Biexciton Dynamics in CdSe Nanocrystals

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Due to decades of research, CdSe NCs can be made with unity exciton quantum yield and with emission wavelengths spanning the visible spectrum rendering them promising materials for lasing and lighting applications.

However, for these applications NCs are subjected to high electrical or optical fluxes, entering a regime where more than one excitation may occur in a nanocrystal simultaneously. Losses in efficiency, even in samples with unity exciton quantum yield, under high-flux illumination are likely due to multiple charge carrier interactions such as Auger recombination. Hence our understanding of what determines the Auger rate, and how it is tied to the NC architecture is crucial for tailoring NC for high-flux applications.

It was long hypothesized that steep potential barriers, such as at a core/shell interface, enhance Auger recombination and by smoothing that barrier with a gradient shell structure, multiexciton yields could be improved. In fact, recent studies have demonstrated unity biexciton quantum yield samples with a bulky, gradient CdS shell.[1] Results in our lab, however, indicate that the shell thickness alone plays a significant role in improving multiexciton quantum yield.[2] These results demonstrate that our understanding of the dynamics of multiply excited states is still incomplete.

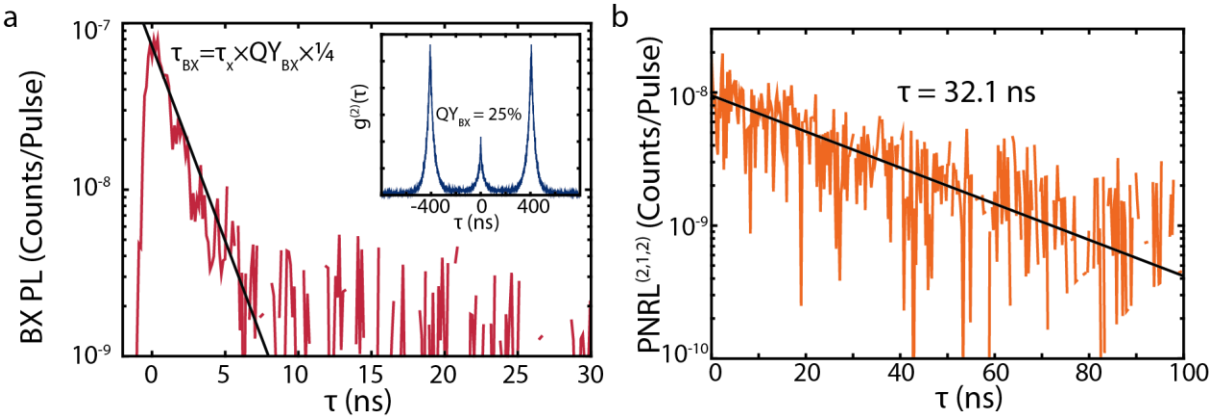

Fig. 1 a Lifetime of the first photon in a two photon emission event, or the biexciton lifetime, in a thin-shell CdSe/CdS NC. **b** Time delay between first and second photon in a two photon emission event, or the exciton lifetime for a decayed biexciton in a thin-shell CdSe/CdS NC.

Our recent developments in analysis of single molecule time correlated single photon counting (TCSPC) data allow us to extract the lifetime of the biexciton, as well as the delay between the first and second photon in a biexciton emission event. Our results indicate, for thin shelled CdSe/CdS NCs, the biexciton lifetime is consistent with a bound biexciton model (fig. 1a). Additionally, the system has no memory, and the lifetime of the second photon matches that of the exciton (fig. 1b). Upon relaxation of confinement either through dimensionality or adding a shell structure, the biexciton lifetime develops multiexponential character which cannot be explained through a simple four carrier band-edge model. Understanding this breakdown may hold the key to continue improving and designing probes for lighting applications.

[1] M. Nasilowski *et al.*, *Nano Letters*, **2015**, 15(6), 3953-3958.
[2] A. Beyler *et al., Nano Letters,* **2014**, 14, 6792-6798.