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Title: HOLE INTRABAND RELAXATION AND EXCITON RADIATIVE LIFETIME IN CSDE QUANTUM DOTS

Author(s): Xu, Su, C-PCS
Mikhailovsky, Alexander A., C-PCS
Hollingsworth, Jennifer A., C-PCS
Klimov, Victor I., C-PCS

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Hole intraband relaxation and the exciton radiative lifetime in CdSe quantum dots

S. Xu, A. Mikhailovski, J. A. Hollingsworth, and V. I. Klimov
Chemistry Division, MS-J585, Los Alamos National Laboratory, Los Alamos, NM 87545
Phone: (505) 665-8284, Fax: (505) 667-7289, E-mail: klimov@lanl.gov

Abstract: We study carrier dynamics in CdSe colloidal quantum dots (QDs) using femtosecond photoluminescence and transient absorption spectroscopies. We resolve hole relaxation between the high- and low-energy fine-structure states that are responsible for the band-edge absorption and emission, respectively. We derive a radiative lifetime of the lowest QD exciton from comparative studies of gated emission intensities in QD and laser-dye samples.
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OCIS codes: (320.7130) Ultrafast processes in condensed matter, including semiconductors

Colloidal synthesis allows preparation of almost monodispersed semiconductor nanoparticles with sizes from 1 to 10 nm and size dispersions as small as 5% [1]. These nanoparticles are also known as nanocrystals or colloidal quantum dots (QDs). The sub-10-nm size range corresponds to a regime of strong quantum confinement for which electronic energy structures exhibit a pronounced dependence on particle size. Tunable electronic structures combined with the ease of chemical manipulation, make colloidal QDs ideal building blocks for electronic and optical nanodevices. An important step towards realization of such devices is development of understanding of carrier relaxation processes in QDs and in particular the effect of QD size and surface properties on competition between radiative and nonraditive decay channels. In the present work, we apply femtosecond (fs) photoluminescence (PL) and transient absorption (TA) spectroscopies to study carrier relaxation dynamics in CdSe QDs and in particular to derive a radiative lifetime of the lowest exciton state.

The cw emission in colloidal QDs recorded under nonresonant excitation is red-shifted with respect to the lowest 1S absorption maximum (Fig. 1A). This shift is believed to be due to a splitting of the lowest hole state as a result of crystal field and electron-hole exchange interactions [2]. The high-energy fine-structure hole states are coupled to the 1S electron state by a strong transition that gives rise to an intense 1S absorption peak (Fig. 1A and B). The low energy fine-structure state is responsible for the cw PL through a weaker transition. To study hole relaxation within the manifold of fine-structure states we applied a fs PL up-conversion experiment [3].

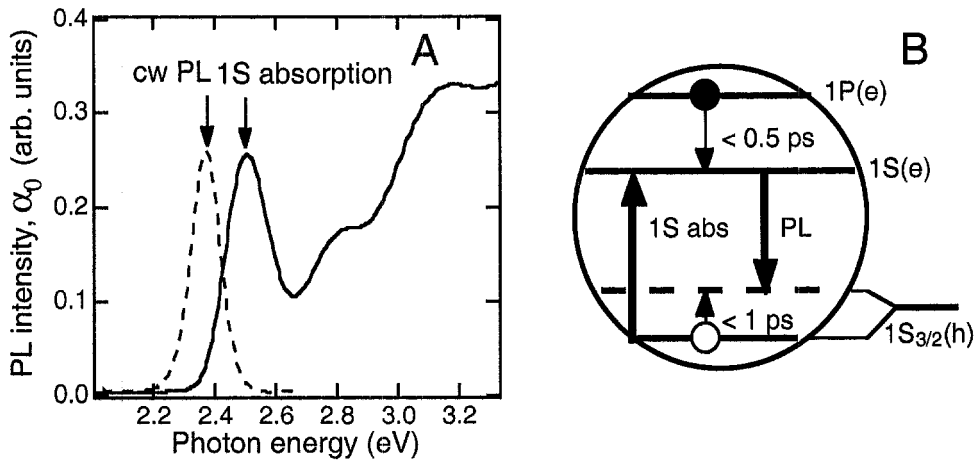

Fig. 1. (A) Absorption and cw emission spectra of CdSe QDs with radius 1.2 nm (300 K). (B) Schematics of "absorbing" and "emitting" transitions in CdSe QDs along with intraband relaxation processes leading to a population buildup of the "emitting" transition.

