to the enhanced Coulomb interaction between charge carriers, MEs in semiconductor NCs are dissipated mainly in a nonradiative Auger process at the sub-nanosecond time scale.3,4 As schematically shown in Fig. 1 for a three-exciton configuration, higher-order excitons of a single NC would transfer their recombination energies to lower-order ones and efficient radiative fluorescence can only be observed from single excitons (SEs). This extremely short Auger lifetime of MEs sets a stringent time window within which one can operate with them and it is obvious that the device applications of semiconductor NCs in photo-detectors,5 solar cells,6 and lasers7 would benefit substantially from the extended storage of MEs.

Förster resonance energy transfer (ET) proceeds through dipole-dipole interactions between optical emitters, and in the case of using semiconductor NCs as donors, it is their excitons that are transferred to the acceptor materials.8,9 In Fig. 1, we also schematically depict the ET processes of SEs, bi-excitons (BEs), and tri-excitons (TEs). It has been demonstrated that SEs could be extracted from the donor NCs within hundreds of picoseconds,9 much shorter than their radiative lifetime of tens of nanoseconds,10 to guarantee a highly efficient ET process. Meanwhile, the respective ET lifetimes of BEs and TEs were predicted11 to be four and nine times shorter than that of SEs to compete with the Auger lifetimes so that efficient ET processes can still be expected. So far, the two commonly used acceptor materials to couple with NC donors are larger-sized NCs,8,9,12,13 and organic dyes,14,15 neither of which is capable of extending the storage of MEs mainly due to the following reasons. In the former case, both the donor and acceptor NCs can absorb the excitation photons8,9 and MEs either directly created in or indirectly transferred to the acceptor NCs would also decay through the Auger recombination channel. In the latter case, direct photon absorption can be avoided in dye molecules14 and their capability of capturing BEs generated in the donor NCs was recently reported.15 However, dye molecules suffer easily from the photo-bleaching effect16 and their nanosecond radiative lifetime17 is only slightly longer than the Auger lifetime of NC MEs.

Here, we show that the above issues can be resolved in an intrinsic ET system of CdSe NCs, where SEs, BEs, and TEs generated in their donor quantized states can be sequentially transferred to the acceptor trap states. This was evidenced by the step-like increase in the intensity and the apparent shortening in the rise time of the trap-state fluorescence when the excitation laser power was increased. With the radiative lifetime being tens of nanoseconds for the trap states, extended storage of MEs has been achieved and marks a crucial step towards flexible manipulations of their optoelectronic properties.

A detailed procedure of synthesizing the CdSe NCs used in our experiment was reported elsewhere.18 One drop of the toluene solution containing NCs was spin-cast onto a quartz coverslip or a silver film to make a solid film. The excitation beam of a 10 MHz, 405 nm picosecond laser was focused onto the NC film at an incident angle of ∼45° relative to the surface normal direction. The laser was set at a low power of ∼1.3 mW so that the average number of excitons generated per pulse in each single NC was ∼0.1 unless otherwise

---

1 a) wxiaoyong@nju.edu.cn
2 b) mxiao@uark.edu

---

[http://dx.doi.org/10.1063/1.4943367]
specified in the text. The sample photoluminescence (PL) was collected vertically by a 60°/C2 objective and sent through a 0.5 m spectrometer to a charge-coupled-device camera or an avalanche photodiode (APD) for the time-integrated or time-resolved (X24 250 ps resolution) PL measurement, respectively. Two bandpass filters were alternatively placed before the APD to detect either the quantized-state or the trap-state PL, respectively. All the optical measurements were performed at room temperature.

