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Testing the fate of nascent holes in CdSe Nanocrystals with sub 10 fs pump-probe spectroscopy

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Numerous studies have reported that transient absorption spectra in core CdSe nanocrystals do not register state filling in $1S_h$, an absence which has profound consequences in light emitting applications. It has been assigned alternatively to rapid hole trapping, or to distribution over a dense degenerated valence band manifold which includes dark states. Here we attempt to observe early contributions of nascent holes to the bleaching of the band edge exciton transition by conducting $1S_e1S_h$ pump - $1S_e1S_h$ probe spectroscopy with <10 fs laser pulses on organic ligand passivated CdSe crystals. Results show no rapidly hole-state filling effects in transient absorption measurements even at the earliest delay, despite use of pulses which are capable of resolving all dissipation mechanisms reflected in the homogeneous $1S_e1S_h$ band width. This proves that neither hole-trapping nor rapid redistribution of the nascent hole over energetically available valence band states can explain absent hole contributions to band edge bleaching, calling for a mechanistic review of this phenomenon.

1. Introduction

Early anticipation of efficient gain media based on quantum confined nanocrystals (NC) have yet to be routinely realized. Rapid Auger recombination of multiexciton states is one wide spread limiting factor. In CdSe[1–3] and other II-VI NCs[4,5] this is compounded with an ill understood inactivity of band edge hole states in facilitating stimulated emission. This absence of hole state filling effects in photo excited NCs has several manifestations in pump-probe spectroscopy. One is that in conventional organic ligand passivated samples a single relaxed exciton induces a 50% bleach of the band edge (BE) absorption abbreviated X1 (see figure 1),[3] and two or more ($NX \geq 2$) render the sample transparent but not emissive.[1,3] Another is the absence of ingrowth of this bleach signal following selective excitation in the $1S_e2S_h$ band (X2, figure 1) during relaxation of the hole to $1S_h$.[6] Still a third is the insensitivity of the BE bleach amplitude to hole-extraction by molecular scavengers.[7] All these have been attributed to the high density of hole-states at the top of the degenerate valence band with contributions from optically dark levels,[8,9] and/or to ultrafast hole-trapping.[1,10] The latter is in accord with another observation showing that capping CdSe cores with very thick layers of high band gap inorganic materials leads to the appearance of stimulated emission from excited NCs.[11–14]

In absence of hole effects on pump-probe BE bleach signals, trapping rates have been deduced from alternative spectroscopic observables.[15] Early on, a rate in the sub-ps to ps range was deduced by probing the IR TA from $1S_h$ to $1P_h$ after inter band photo excitation, and assigned to hole trapping in intrinsic electron donor sites within the NC.[16] This was later refined to ~1 ps for a fast majority component of trapping in particles of equal size, using high time resolution fluorescence upconversion.[17,18] A significantly longer hole trapping time of several ps was deduced from sub-band gap photo induced absorption signals.[19] Despite the initial excitation being above band gap in these experiments, the dynamics of hole-trapping was resolvable with routine femtosecond laser systems. Furthermore, the range of trapping times along with much faster hole cooling would leave ample time for observing relaxed hole effects on the X1 bleach if they were present. Uniformly, none were reported. This invisibility of holes in the X1 transition after relaxation from $2S_h$ even in well passivated core/shell samples has led others to postulate hot-hole trapping which bypasses relaxation to the band edge altogether.[20] No less baffling is the observation that ultrafast laser pumping directly into X1 has also not shown evidence for a short lived hole induced bleaching of this band in femtosecond transient absorption (TA) experiments.[6]

Revealing the mechanism which inactivates the availability of holes for bright near BE transitions in CdSe NCs is of the utmost importance. From a basic point of view this blind spot renders photophysics of the most extensively studied family of semiconductor NCs fundamentally ill understood. From a practical perspective its elucidation is vital for using these systems as stimulated emitters. Recent studies have accordingly attempted to clarify the source of these phenomena. The first compared state selective TA in CdSe cores with CdSe/CdS/ZnS core-shell-shell NCs, assuming that the main effect of the double layer capping is elimination of surface traps. Contrary to observations in CdSe cores, BE bleach ingrowth during $2S_h$ to $1S_h$ relaxation was detected for the double capped cores.[10] The authors concluded that similar hole-contributions to the 1S band-bleaching are absent in conventional CdSe and CdTe core NCs due to rapid hole-trapping by surface defects. Another study has compared time resolved emission with TA on cores and core/sell NCs with and without hole-scavengers, but takes a different view on the cause, maintaining that thermal distribution over both bright and dark exciton levels suffices to explain the observations.[21] In both cases the absence of prominent

