

# Impact of excitonic-vibrational coupling in a single colloidal quantum dot emission spectrum<sup>1</sup>

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Colloidal quantum dots (CQDs) implementation in optoelectronics is limited by internal material imperfections such as a fluorescence intermittencies (blinking) and its spectral stability (spectral diffusion). Both the effects originate in the material ability of extra energy exclusion from the system and closely packed charges. A turning point occurred when a few distinctive systems with blinking free behavior were reported in CQDs with either type – I, type – II or *quasi* – type – II core/shell configurations. The particular interest gains the material with *quasi* – type – II configuration and a graded interface composition such as  $\text{CdTe/CdTe}_x\text{Se}_{1-x}$ <sup>2</sup>. This graded composition gives rise to the smooth quantum confined boundaries resulting in the reduction of the non – radiative Auger process and paving the way for non – blinking material and permitting the carrier to interact with a particle surrounding. Since, the CQDs prepared in the wet chemical method, they passivated with organic ligands protecting shell. The ligands shell plays an important role for hot carriers cooling preventing phonon bottle neck in the inter band relaxation processes<sup>3</sup>. This occurs due to sufficient energy losses of the hot carriers to the ligands vibrational modes.

In this work we explore the role of the ligands vibrational degrees of freedom on band edge exciton recombination and the blinking effect/ spectral stability in single (A)  $\text{CdTe/CdTe}_x\text{Se}_{1-x}$  and (B)  $\text{CdSe/CdSe}_x\text{S}_{1-x}$  CQD capped with oleic acid (OA). Along this we present an ability of simultaneous detection of both infrared - and Raman active modes using CQDs spectroscopy.

The major difference between the materials lies in their ability for electron delocalization over the entire core/shell structure.  $\text{CdTe/CdTe}_x\text{Se}_{1-x}$  builds pronounced type – II structure while in  $\text{CdSe/CdSe}_x\text{S}_{1-x}$  an uncertainty in the conduction band alignment between CdSe and CdS enables carrier delocalization depending on the shell thickness and composition. Electron wave function penetration to the particle surface enhances the exciton coupling to the ligands vibrations opening the alternative channel for the relaxation. Control experiments with ligand exchange to hexadecylamine (HDA) and performing ZnS buffer shell were done. In the first, we observed a change in vibrational modified emission lines. While in the last, no exciton – ligand vibrational modes coupling was observed.

A representative spectra of  $\text{CdTe/CdTe}_x\text{Se}_{1-x}$  - OA (green),  $\text{CdTe/CdTe}_x\text{Se}_{1-x}$  - HDA (black)  $\text{CdSe/CdSe}_x\text{S}_{1-x}/\text{ZnS}$  - OA (red) and FTIR of free OA (blue) are shown in figure (left panel). The  $\text{CdTe/CdTe}_x\text{Se}_{1-x}$  - OA shows similar emission lines detuned from the exciton transition, while  $\text{CdTe/CdTe}_x\text{Se}_{1-x}$  - HDA possesses a different emission lines. This occurs due to the exciton coupling to the different vibrational modes of the surface capping ligands. At the same time ZnS passivated particle does not exhibit any vibration induced structure due to the spatial separation of the exciton wave function from the particle surface. The left panel of the figure shows a representative plots of PL spectra recorded over time span with acquisition time 1 sec of  $\text{CdTe/CdTe}_x\text{Se}_{1-x}$  - OA (upper) and  $\text{CdSe/CdSe}_x\text{S}_{1-x}/\text{ZnS}$  - OA (bottom). The insets show the TEM image of the measured material. One can see that the exciton coupling to the ligand vibration stabilize the material emission, i.e. the material has a non-blinking behavior and has less pronounced spectral diffusion.

# References:

- 1 in preparation
- 2 Osovsky *et al.*, Phys. Rev. Lett. 102, 197401 (2009)
- 3 Guyot-Sionnest *et al.*, Journal of Chemical Physics 123, 074709 (2005)

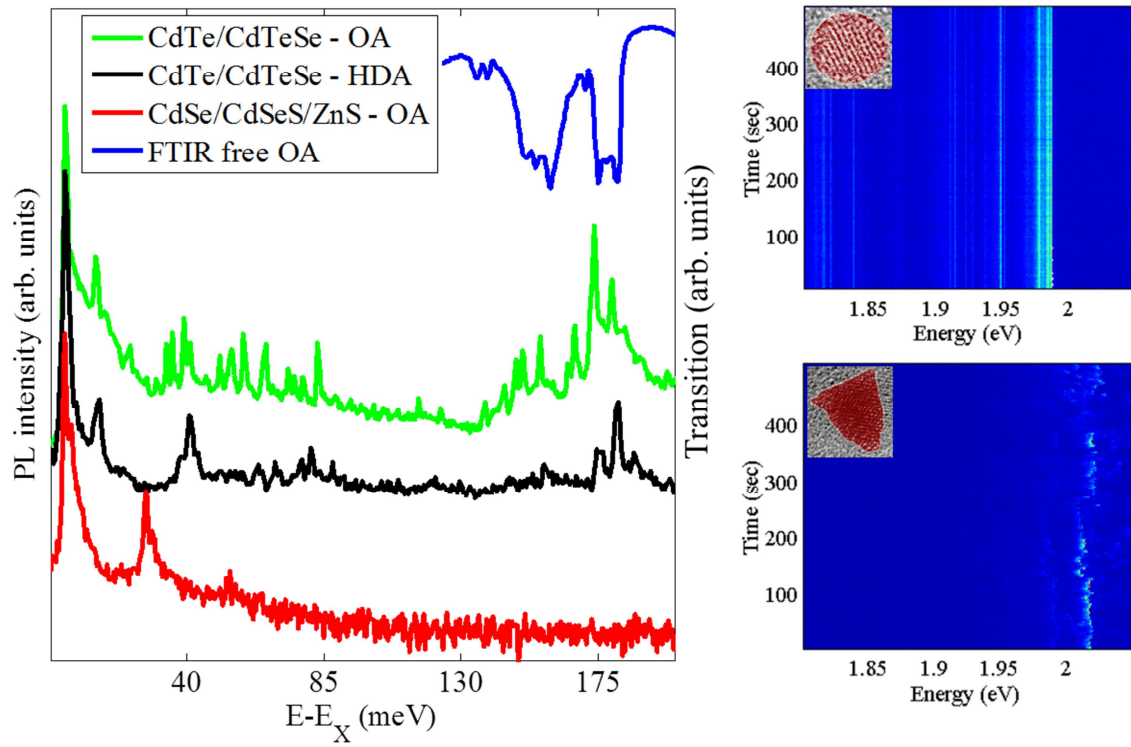


Figure: Left panel: FTIR spectrum of free OA (blue), PL spectra of CdTe/CdTe<sub>x</sub>Se<sub>1-x</sub> - OA (green), CdTe/CdTe<sub>x</sub>Se<sub>1-x</sub> - HDA (black) and CdSe/CdSe<sub>x</sub>S<sub>1-x</sub>/ZnS - OA (red). Right panel: PL spectra recorded over time span with acquisition time 1 sec of CdTe/CdTe<sub>x</sub>Se<sub>1-x</sub> - OA (upper) and CdSe/CdSe<sub>x</sub>S<sub>1-x</sub>/ZnS - OA (bottom). Insets: TEM images of the measured materials.