

Fundamental properties of the ground state exciton in PbSe core and PbSe/PbSeS core-shell nanocrystals quantum dots and their application in a gain device

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Colloidal PbSe nanocrystals quantum dots (NQDs) are the focus of widespread interest due to their unique electronic and optical properties, associated with the tunability of their band-gap in the near infra-red spectral regime (between 0.9 to 3.5 eV), relatively high dielectric constant ($\epsilon_{\infty}=24$) and the recent reported impact ionization process (multi carriers' generation)¹, with feasibility of application in photonic crystals, near infrared (NIR) lasers, biological markers, photovoltaic solar cells, NIR light emitting diodes (LEDs), and Q-switches. Despite the potential vision, there are still controversial opinions regarding the excitonic properties in those materials. Calculations within the framework of effective-mass theory revealed that the conduction and valence bands of PbSe are nearly symmetric, due to the close similarity of the electron and hole effective masses, with level spacing larger than room temperature energy, and ground-state exciton degeneracy of 64.² However, recent tight binding and atomistic pseudo potential calculations³ revealed that inter-valley coupling, anisotropy of effective masses, Coulomb and electron-hole exchange interactions lift the degeneracy of the excitonic states.

This work explores the unique properties of the ground-state exciton in colloidal PbSe core NQDs and of a number of PbSe core-shell structures, denoted as PbSe/PbS, PbSe/PbSe_xS_{1-x} and PbSe_xS_{1-x}/PbSe_yS_{1-y} (the core or/and the shell may have an alloy composition with $x \leq 1$ and $y \geq 0$), with an overall diameters varying between 2.0 nm to 6.5 nm.⁴ The composition was accurately determined by an energy dispersive analysis of X-ray and Raman spectroscopy. The study investigated a few peculiar phenomena in the luminescence spectra of the core NQDs: (a) Appearance of an anti-Stokes emission in NQDs with a diameter > 5 nm (see inset in Figure 1A); (b) Appearance of two emission bands in the continuous wave photoluminescence spectra, recorded at low temperatures; (c) Existence of two decay processes, with a time constant τ_1 of tenths of ns and additional slow component with time constant τ_2 of hundreds of ns (Figure 1A). The lifetimes of both components decreased with the increase of the NQDs size, and the fast component grew to be the dominant one, and consequently shortens the value of the weighted average lifetime, τ_{eff} . The mentioned properties can be correlated with a recent proposed model, predicting a splitting of the 64 degenerate ground-state excitons, by the inter-valley (δ), coulomb and exchange (Δ_x) interactions, into a few manifolds, with the lowest energy angularly allow ones (separated by $\delta=17-80$ meV and $\Delta_x=2-17$ meV, depending on the NQDs' size) responsible for the two emission processes observed in a-c. The lifetime of the core-shell structures showed substantially longer weighted averaged lifetimes, τ_{eff} , in the core-shell NQDs, both with respect to their corresponding cores and with respect to the lifetime of a PbSe core with a similar overall size. This was associated with a reduced overlap between the electron and hole wave-functions spread differently over the core-shell interface, a preferred situation that reduces the Auger effect and may be of a beneficial in a gain and solar cell devices. This work also exhibits a representative example of the utilization of the PbSe core and their corresponding core-shell structures in a gain device (schematically described in the inset of Figure 2), composed a NQDs' monolayer, sandwiched between dielectric TiO₂/SiO₂ Bragg reflectors, spaced apart by $\lambda/2$ (λ =emission energy of the NQDs) and with the appropriate transmittance properties at the NIR spectral regime (Figure 1B). The amplified spontaneous emission is shown by the red curve in the Figure.

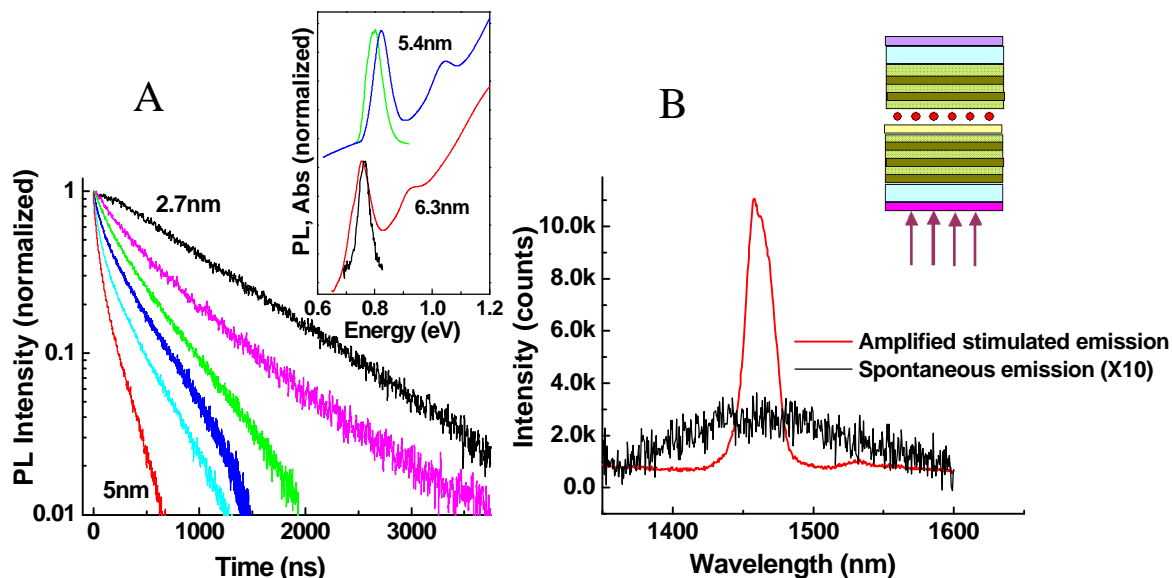


Figure 1: (A) PL decay curves of PbSe core NQDs, measured at room temperature. Inset: representative absorption and cw-PL spectra of PbSe core NQDs. The relevant NQDs diameters are labeled in the Figure; (B) Amplified stimulated emission (red curve) of PbSe/PbS core-shell NQDs, with a 4.2 nm core and a 1.8 nm shell inserted to an air spaced micro-cavities. Inset: A single layer of QDs in an air filled micro-cavity with the following components from bottom to top: 800 nm AR coating, Zerodur (substrate), Sapphire (substrate), TiO₂ and SiO₂ dielectric $\lambda/4$ layers, organic layer, PbSe NQDs and 1.54 μ m AR coating.

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