PL dynamics for QDs with radius R = 1.3 nm (Fig. 2) recorded at the positions of the 1S absorption ("absorbing" transition) and the PL maximum ("emitting" transition) show a rapid 700-fs decay of the 1S emission. This decay is complementary to the growth of the emission at the center of the cw PL band. Band-edge TA

dynamics recorded on the same time scale are significantly slower than those observed in PL. Since band-edge absorption bleaching in CdSe QDs is dominated by electrons [4], the fast PL dynamics should be attributed to hole relaxation (the PL signal is proportional to the product of electron and hole occupation numbers), namely, to the sub-ps hole transition from the "absorbing" to the "emitting" fine-structure state. Studies of samples with different degrees of surface passivation show that this initial hole relaxation is not affected by the number of surface defects, indicating that the "emitting" hole state is not defect-related but is intrinsic to nanocrystal QDs, consistent with the model proposed in Ref. 2.

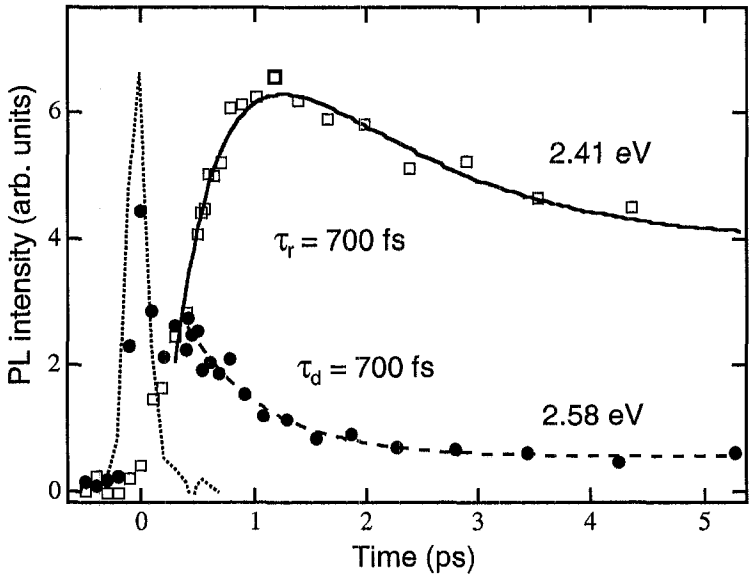

Fig. 2. PL dynamics detected at the positions of the "absorbing" (circles) and the "emitting" (squares) transitions in 1.2-nm CdSe QDs (dotted line is a pump pulse autocorrelation).

We also use PL up-conversion to study the decay of the band-edge exciton in the stage following initial intraband relaxation. The decay of the band-edge PL is strongly nonexponential, indicating the presence of relaxation components with time constants from several ps to sub-μs. Such complex relaxation behavior does not allow one to reliably determine the exciton radiative lifetime (τ_r) by simply fitting PL time transients. An alternative approach to determining radiative time constants from the up-conversion PL data is by analyzing the gated PL intensities. For a short sub-ps gate pulse, time-resolved (gated) PL signal is inversely proportional to τ_r. By comparing gated signals in QDs with those in well characterized laser dyes we obtain that radiative time constants in CdSe QDs are in the range from 30 to 60 ns. The reliability of the proposed method was verified by measuring QD samples with different surface passivations. Despite the fact that these samples demonstrated strongly different PL relaxation behavior and the difference in PL quantum yields up to a factor of 10, they all showed almost the same magnitude of the gated signals at early times after photoexcitation indicating almost identical radiative time constants.

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