In Fig. 2(a), we plot the PL spectrum of CdSe NCs deposited on the quartz coverslip with a low density, which is similar to that measured in a solution and consists of two peaks at ~560 nm and ~720 nm from the core quantized states and the surface trap states, respectively.19–29 This trap-state PL was used to be an unwanted property that should be eliminated to increase the PL quantum yield (QY) of quantized states;20 however, it has attracted great attention recently due to the white-light emitting applications.18,23–25 As shown in Fig. 3, PL decay of the quantized states (curve 3) can be best described by a bi-exponential function with two lifetime components of ~2.1 ns and ~20.7 ns, respectively, the latter of which is due to the radiative recombination of SEs.9,10 In contrast, the trap-state PL has a single-exponential decay (curve 1) with a radiative lifetime of ~62.3 ns. Very similar transient PL dynamics were observed from the solution of CdSe NCs so that ET interaction between the neighbouring NCs deposited on the quartz substrate can be safely ruled out for a simple interpretation of our experimental results.

Surface trap states of the semiconductor NCs might have their structural origins from stoichiometric vacancies,19,22,25 dangling bonds,19,20,23 or external adatoms,19 and their PL mechanisms are still being highly debated. Both electron and hole traps could be located on the NC surface with a donor-acceptor-like configuration19,21 and carrier recombination would be realized through the tunneling of trapped electrons to trapped holes.19 Alternatively, only one kind of carrier traps might be located on the NC surface to interact with the core quantized states through a carrier transfer process.22,23,25,27–29 For example, photo-generated holes could be trapped by the surface chalcogenide vacancies and recombine with delocalized electrons from the quantized states.23,25 In the above two scenarios with either one or two kinds of carrier traps on the NC surface, the reduced overlap between electron and hole wave functions would result in an elongated radiative lifetime,19,20,25 as compared to that of quantized-state emission (see Fig. 3). As shown in the inset of Fig. 2(a) from the absorption spectrum of solution CdSe NCs, despite the presence of trap-state PL, there is no detectable feature at its wavelength range. This is consistent with the previous PL excitation measurement of CdSe NCs, showing that the trap-

FIG. 1. Schematic diagram showing the energy level structure of a single NC with both core quantized states and surface trap states that interact with each other through an ET process. When SE, BE, and TE are present in the quantized states simultaneously, the BE and TE can go through the Auger interaction process or be transferred to the trap states. The remaining SE can recombine to yield a PL photon or be transferred to the trap states. The BX energy is assumed to be lower than that of SE from an attractive interaction and the TX energy higher than that of SE due to the involvement of higher-lying excited state.

FIG. 2. (a) PL spectrum of CdSe NCs measured on the quartz coverslip with optical emissions from both quantized and trap states. Inset: Absorption spectrum of solution CdSe NCs. (b) PL spectrum of CdSe NCs measured on the corrugated silver film.

FIG. 3. PL decay curves of CdSe NCs. Curves 1 and 2 were measured for the trap-state PL on the quartz coverslip and corrugated silver film, respectively. Curves 3 and 4 were measured for the quantized PL on the quartz coverslip and corrugated silver film, respectively. Inset: Rising part of the trap-state transient PL measured on the quartz coverslip and fitted with the solid line using a single-exponential function.
state PL became obvious only when the excitation wavelength was tuned within the quantized absorption band. It is very likely that the small surface volume of trap states could prevent their efficient absorption transitions and charge carriers should be present mainly at the quantized states right after laser excitation.

Direct trapping of quantized electrons/holes from higher-lying excited states or band-edge states into surface traps normally occurs on the picosecond timescale. As can be seen from the rising part of the trap-state transient PL in the inset of Fig. 3, it can be well fitted with a single-exponential lifetime of ~1.9 ns that is comparable to the ~2.1 ns fast component of the quantized PL decay in Fig. 3. This relatively slow buildup time of trap-state PL falls within the reported ET component of the quantized PL decay in Fig. 3. This relatively slow buildup time of trap-state PL falls within the reported ET lifetime range of semiconductor NCs, which strongly suggests that both electron and hole traps are located on the NC surface to capture quantized excitons through an ET process. In principle, both the direct trapping and ET processes are able to extract MEs from the quantized states, although there may exist discrepancies in the times required to finish these two processes and, consequently, the associated efficiencies.

