The Role of Electron Delocalization on Exciton-Phonon Coupling in CdSe/CdS Nanocrystals

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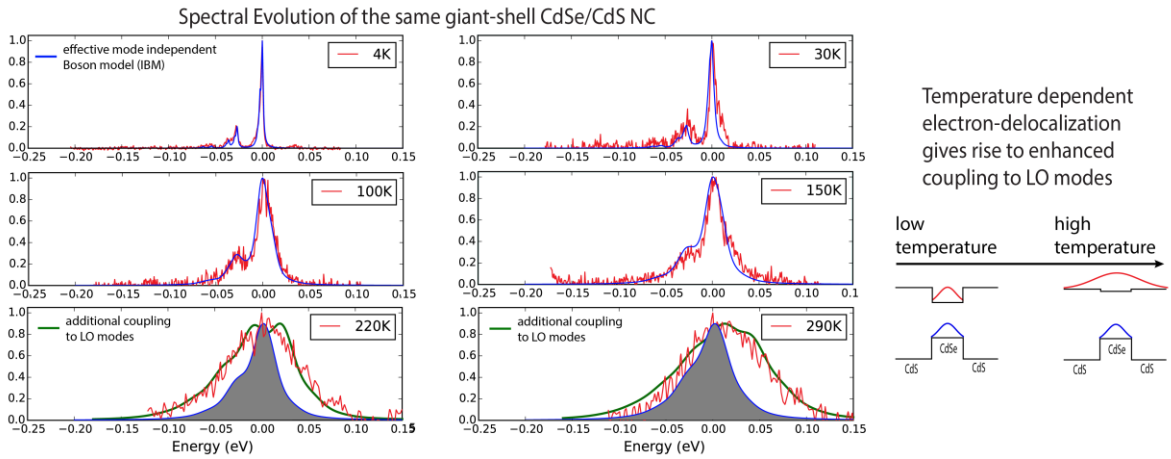
The exciton-phonon interaction in nanocrystals crucially determines the application relevant emission lineshape. However, the strength and nature of exciton-phonon interaction in nanocrystals remains poorly understood, and has been subject to a multitude of discrepant studies in the past.[1,2] In particular, it has proven difficult to reconcile the narrow (<1 meV) low temperature (~4 K) linewidths and weak phonon sidebands with the broad room temperature emission linewidth (60-100 meV) within the framework of a suitable model. Moreover, clear relationships between exciton-phonon coupling parameters and the architecture of nanocrystals are not yet established.



To elucidate the exciton-phonon interaction in nanocrystals, we have studied a series of CdSe/CdS core/shell nanocrystals with vastly different shell-thicknesses. The quasi type-II band alignment in these materials allows tuning of the excited state electron-hole separation with the shell-thickness.[3,4] Using a combination of single dot emission spectroscopy over a wide temperature range and time dependent fluorescence spectroscopy, we have investigated the role of the shell-growth induced carrier separation on the exciton-phonon coupling parameters.

We find that the room temperature single NC lineshape of thin-shell CdSe/CdS and the lineshape at 4 K can be reconciled within the framework of a self-consistent model taking a single set of exciton-phonon coupling parameters into account. For thick-shell NCs, our model systematically underestimates the linewidth above 220 K, coninciding with electron-delocalization into the shell.[4] We explain this additional broadening with enhanced exciton-phonon coupling to LO modes via the dipolar Fröhlich mechanism due to the larger exciton dipole.

For the first time, our study allows the dissection of the room temperature linewidth in terms of exciton-phonon coupling parameters. Moreover, it highlights the importance of the electron-hole separation in determining the application relevant linewidth, and can directly be translated into synthetic guidelines to minimize the emission linwidth of core/shell nanocrystals.

1) M.Salvador *et al. J.Chem.Phys.* **2006**,125,18.
2) C.Lin *et al.*, *ACS Nano*, **2015**, 9 (8),8131-8141.
3) J.Cui *et al.*, *Nano Lett.*, **2015**, *16*, 289-296.
4) C.Javaux *et al.*, *Nat. Nano.*, **2013**, *8*, 206-213.