

Temperature dependence of the ground-state exciton in PbSe core, and relevant core-shell colloidal quantum dot structures

A. Sashchiuk, G. I. Maikov, A. Kigel, R. Vaxenburg, D. Yanover, E. Lifshitz
Schulich Faculty of Chemistry and Solid State Institute, Technion, Haifa, Israel
chaldona@techunix.technion.ac.il

PbSe and PbS colloidal quantum dots (CQDs) are the focus of widespread interest due to their unique electronic and optical properties, with feasibility of applications in near infra-red (NIR) lasers, biological markers, photovoltaic solar cells, Q-switches and nano-electronic devices [1,2]. These semiconductors have a simple cubic crystal structure with nearly identical lattice constants 5.93 Å and 6.12 Å at 300 K, respectively, which facilitates the formation of heterostructures. Recently, [3] high quality PbSe/PbS core-shell and completely original PbSe/PbSe_xS_{1-x} core-alloyed shell CQDs structures produced using a single injection process, offering the potential to tailor the crystallographic and dielectric mismatch between the core and the shell, forming a perfect crystalline hetero-structure. These structures present a tunability of the band-edge offset with variation of the shell thickness and composition, eventually controlling the electronic properties of the CQDs.

The present study describes a thorough investigation of the temperature influence on luminescence spectra and their decay processes in the PbSe/PbS core-shell (CS) (produced using two injection process) and PbSe/PbSe_xS_{1-x} core-alloyed shell CQDs (with 0 ≤ x < 1 produced using a single injection process with an initial Pb/Se/S molar ratios of 1/1/1.5 and 1/0.6/0.8) in comparison with luminescence spectra of the PbSe core CQDs dispersed in glass solution. The compositional and crystallographic structural properties of the studied samples were confirmed by a high-resolution transmission electron microscopy, and energy dispersive analysis of x-ray. The ground-state exciton lifetime was measured and recorded at laser fluence ~0.2 mJ/cm², ensuring the formation of a single exciton per a single CQD.

Figure (A) and (B) shows the representative continuous-wave (cw) photoluminescence (PL) spectra of PbSe with a radius (R) of 2 nm and of PbSe/PbS CS CQDs with R=1.65 nm and shell thickness (Th) of 0.55 nm, measured at various temperatures as indicated in the legend. The absorbance first exciton transition (1.03 eV) at room temperature (RT) is the same for these structures. Figure (C) presents the plots of the PL peak energy versus the temperature (see legends) of PbSe/PbS CS CQDs and of PbSe/PbSe_{0.3}S_{0.7} core-alloyed shell CQDs structures produced with an initial Pb/Se/S molar ratio of 1/0.6/0.8, in comparison with the PL spectra of PbSe core CQDs as indicated in legends. Figure (D) demonstrates the transient PL curves of CQDs shown in Figure (C) according to the legend notations and measured at RT.

PL spectroscopy analyses of these nanostructures, electronic band-gaps and photo-emission demonstrate that compositional, and phonon-electron interactions properties play important roles in these structures. The influence of a dark-bright states thermal activation on the energy and dynamics of a ground-state exciton of PbSe/PbS CS and PbSe/PbSe_xS_{1-x} core-alloyed shell CQDs respect to these of PbSe core CQDs [4] would be discussed.

PL-decay time investigations shows that PL decay process of PbSe/PbS CS CQDs differ from that of PbSe core CQDs, which shows only single exponent behavior. The ground-state lifetimes of the core-shell structures presented in Figure D, in particular the PbSe/PbS CS CQDs, showed substantially longer lifetime on the microsecond time scale at RT, both with respect to their corresponding cores and with respect to that of a PbSe core with a similar overall size. The significant difference in lifetimes between cores and CS CQDs (particular

with smallest core) is a demonstration of the excellent passivation of the shell which prevents non-radiative quenching of the excitons by the Auger effect and is responsible of PL quantum efficiency increasing in core-shell CQDs. This may be beneficial in gain and solar cell devices.

References:

- [1] V. I. Klimov, J. Phys. Chem. B 110 (2006)16827.
- [2] M. D. Fischbein, M. Drndic, Appl. Phys. Lett. 88 (2006) 063116.
- [3] E. Lifshitz, M. Brumer, A. Kigel, A. Sashchiuk, M. Bashouti, M. Sirota, E. Galun, Z. Burshtein, A.Q. Le Quang, I. Ledoux-Rak, J. Zyss, J. Phys. Chem. B 110 (2006) 25356.
- [4] A. Kigel, M. Brumer, G.I. Maikov, A. Sashchiuk, E.Lifshitz, Small (2009) in press.

