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The influence of intrinsic and surface states on the emission properties of colloidal nanocrystals

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Abstract

Time Resolved Photoluminescence (TRPL) measurements on the picosecond time scale (temporal resolution of 17 ps) on colloidal CdSe and CdSe/ZnS Quantum Dots (QDs) were performed, to elucidate the role of intrinsic and surface states on the emission process. Transient PL spectra reveal three emission peaks with different lifetimes (60 ps, 460 ps and 9–10 ns, from the bluest to the reddest peak). The energy separations among the states, together with their characteristic decay times, allow us to attribute the two higher energy peaks to $\pm 1^U$ and $\pm 1^L$ bright states of the fine structure picture of spherical CdSe QDs, and the third one to surface states emission, respectively. We show that the contribution of surface emission to the PL results to be different for the two samples studied (67% in the CdSe QDs and 32% in CdSe/ZnS QDs), confirming the decisive role of the ZnS shell in the improvement of the surface passivation.

Keywords: Colloidal nanocrystals; Time resolved measurements; Picosecond; Photoluminescence decay time

1. Introduction

Colloidal II–VI highly luminescent nanocrystals are important both in fundamental studies, due to their peculiar optical properties, and in technological applications such as diodes, lasers, photovoltaic cells. In the last years, great improvement in the Quantum Yield (QY) has been obtained by optimizing inorganic surface passivation techniques [1]. The knowledge of

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the dependence of radiative and nonradiative processes on the QDs structure, with particular attention on the role of surface states in the carrier relaxation upon laser excitation, is fundamental in order to make improvement on the QD QY. To this aim, we have performed TRPL measurements on the picosecond time scale on colloidal CdSe core and CdSe/ZnS core/shell QDs in a temperature range from 15 to 300 K. We show that in the first 2 ns the PL arises from three states with different lifetimes. By considering typical decay times and the energetic separation among the states extracted from the transient spectra, we conclude that the two peaks at higher energies can be assigned to emission from the lowest intrinsic bright states $\pm 1^U$ and $\pm 1^L$ of the fine structure of spherical CdSe QDs, whereas the low energy peak is due to emission from surface states. Moreover, in a low temperature range (15–60 K) an interplay among the states occurs. In particular, we had evidence for thermal filling of $\pm 1^U$ and $\pm 1^L$ states, fed by surface states.

2. Experiment

We have prepared CdSe cores (4.5 nm in diameter) following the method described in Ref. [2], and we have grown the ZnS shell by using the approach described in Ref. [3]. The QDs have been deposited by drop casting from chloroform solution on Si–SiO_2 substrates. For each sample we performed TRPL measurements in the temperature range of $15 \div 300$ K, in steps of 10 K. The QDs were excited by the second harmonic (397 nm) of a Ti:sapphire laser (pulse duration of 80 fs, repetition rate of 80 MHz). The sample emission was dispersed by a spectrograph (0.35 m focal length) and detected by a streak camera (temporal resolution of 17 ps). All the measurements were performed at low excitation density, in order to overcome multiexciton generation.

3. Results and discussion

In Fig. 1(A) the temporal evolution of CdSe/ZnS QDs PL spectra is shown. The spectra consist of three emission peaks evolving in time. The blue peak $|1\rangle$ evolution is the fastest (see Fig. 1(A)) and the red one $|3\rangle$ is the slowest. After 1.7 ns a small red shift is observed because of the disappearance of feature $|1\rangle$, while after 12 ns peak $|3\rangle$ becomes dominant. Such a time evolution suggests that three emitting states, with different relaxation times, contribute to the PL of these quantum dots. We have fitted the PL spectra to a superposition of three lorentzian curves, obtaining the energetic separations among the three states, $E_{1,2}$ and $E_{2,3}$. We found $E_{1,2} = 21$ meV and $E_{2,3} = 16$ meV for core QDs and $E_{1,2} = 21$ meV and $E_{2,3} = 13$ meV for core/shell QDs. The PL time decay for core and core/shell samples (shown in Fig. 1(B)) is well reproduced by a triexponential decay function at all the temperatures and for both samples

$$I(t) = A_1 \cdot \mathrm{e}^{-(t-t_0)/t_1} + A_2 \cdot \mathrm{e}^{-(t-t_0)/t_2} + A_3 \cdot \mathrm{e}^{-(t-t_0)/t_3} \tag{1}$$

where t_0 is the delay at which $I(t)$ is maximum, t_1, t_2, t_3 are the lifetimes and A_1, A_2, A_3 are the weights of each process, respectively. At low temperature (15 K) the parameters values for CdSe sample are shown in the Table 1. Noteworthy, the non exponential behaviour can be neither due to Auger recombination, as the experiment is performed in a low excitation regime, nor to energy transfer, since similar relaxation dynamics were also obtained in solution, where the average interparticle distance is too large to allow for efficient Förster Resonant Energy Transfer (FRET). We observe that the time constant t_1 and t_2 are the typical carrier relaxation times from intrinsic bright states of the fine structure of spherical CdSe QDs [5] into the surface defect states [4], and t_3 is comparable with typical lifetime of surface-related emission in CdSe QDs [6].