Delayed exciton emission in InP-based nanocrystals

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Delayed exciton emission is the observation of photoluminescence (PL) on time scales much longer than the intrinsic luminescence lifetime and has recently been reported for various types of semiconductor nanocrystals (NCs), such as CdSe/CdS core-shell QDs, CdSe nanoplatelets, (Cu-doped) CdSe QDs, and $CuInS_2$ NCs [1-3]. Delayed luminescence occurs if absorption of a photon is followed by temporary charge carrier trapping and subsequent slow recovery of the exciton state. The resulting delayed exciton emission will have the same emission wavelength as direct exciton recombination, but is delayed due to the time that the charge carrier was trapped in the metastable state. Until recently, the delayed PL component was often overlooked because the delayed luminescence amplitude is small relative to the total PL amplitude during photoexcitation. However, it can account for a large fraction (10-50%) of the total emission after an excitation pulse. Interestingly, the decay of delayed emission follows a power law and has therefore been related to blinking.

In this work, we studied the photoluminescence decay dynamics of colloidal InP-based core/shell NCs on time scales up to tens of microseconds. For InP/ZnS NCs we observe a mono-exponential decay with a lifetime of 40 ns on short (<100 ns) time scales. At long (>100 ns) time scales the decay curve deviates from mono-exponential behavior and follows a power law as expected for delayed emission (Fig.1). Using the theoretical model of Rabouw *et al*. we obtain a 20% probability of charge separation, which is a significantly higher trapping probability than observed in CdSe/CdS NCs. Moreover, we find that the energy spectrum of the delayed emission deviates from that of prompt emission. A second emission peak appears in the spectrum 500 ns after excitation caused by radiative recombination from deep trap states. These measurements demonstrate the existence of (at least) two different types of delayed emission in InP/ZnS NCs: (I) delayed emission due to carrier trapping and recovery to the exciton state, and (II) delayed emission from trap states that can decay by emission of midgap photons.

In addition, we compare the results obtained for InP/ZnS and InP/ZnSe NCs and study the temperature dependence of the delayed emission to provide insight in the recombination mechanism.

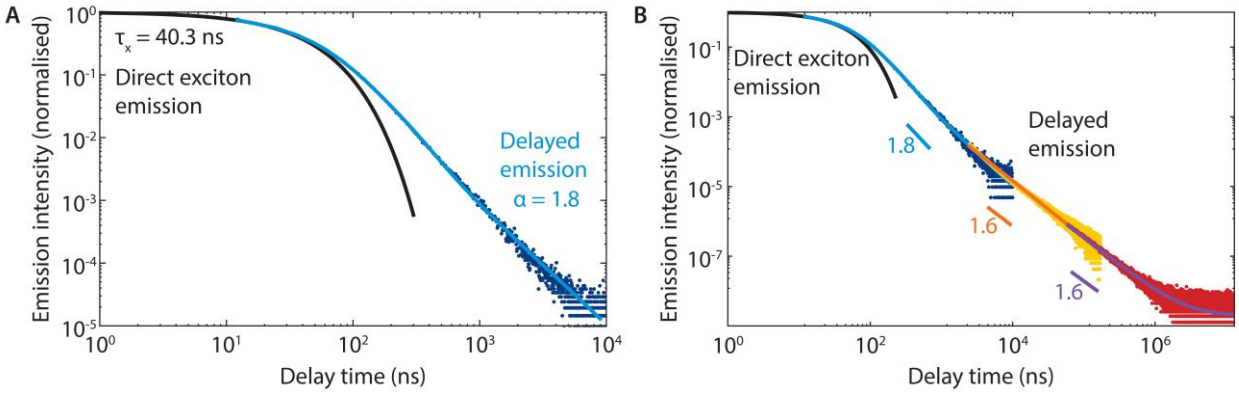

Fig. 1 Photoluminescence decay dynamics for InP/ZnS core shell nanocrystals in (a) the first 10 µs after excitation. The blue line is a fit obtained using the delayed emission model of Rabouw *et al*. The black line represents a mono-exponential fit of the direct exciton emission using the lifetime fitted by the model. (b) Decay dynamics for times up to 10 ms after excitation obtained during three different measurements and fitted with a power law.

1) F.T. Rabouw *et al*., *Nano Lett.*, **2015**, *15*, 7718-7725.
2) A. Marchioro *et al.*, J. *Phys. Chem. C*, **2016**, *120, 27040-27049.*
3) F.T. Rabouw *et al*., *Nano Lett.*, **2016**, *16*, 2047-2053.