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Evidence of electron wave function delocalization in CdSe/CdS asymmetric nanocrystals

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ARTICLE INFO

Article history:

Available online 1 October 2009

Keywords:

Ultrafast dynamics
Core-shell nanocrystals
Pump-probe

ABSTRACT

We studied the delocalization of electron wave function in asymmetric CdSe/CdS nanocrystals, consisting of a spherical CdSe dot embedded in an elongated CdS shell, by means of a pump-probe technique. By comparing the transient spectra obtained upon pumping the band edge transition of the CdSe in CdSe/CdS heterostructure and in a bare CdSe dot, we observed the delocalization of electron wave function at the CdSe/CdS interface.

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1. Introduction

Colloidal nanocrystals are very attractive materials both for fundamental studies and technological applications mainly due to the possibility of tuning their optical and electronic properties by modifying their size and shape [1,2]. In these materials the strong confinement leads to discrete electronic levels and a blue shift of the energy gap. Furthermore, the increase of the surface-volume ratio at low dimensionality enhances the role of surface states, thus changing the carrier relaxation path, introducing trapping and non-radiative decay channels [3–5].

Core-shell nanocrystals, composed of a semiconductor core covered by a shell of another material, have been extensively investigated due to the passivating role of the shell which increases the photoluminescence quantum yield [1,6] and the possibility of tuning the charge confinement inside the core. In fact, the band alignment at the interface can be tuned by changing the shell material so

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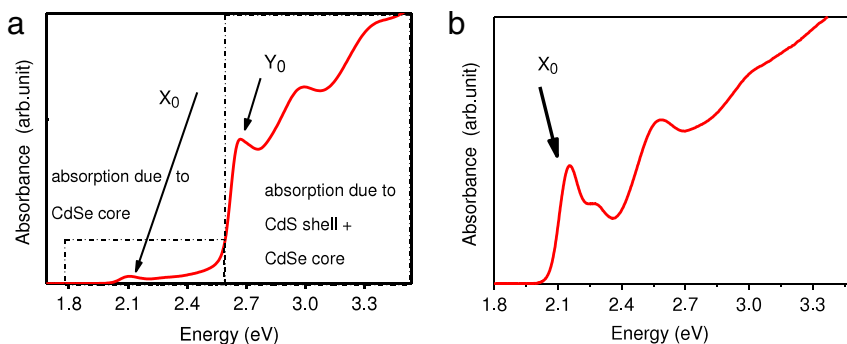


Fig. 1. Absorption spectra of CdSe/CdS dot/rod (a) and of CdSe dot (b). X_0 and Y_0 refer to the first absorption peak in CdSe and CdS, respectively.

that different heterostructures can be realized in which electrons and holes are either both confined inside the core or remain separated in the two materials [6,7].

Core-shell nanocrystals consisting of a rod-shaped CdS embedding a spherical CdSe domain exhibit high fluorescent quantum yields (reaching 70%) and linearly polarized emission [8]. These dot/rod core/shell CdSe/CdS nanocrystals have been recently synthesized with a seeded growth approach at high temperature, which yields high uniformity in terms of rod length and diameter distribution [8]. These nanorods have a quasi-1D electronic structure due to their small diameter, while the dot inside each nanorod has 3D confinement and fully quantized states. It is worth noting that the CdSe spherical domain is most often located closer to one end of the rods across the rod length, rather than at its center, and that is why these nanostructures are also referred to as “asymmetric core/shell nanorods”.

Here we investigate CdSe dots, which are the starting ‘seed’ for the growth of the CdSe/CdS heterostructure [8], and CdSe/CdS dot/rod heterostructures. By means of a pump-probe technique we study ultrafast excited-state dynamics in these samples by resonantly pumping at the band edge and obtain evidence of delocalization of the electron wave function in CdSe/CdS heterostructures.

2. Results and discussion

The laser system is based on a chirped-pulse-amplified Ti: sapphire source, with maximum output energy of about 800 μ J, 1 kHz repetition rate and central wavelength of 780 nm. Excitation pulses are generated by non-collinear optical parametric amplification in a β -barium borate crystal, with pulse duration around 100 fs. Pump pulses are focused onto a 200 μ m spot. Probing is achieved in the visible region by using white light generation in a thin sapphire plate. Chirp-free two-dimensional transient transmission maps as a function of probe delay and wavelength are collected using a fast OMA (optical multichannel analyzer) with a de-chirping algorithm. The measured quantity is the normalized transmission change, $\Delta T/T$, that is proportional to the absorbance change ΔA in the small signal limit. All measurements were performed with rods dispersed in a toluene solution at room temperature.

