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The Role of Intrinsic and Surface States on the Emission Properties of Colloidal CdSe and CdSe/ZnS Quantum Dots

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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. 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). By considering the characteristic decay times and by comparing the energetic separations among the states with those theoretically expected, we 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. 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.

Introduction

Colloidal II-VI highly luminescent nanocrystals are important both in fundamental studies, due to their peculiar

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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 the inorganic surface passivation techniques [1]. The knowledge of 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 separations 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, we found that, 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.
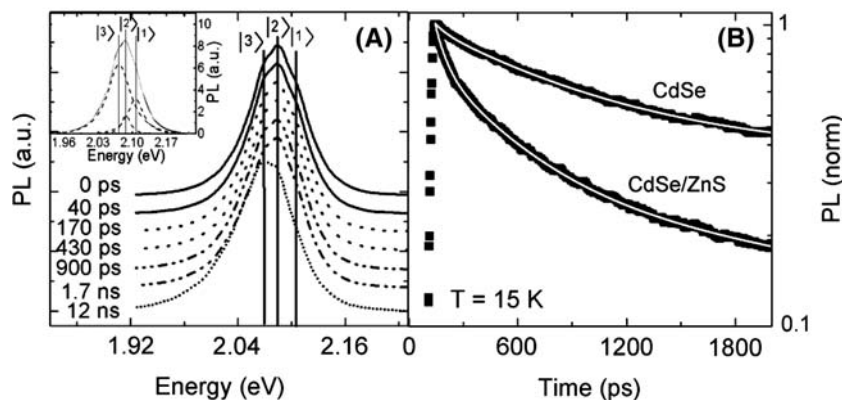
Experimental Section

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 15–300 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.

Results and Discussion

In Fig. 1A 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. 1A) and the red one $|3\rangle$ is the slowest. After 1.7 ns a small red shift is observed because of the disappearence 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 (see inset of Fig. 1A), 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.1B) is well reproduced by a triexponential decay function at all the temperatures and for both samples:

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

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 parameter values (obtained by analysing all the emission wavelengths) for the two samples are shown in the Table 1. We note that by studying the decays at the different emission wavelengths (corresponding to the three transitions) the general nonexponential behavior, along with the lifetimes,

does not change apart from the relative weights of each process, the longest component being more and more important by detecting wavelengths from the blue to the red side of the whole emission spectrum. Moreover, the nonexponential decay 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). The PL spectra obtained in continuous wave (CW) excitation (not shown here) show a symmetric line-shape, confirming that the relative weights of the two fastest components is too slight to feature the CW time integrated PL spectrum. 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 [4] into the surface defect states [5], and t_3 is comparable with typical lifetime of surface-related emission in CdSe QDs [6]. Moreover, the extracted energy splitting $E_{1,2}$ is the same in core and core/shell sample, and it is similar to the theoretically predicted splitting between the lowest bright states $\pm 1^U$ and $\pm 1^L$ in CdSe QDs [4] (20 meV), whereas $E_{2,3}$ is different in the two studied samples, suggesting that the nature of the transition $|3\rangle$ (Fig. 1A) is extrinsic. Also, we can rule out that the longest decay arises from an intrinsic state, like the ± 2 "dark" state, because in that case the splitting $E_{2,3}$ should be the same in the two samples, and the found lifetime (10 ns) is much lower than the expected "dark exciton" decay time (from μs to ms) [7]. Nevertheless, if "dark" emission occurs, it cannot be discerned because of the relatively short temporal range studied in our experiments. In light of these results we can associate the transitions $|1\rangle$ and $|2\rangle$ to carrier recombination from $\pm 1^U$ and $\pm 1^L$ states and the transition $|3\rangle$ to a surface states emission.