Figures:

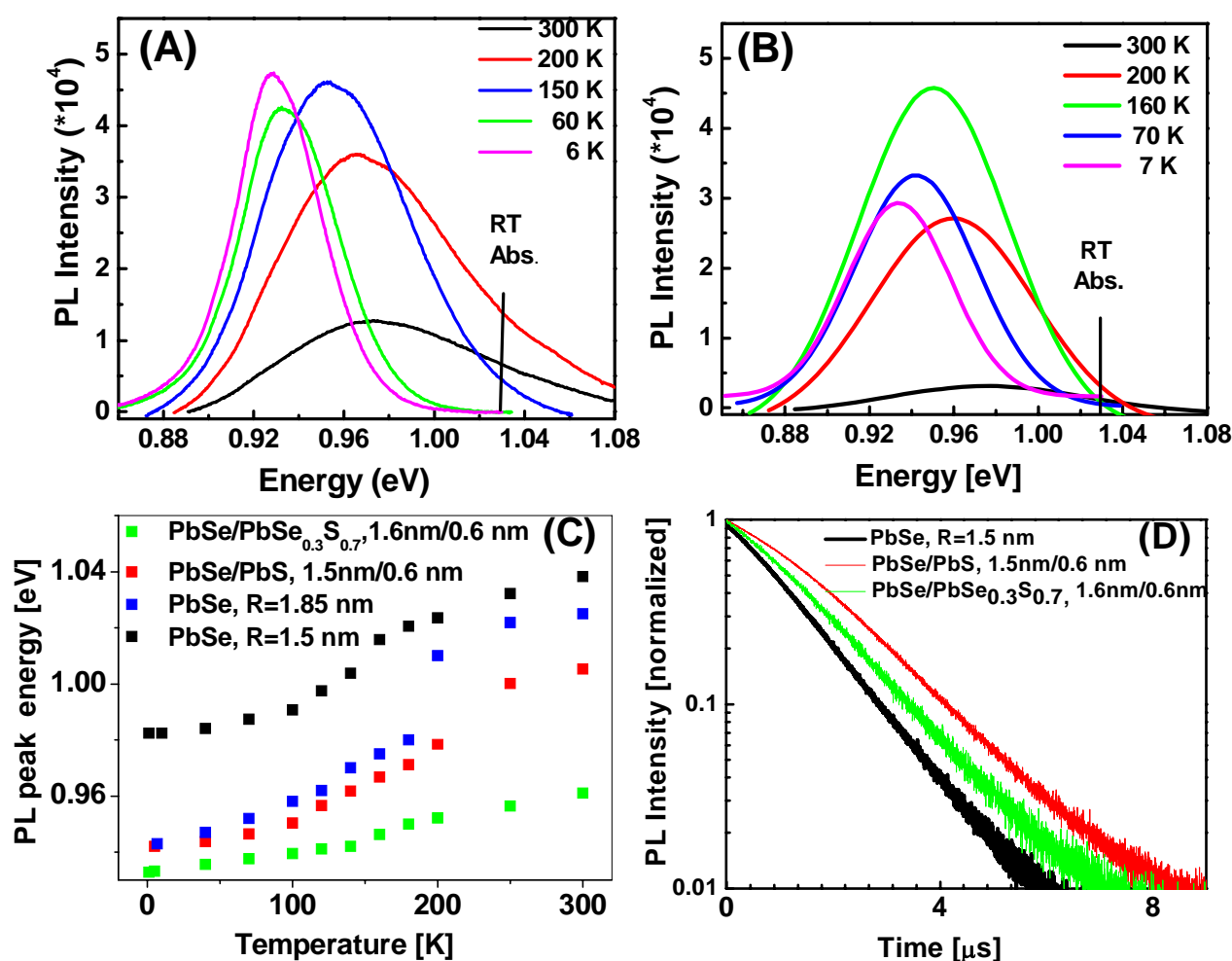


Figure (A) Representative cw-PL spectra of PbSe CQDs; with R= 2 nm; **(B)** Representative cw-PL spectra of PbSe/PbS CS CQDs with R=1.65 nm and Th =0.55 nm, measured at various temperatures as indicated in the legend; Absorbance first exciton transition (1.03eV) at RT is labeled; **(C)** Plots of the PL peak energy versus the temperature, according to the legend notation. (■) PbSe core CQDs with R=1.5 nm, (■) PbSe CQDs with R=1.85 nm; (■) PbSe/PbS CS CQDs with R=1.5 nm and Th =0.6 nm (■) PbSe/PbSe_{0.3}S_{0.7} CQDs with a R=1.6 nm and Th =0.6 nm prepared with a initial Pb/Se/S molar ratio of 1.0/0.6/1.8.; **(D)** The transient PL curves of CQDs shown in (C) according to the legend notations.