Novel Spectral Decay Dynamics of Hot Excitons in PbSe Nano-Crystals.

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Abstract: Ultrafast exciton cooling in highly mono-disperse PbSe nanocrystals (NC) is followed with tunable pump - Hyperspectral near-IR probe spectroscopy. Unexpected kinetic and spectral correlations are revealed arguing against the standard models for excited NC absorption.
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1. Introduction

Hot exciton cooling dynamics are of fundamental interest, and are also of practically significance. Before excess photon energy is dissipated, it is proposed to be utilizable via quantum dot (QD) specific mechanisms for boosting the production of additional carriers in solar cells [1]. This proposal was based on the sparse spacing of electron states near the band edge, expected to slow down energy dissipation. Experiments show this expected phonon bottleneck is absent in many semiconductor NC samples. Fast excess energy transfer from electron to hole, which later loses it rapidly by phonon emission, otherwise known as Auger cooling, [2] was suggested to facilitate this rapid decay. In PbSe QDs, which also exhibit rapid carrier cooling, electrons and holes have similar effective masses, predicting symmetry in level spacing between the conduction and valence bands, possibly reducing the effectiveness of this mechanism. To better characterize energy relaxation in hot excited PbSe QDs, we have used ultrafast hyperspectral transient absorption spectroscopy. The high degree of size uniformity in the samples studied allows selective pumping and probing in particular optical transitions, which is essential for deciphering the spectral evolution associated with hot exciton cooling. The broadband hyperspectral probing apparatus used offers detailed spectral characterization of the sample during exciton cooling, demonstrating that the accepted mechanisms underlying TA of QDs are insufficient for explaining all our observations. Finally, the transient spectra recorded are also at odds with recent theoretical predictions concerning the effective cooling mechanisms of hot excitons in PbSe QDs.

2. Results and Discussion.

The initial 3 psec of spectral evolution following excitation at t=0 of PbSe QDs with varying pump wavelength is presented in figure 1 panel a to d as sequences of transient difference absorption spectra at delays indicated in the figure legend. Pump photon fluxes in both were controlled to deposit ~1 exciton per QD on average at the front surface of the sample, which had an OD of 0.5 at 1500nm.

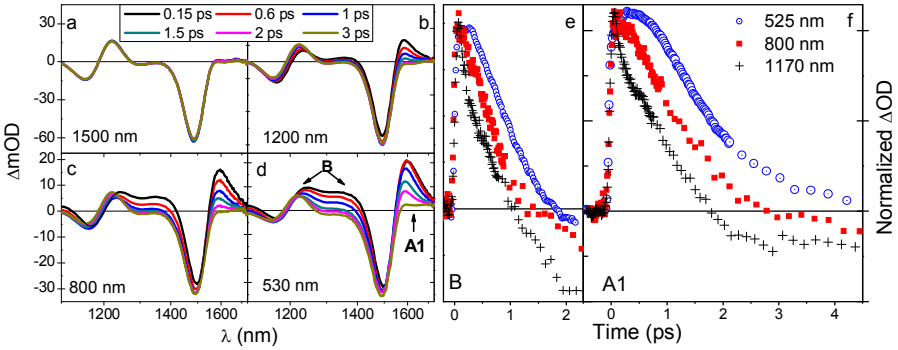

Fig. 1. Transient difference spectra presented as temporal cuts at the designated pump–probe delays, after excitation at 1500 nm(a), 1170 nm(b), 800 nm(c) and 525 nm(d). Panel e and f present the decay kinetics of the B and A spectral bands.

At all four excitation wavelengths photon absorption leads to an immediate buildup of an intense bleach feature centered near the 1S and 1P absorption peaks. Along with them a broad absorption which extends from below to well above the absorption threshold appears promptly when exciting above the band edge. The amplitude and the spectral range are enhanced with the increase of exciting photon energy, farther more the decay in absorption does

not take place with the same rate throughout, the prompt broad induced absorption spanning the 1S and 1P peaks (B) decays faster than the sharp induced absorption peak just below the 1S band (A1), as demonstrated in the table below which quantified these decays. finally, at delays >3 psec, the signal converges to that observed immediately following excitation at 1500.

	A1			B		
Pump wavelength (nm)	1150	800	500	1150	800	500
$t_{(1/2)}$ (fsec)	850	1300	1650	650	700	1050
Normalized amplitude	0.49	0.53	0.55	0.05	0.2	0.27
trailing edge lifetime (fsec)	1150± 50	1200± 30	1170± 30	930± 20	825± 10	850± 10

Table 1. Normalized amplitudes and decay kinetics of the major cooling spectral features for above band edge excitation wavelengths

These results are at odds with the accepted paradigms of transient spectra in hot excited QDs, which are based on two mechanisms - that of biexciton interactions where Coulomb interactions lead to modifications in level energies which result in shifts in the related optical transitions, and that of state filling where filling of electronic states leads to blocking of the corresponding optical transitions. Not only would these mechanisms predict a slow rise in band edge bleach but prior to exciton cooling, any such feature would be the negative portion of a correleted spectral shifting feature, both spectrally shifted from the initial band center.

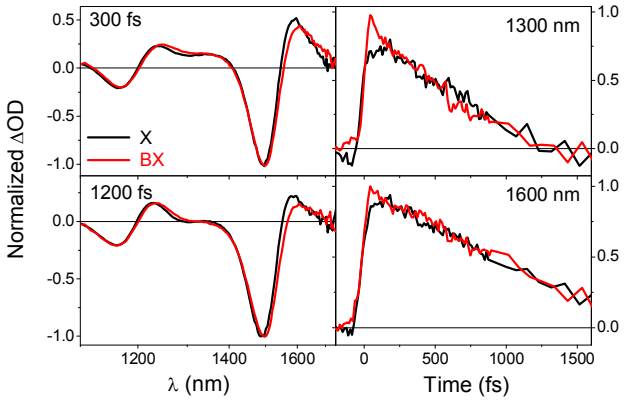

Fig. 7. Comparison of single- and bi-exciton transient spectra after 800 nm excitation. Left - transient difference spectra at the designated pump–probe delays. Right - decay kinetics of TA at 1600nm and 1300nm.

To study the bi-exciton effects on cooling dynamics, the contribution of the double exciton to the spectral evolution mas isolated and compered to the single exciton. The results are presented in figure 2 both as time and spectral cut which display the dynamics of features associated exclusively with hot excitons. The match between the spectra and the time traces evolved is almost perfect. If the cooling was a multi body process then the rate will grow at least linearly with the number of excitons since more exciton generate additional number of potential partners. Thus the identical rates for cooling of single and multi-excitons demonstrates the ineffectiveness of Auger cooling in this material.

3. Conclusions

- The sudden rise of band edge bleach and surrounding induced absorptions following excitation high above the band gap are at odds with the expectation that this feature arises from state filling. Its kinetic independence from the hot below band gap induced absorption, expected to arise from strong interactions in hot biexcitons compounds this quandary - demonstrating the need for revising our understanding of TA in QDs.
- Data analysis has allowed the separation and kinetic characterization of single and double exciton contributions to changes in transmission. The remarkable similarity of both in appearance and decay dynamics clearly indicates no involvement of Auger cooling in the rapid exciton relaxation in PbSe QDs.

References

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