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hole-state filling contributions even when exciting directly at the band edge of core samples was assigned to trapping and/or population redistribution being too fast to be detected with the employed time resolution of a few tens of fs. This is ~100 times faster than previously suggested for surface trapping,[17,19] and even faster than the process of Auger cooling of hot electrons which presumably requires a free hole.[22,23]

Given the wide range of time scales assigned to hole trapping in II-VI NCs, and the controversial absence of hole state filling effects on BE bleach signals, in this study we look for early hole contributions to the band edge absorption feature with superior time resolution. Since the transition dipole depends on correlations of both carriers, such contributions are expected following photoexcitation even for a brief time. Pump-probe measurements are reported on organic ligand passivated CdSe samples using sub- 10 fs laser pulses whose spectrum overlaps exclusively with the lowest exciton transition. These transform limited pulses have spectral widths several times that of the X1 feature, and are accordingly capable of capturing all the ensuing dissipation processes. As demonstrated below, no ultrafast BE bleach decay which would be expected to accompany hole-trapping is observed, even with this extreme time resolution. This casts doubt on the assignment of the missing hole contribution to the BE bleach signal to rapid trapping, and renews the enigma concerning the source of its absence in this and other conventionally passivated nanocrystal.

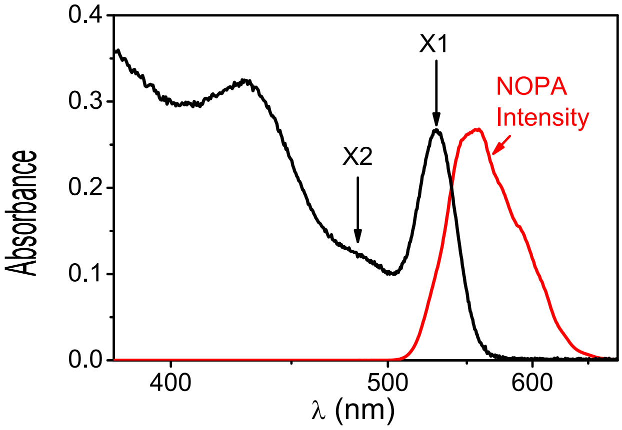

Figure.1. Absorption of CdSe quantum dot sample dissolved in hexane and NOPA intensity (red one) spectra.

2. Experimental section

2.1 Synthesis of zinc-blend core CdSe QDs

We prepared CdSe core NCs after following our previous report.[24] To synthesise the CdSe QDs, first we prepared cadmium and selenium precursor separately. Cadmium precursor was prepared after mixing of Cadmium oxide (CdO) and oleic acid (OA) of a molar ratio 1:4 in 37 mL of 1-octadecene (ODE) into a three-neck flask. To deaerate the mixture was degassed for 1 h at 110°C under vacuum. The temperature of this mixture was increased to 300°C under nitrogen flow until the solution turned optically transparent, representing the formation of cadmium oleate. Then the solution was allowed to cool down to room temperature and hexadecylamine (HDA) in a molar ratio of 1:8 (Cd/HDA) was added to Cd-precursor. Then after the mixture was degassed for 1 h under vacuum at 110°C and it was heated up to 280°C in nitrogen atmosphere. 8 mL of 0.1M selenium in trioctylphosphine (TOP) as selenium precursor was injected to the flask at 280°C at a single shot. To grow the desired particle size we waited for 1 min after addition of selenium precursor and the reaction was quenched after cooling down the reaction mixture to room temperature with water bath and addition of 10 mL ODE. To clean the formed CdSe QDs, cooled reaction mixture was precipitated with 1:1 ratio of 2-propanol/ethanol mixture, separated by centrifugation at 3600 rpm for 30 min, and then re-dissolved in hexane.