The samples we study consist of a small CdSe quantum dot of about 3.2 nm in diameter, either isolated or embedded inside a CdS shell with about 50 nm length and 5 nm diameter. The absorption spectra of CdSe/CdS and of CdSe nanocrystals are reported in Fig. 1. The first electronic transition in CdSe is red shifted (by 0.12 eV) in the dot/rod with respect to the corresponding transition in the CdSe dot due to the lower confinement induced by the shell. Two different regions can be evidenced in CdSe/CdS absorption spectrum (see Fig. 1(a)): absorption at energies lower than 2.48 eV is due to CdSe, while at higher energies the main contribution is from the CdS shell [9]. We label X_0 and Y_0 the first absorption peak in CdSe (both in dot and dot/rod nanocrystals) and CdS, respectively.

Fig. 2 reports the transient spectra for both the CdSe/CdS heterostructure and the CdSe dot, obtained upon resonant excitation of the X_0 transition, thus directly generating photo-carriers into the CdSe. In order to compare the experimental results, we superimposed the two spectra by plotting

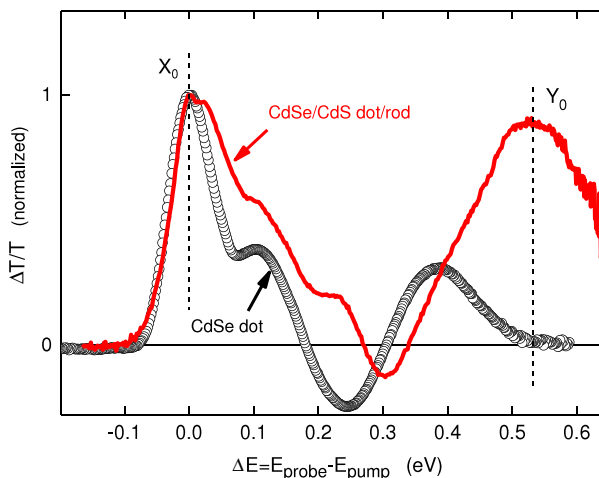


Fig. 2. Normalized differential transmission spectra, at a probe delay of 2 ps, for CdSe dot (black circles) and CdSe/CdS dot/rod (red solid line). The pump excitation is resonant with X_0 for each sample.

them as a function of the energy difference between the probe and the pump photons. As expected, we detect in both samples a positive $\Delta T/T$ signal at zero energy difference, due to photo-bleaching of the X_0 transition. In the CdSe/CdS heterostructure we also detect a strong positive $\Delta T/T$ signal when probing at ≈ 0.55 eV above the band edge (see red solid line in Fig. 2), corresponding to transitions inside the CdS shell. This signal is not present in the CdSe dot (see black circles in Fig. 2), so it cannot be ascribed to any photo-bleaching signal due to transitions inside the CdSe dot at energies higher than the band edge. For these reasons, we assign it to photo-bleaching from the band edge Y_0 transition inside the CdS shell. Due to hole localization inside the core [10], this indicates that photo-generated electrons inside the CdSe dot delocalize inside the CdS shell, filling its band edge levels. We can exclude that the bleaching at Y_0 is due to two-photon absorption because: (i) the pump fluence is < 1 e-h pair per dot; (ii) we do not observe the characteristic dynamics associated to hole transfer. Indeed, two photon excitation would give rise to generation of an electron-hole pair in the CdS rod and subsequent hole transfer to CdSe dot [9] with a time constant of about 700 fs. The later is not present in data here reported, where the rise time is below our time resolution of 200 fs. Temperature activated electron delocalization over of a barrier of 0.3 eV (as reported by other authors, [11]) can also be ruled out, while other temperature effects are unlikely and not observed in any other experiment.

3. Conclusions

In conclusion, by comparing the differential transmission spectra of the CdSe seed with the CdSe/CdS dot/rod heterostructure, we observe the delocalization of the electron wave function at the interface between CdSe and CdS in core/shell asymmetric nanocrystals and corroborate the previously-reported study [9] based on experimental results and theoretical calculations.

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