By analysing the temperature dependence of the PL intensities I_1, I_2 and I_3 for the three states, we found evidence for thermal population of $\pm 1^U$ and $\pm 1^L$ states, fed by

Table 1 Best fit values of t_1, t_2, t_3 and of the relative weights A_1, A_2, A_3 for the two samples at 15 K

Sample	t_1 (ps)	t_2 (ps)	t_3 (ns)	A_1	A_2	A_3
CdSe	62 ± 4	490 ± 11	10 ± 1	0.034 ± 0.001	0.29 ± 0.03	0.67 ± 0.02
CdSe/ZnS	61 ± 1	450 ± 10	9.5 ± 0.7	0.199 ± 0.003	0.474 ± 0.002	0.326 ± 0.005

Fig. 2 (**A**) PL intensity of the three states as a function of temperature for CdSe/ZnS QDs (symbols). The same behaviour characterizes the CdSe QDs. The continuous lines are the best fit of experimental data from 15 to 60 K to the expressions obtained by solving a set of rate equations. (**B**) Four-level model
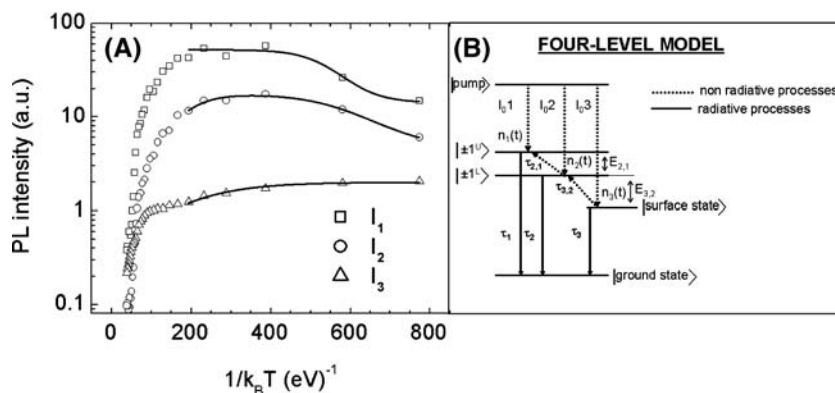
surface states, in the range of 15–60 K (see experimental data of Fig. 2A). After 60 K all the intensities fall abruptly due to activation of nonradiative processes involving all the states, such as thermal escape induced by optical phonons absorption. To explain the behaviour up to 60 K, we have developed a four-level model (Fig. 2B). By considering only thermal population effects in the range of 15–60 K, we have imposed and solved a set of rate equations. The solutions gave us the expressions for the intensities I_1, I_2 and I_3:

$$I_1(T) = I_{01} + \frac{\tau_2}{\tau_{2,1}} \cdot e^{-E_{2,1}/k_B T}(I_{02} + I_{03} \cdot \rho) \quad (2)$$

$$I_2(T) = \frac{I_{02} + I_{03} \cdot \rho}{1 + \frac{\tau_2}{\tau_{2,1}} \cdot e^{-E_{2,1}/k_B T}} \quad (3)$$

$$I_3(T) = \frac{I_{03}}{1 + \frac{\tau_3}{\tau_{3,2}} \cdot e^{-E_{3,2}/k_B T}} \quad (4)$$

where

$$\rho = \frac{\frac{\tau_3}{\tau_{3,2}} \cdot e^{-E_{3,2}/k_B T}}{1 + \frac{\tau_3}{\tau_{3,2}} \cdot e^{-E_{3,2}/k_B T}} \quad (5)$$

By fitting the experimental data to the theoretical I_1, I_2 and I_3, we have extracted the energetic separations among the three states $\Delta E_{1,2}$ and $\Delta E_{2,3}$. We found $\Delta E_{1,2} = 20 \pm 1$ meV and $\Delta E_{2,3} = 16.5 \pm 0.3$ meV for CdSe QDs, $\Delta E_{1,2} = 20 \pm 1$ meV and $\Delta E_{2,3} = 12 \pm 1$ meV for CdSe/ZnS QDs. These values are very similar to the respective energy splittings extracted from the deconvolution of the spectra in Fig. 1A. This analysis confirms the previous assignation of the three emitting states to the two lowest bright states of spherical CdSe QDs and to surface states.

Conclusions

In summary, we have demonstrated that the PL of CdSe core and CdSe/ZnS core/shell QDs in the first 2 ns arises from the intrinsic bright $\pm 1^U$ and $\pm 1^L$ states with lifetime of about 60 ps and 450 ps, respectively, and from surface states with lifetime of 9–10 ns. The contribution of surface states to the PL is considerably reduced after inorganic passivation of the CdSe core QDs.

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