Ultrafast Carrier Dynamics in PbS Quantum Dots

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Abstract: We report studies of multi-carrier dynamics in PbS quantum dots. Nanosecond recombination times are observed for the $1S_{el}$–$1S_{3/2}$ transition and evidence of direct radiative recombination from $1P_{el}$-$1P_{3/2}$ is observed on picoseconds time scales.

OCIS: (300.6420) Nonlinear spectroscopy; (190.4400) Nonlinear optics, materials

1. Introduction

Semiconductor quantum dots (QD's) are of great interest because of our ability to tailor their optical properties by controlling the size. For example, the band-edge luminescence, with quantum yields of better then 10% [1], is tunable over a wide range (500-1700nm). Understanding their electronic structure and carrier dynamics is of fundamental importance for future application of these materials.

In this paper we present studies of the multi-carrier dynamics in PbS QDs measured with femtosecond white-light-continuum transient-absorption experiments. We identify different relaxation processes and measure their time constants. We investigate different sizes of QDs with bandgap energies spanning the wavelength range from 700-1500nm, and we demonstrate the influence of the varying degrees of quantum confinement on the carrier dynamics.

2. Results and Discussion

Colloidal PbS quantum dots dispersed in toluene, with sizes ranging from 3.2 to 6.0nm in diameter are investigated using a white-light-continuum pump - probe setup [2]. The pump was chosen to excite either the $1S_{el}$ - $1S_{3/2}$ or the $1P_{el}$ – $1P_{3/2}$ transition for each sample, and then the transient absorption is probed over a wide range from the transparent region all the way to the $1P_{el}$ – $1P_{3/2}$ transition.

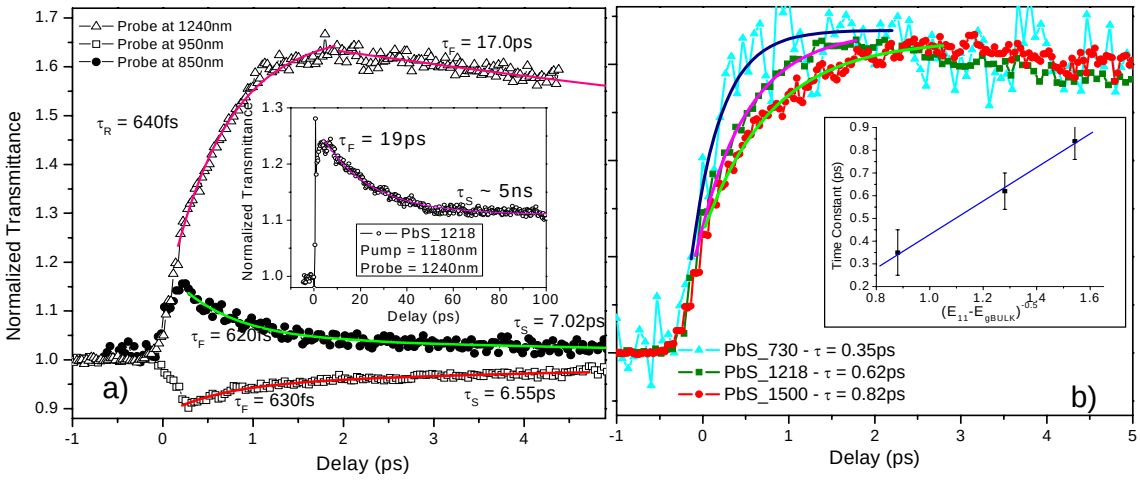

Fig. 1 a) Time evolution for different probe wavelengths for PbS1218 when the pump is at 740nm. The inset shows the $1S_{el}$ - $1S_{3/2}$ decay when pumped at 1180nm and probed at 1240nm; b) 1P-1S saturation dynamics for different sizes of QDs. The inset shows the 1P-1S decay 'time constant' vs. $(E11 - E_{gBULK})^{-0.5}$ which shows how the 1S rise time changes with the QD size.

Figure 1a shows the transient absorption spectra for PbS QD's with the first absorption peak at 1218nm (PbS1218) when pumped at 740nm ($1P_{el}$ – $1P_{3/2}$) or 1180nm ($1S_{el}$ - $1S_{3/2}$). The probe wavelength is varied as noted in Fig. 1a. Exciting at 740nm and probing at 1240nm using 140 fs pulses, the time constant for the saturation of the absorption is determined to be ~600fs. This rise time for the $1S_{el}$ - $1S_{3/2}$ saturation

is due to the 1P-1S intraband relaxation and corresponds to the fast relaxation times measured with the probe at 950nm and 850nm ($1P_{el} - 1P_{3/2}$).

Figure 1b compares the 1P-1S decay time for three different PbS QD sizes. This decay is faster for smaller QDs, and for this QD radius range the rise time is linearly proportional to the QD size (inset in Fig. 1b), indicating the enhancement of the intraband energy relaxation due to the quantum-confinement and that the process is not assisted by electron-phonon interaction, in agreement with ref. [3] for CdSe QDs. When probing the $1P_{el} - 1P_{3/2}$ transition (850nm for PbS1218) the second decay constant (~7 ps)is probably the direct radiative $1P_{el} - 1P_{3/2}$ relaxation time. These transitions have previously been observed with time-resolved fluorescence measurements for PbS QDs [4].

Figure 2 shows the time evolution of the transient absorption for PbS1218. For a 200fs delay, the electronic 1S states are still not completely populated as the carriers are still residing in the 1P states. Probing with photon energies between the $1S_{el} - 1S_{3/2}$ and $1P_{el} - 1P_{3/2}$ transitions, we observe an increase in absorption. This photo-induced absorption is thought to be due to multi-particle interactions since we excite more than 1 e-h pair per QD.[3] This influence becomes negligible for delays longer than 10ps when the 1P states are mostly depopulated.

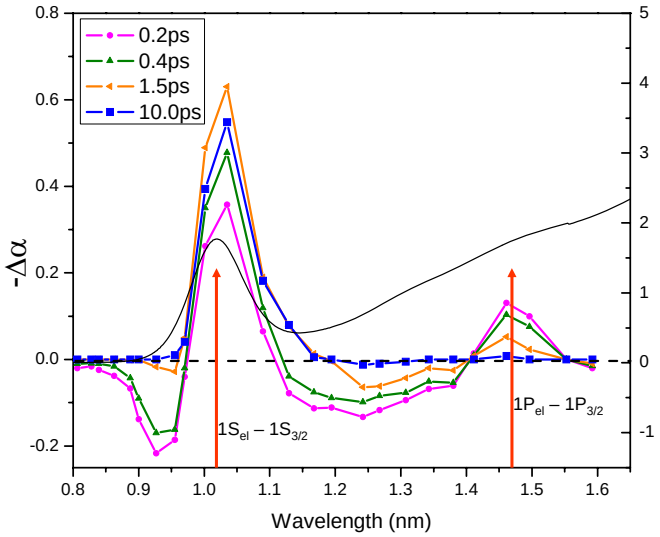

Fig. 2 Time evolution of the transient absorption for PbS1218. For 200fs the influence of the multi-carriers on the 1P states is strong. For a 10ps delay the influence of the 1P population is considerably reduced and the signal is dominated by the 1S saturation. The black continuous line is the linear absorption of the sample

In conclusion, we show the e-h dynamics in PbS QDs, identifying the different processes involved and their different time scales. We also directly measure the position of the $1P_{el} - 1P_{3/2}$ transitions and study their shift as a function of the QDs sizes.

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3. References

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