Now equipped with the long-lived trap states on the NC surface that are coupled with the core quantized states through an ET channel, we can start testing whether they are capable of accepting MEs for the extended storage. In Fig. 4(a), we plot spectrally integrated PL intensities of the CdSe quantized and trap states measured on the quartz coverslip as a function of the excitation laser power. The quantized PL intensity increases at first and then gets saturated with the increasing laser power, as expected for CdSe NCs whose PL QYs of MEs should be extremely low due to their nonradiative Auger recombination. In contrast, almost no saturation behavior is observed from the trap-state PL in Fig. 4(a), implying that MEs received by the trap states should be free of Auger recombination due to reduced Coulomb interaction between charge carriers from bulk-like energy states.

However, the slope for the trap-state PL intensity decreases twice with the increasing laser power, and the two turning points for the slope decrease roughly occur at the laser power to just saturate the quantized PL and when it is doubled, respectively. This discrete slope change thus reveals that the ET process between quantized and trap states can be divided into three stages dominated by the generation and transfer of one, two, and three excitons, respectively. Under a simple assumption that the number of excitons initially generated in the quantized states is linearly dependent on the excitation laser power, the ratio of these three consecutive slopes would provide an approximate estimate for the relative ET efficiencies of SEs, BEs, and TEs, which is about 5.8:1.3:1 as calculated from the three linear fittings in Fig. 4(a). These relatively smaller ET efficiencies measured for MEs might reflect the fact that their ET processes have to compete with the Auger recombination that normally occurs at the hundreds of picoseconds time scale.

Since the NC ET rates are expected to increase from SEs, BEs to TEs, it would be interesting to see how the rise time of the trap-state PL evolves with the step-like decrease of its intensity slope. In our experiment, we set the laser power around the middle point of each slope line in Fig. 4(a) and measured the rise times of the trap-state PL. As shown in Fig. 4(b), the apparent shortening of the rise time can be observed when the trap-state transient PL is sequentially dominated by the one-, two-, and three-exciton ET processes. With the increasing laser power, the three rising curves in Fig. 4(b) can be roughly fitted by single-exponential functions with the lifetimes of 0.94 ns, 0.61 ns, and 0.34 ns, respectively, which, however, cannot be taken directly as the ET lifetimes. For example, in the middle curve of Fig. 4(b), both the SE and BE ET processes, together with the Auger recombination of BEs, should jointly determine the buildup time of trap-state excitons. While all the above factors need to be considered in future work for a more precise fitting of

---

**Fig. 4.** (a) Spectrally integrated PL intensities of CdSe quantized and trap states measured on the quartz coverslip as a function of the laser power. The solid lines are linear fittings for the PL intensity increase with three different slopes. (b) Three rising curves of the trap-state transient PL, each of which was measured with the laser power around the middle point of one specific slope line in (a). Similar PL intensity and lifetime results are plotted in (c) and (d), respectively, for the CdSe NCs deposited on the corrugated silver film.
the trap-state PL rise time, we believe that the time-resolved measurements in Fig. 4(b) have provided an additional evidence for the extraction of MEs to the trap states. The trap-state PL intensity in Fig. 2(a) is significantly lower than that of the quantized states, making it impractical for both fundamental studies and device applications of ME storage. While there exists a variety of synthesis approaches to enhance the trap-state PL, including structure design,23 size control,23,25 and ligand exchange,25 here we adopt a post-synthesis method utilizing the interaction between semiconductor NCs and localized plasmons.18,36 For this purpose, one drop of the CdSe NC solution was spin-cast onto a silver film (~60 nm thick) grown on a silicon wafer by thermal evaporation. The as-prepared film was then annealed at 150 °C for 30 min to introduce corrugated silver islands for enhanced coupling between localized plasmons and CdSe NCs.18 Due to the oxidation-induced shrinkage of the NC size in the thermal annealing process, the quantized PL peak was shifted from ~560 nm in Fig. 2(a) to ~540 nm in Fig. 2(b). Meanwhile, the trap-state PL peak showed a larger blue shift from ~720 nm in Fig. 2(a) to ~620 nm in Fig. 2(b), which may reflect the fact that trap-state energy positions are strongly dependent on those of the quantized states.21,25 Besides the blue shifts, another dramatic difference observed between the two PL spectra in Figs. 2(a) and 2(b) is that the placement of CdSe NCs on a corrugated silver film makes the trap-state PL more enhanced relative to that of the quantized states. This has increased the QY value of CdSe NCs from ~1% on the quartz coverslip to ~20% on the silver film.18

It has been well documented that the NC PL could be enhanced by rough metal films or spherical metal particles through plasmonic couplings, which was normally associated with a shortened radiative lifetime of the NC excitons.37–39 In Fig. 3, we also plot the PL decay curves measured for both quantized and trap states on the corrugated silver film. The trap-state PL now shows a bi-exponential decay (curve 2) with the emergence of a fast component of ~2.6 ns that can be attributed to nonradiative quenching of excitons by the silver film.11,40 The slow component of ~27.2 ns, which should still originate from the radiative decay of trap-state excitons, has been shortened by ~56.4% due to the plasmonic coupling effect, as compared to the ~62.3 ns value measured on the quartz coverslip. On the other hand, the quantized PL decay measured on the corrugated silver film is still bi-exponential in Fig. 3 (curve 4). The fast component has decreased from ~2.1 ns on the quartz coverslip to ~1.6 ns, which can also be attributed to nonradiative quenching of excitons by the silver film. The shortening of ~22.0% for the slow component (from ~20.7 ns to ~16.2 ns) from the radiative decay of quantized excitons is significantly lower than that of ~56.4% for the trap-state excitons, implying that the plasmonic coupling between surface trap states and corrugated silver film should be relatively stronger to cause their more enhanced PL in Fig. 2(b).

In Figs. 4(c) and 4(d), we also plot time-integrated PL intensities and time-resolved PL dynamics measured on the silver film for CdSe quantized and trap states as a function of the excitation laser power, where similar trends to those in Figs. 4(a) and 4(b) can be observed. Specifically, the ratio between three PL intensity slopes in Fig. 4(c) is about 14.6:4:2.1 and the PL rising time in Fig. 4(d) decreases from ~0.90 ns, ~0.59 ns, to ~0.33 ns at the three increasing laser powers. These experimental results not only confirm again the extraction of MEs from the quantized states to the trap states but also show that this process can be effectively manipulated through the plasmonic coupling effect.

In summary, we have performed time-integrated and time-resolved optical measurements on CdSe NCs with optical emissions from both quantized and trap states. Due to the long buildup time of ~1.9 ns measured for the transient PL of the trap states, we tentatively assume that they interact with the quantized states through an ET process, instead of direct carrier trapping or Auger-assisted carrier transfer through the ME ionization effect. With the increasing laser power, MEs created in the quantized states were transferred to the trap states of CdSe NCs deposited on both a quartz coverslip and a silver film. Since the bulk-like trap states have a radiative lifetime of tens of nanoseconds, the survival time of MEs limited by the Auger effect in the quantized states has been greatly extended. Given the importance of exciton storage in the semiconductor nanostructures,41,42 the realization of ME storage here in CdSe NCs would promote a variety of their applications such as in lasers (optical gain), solar cells (charge separation), and quantum optics (multiple photons).

This work is supported by the National Basic Research Program of China (No. 2012CB921801), the National Natural Science Foundation of China (Nos. 11574147, 91321105, 11274161, 61307067, and 11321063), Jiangsu Provincial Funds for Distinguished Young Scientists (No. BK20130012), and the PAPD of Jiangsu Higher Education Institutions.

---

32Y. Yang, W. Rodríguez-Córdoba, and T. Lian, Nano Lett. 12, 4235 (2012).