2.2. Femtosecond Pump-Probe Measurements

To perform the Pump-probe measurements, NC samples were dissolved in hexane and placed in a 0.2 mm path-length quartz cell under inert atmosphere. Pump-probe measurements were carried out on a home built amplified Ti-sapphire laser generating pulses of 1 mJ, duration of 30 fs, and peak wavelength of 790 nm. 7 fs pulses were generated in a home built Non collinear Optical Parametric Amplifier (NOPA) tuned to excite the CdSe sample exclusively at the BE transition. The high time resolution experiments derived both pump and probe beams by splitting the output of the NOPA. For saturation experiments depicted in figure 4 pump pulses were derived by frequency doubling part of the 790 nm amplifier output in BBO. This choice stems from the insensitivity of the cross section at 400 nm to the number of absorbed photons allowing the assumption of Poisson exciton statistics. Once the cross section at 400 nm is deduced, that at other wavelengths can be calculated from the absorption spectrum. Probe pulses in the range of 350-750 were generated by focusing 1300 nm pulses from an optical parametric amplifier (TOPAS 800, Light Conversion) on 2 mm of CaF2. In both cases the probe was dispersed in a SpectraPro 2150i imaging spectrograph (Acton Research Corporation) equipped with a CCD camera (EntwicklungsbüroStresing).

3. Results and Discussion

The NC sample consisted of Oleic acid (OA) passivated CdSe cores with a BE peak absorption at 528 nm. An absorption spectrum is shown in figure 1 along with an intensity spectrum of the NOPA pulses which were tuned to overlap only with X1. Figure 2 presents high time resolution TA data in the form of 2 D colour coded contour maps, the lower presenting an expanded view of pump-probe temporal overlap. NOPA pulses serve both for photo excitation and probing. These maps are obtained after subtraction of a nonlinear artefact due to the window material and the non-absorbing solvent as described in the SIO. The maps have not been time-corrected in any way, demonstrating the high level of pulse compression achieved in the NOPA setup.

Close to the origin of pump-probe delay, periodical spectral structure is observed which is characteristic of degenerate pump-probe on resonance.[25–27] As reported for such samples, the TA spectra following BE excitation consists of a bleach at the two lowest transitions involving the 1S electron state due to state filling.[16,19] Additional weaker positive and negative features appear when probing deeper to the blue assigned to spectral shifts of absorption bands due to bi-exciton interactions.[16,19] Following the sudden rise of these features very little change is observed over the first ps or

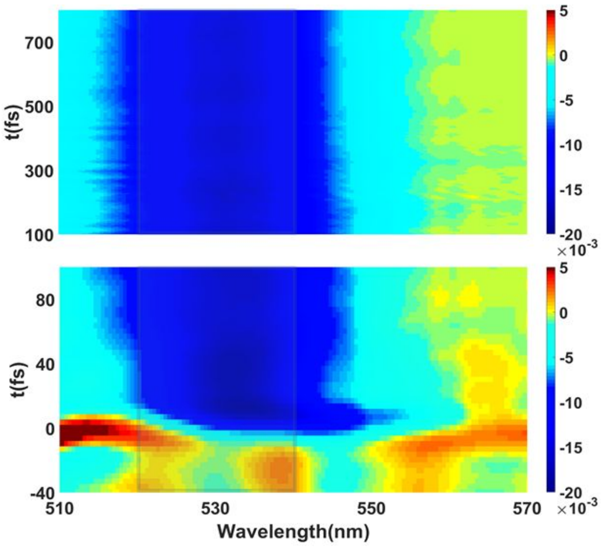

Figure 2. Contour maps of NOPA pump- NOPA probe data for CdSe QDs after subtraction of the nonlinear artefact. Upper and lower panels are the maps for time delay up to 100 fs and 100-800 fs, respectively.

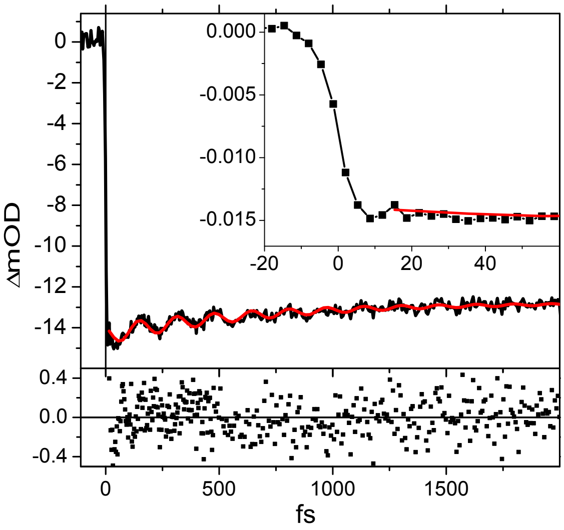

Figure 3. Bleach dynamics of CdSe QDs after integration over the wavelength range between the two dark lines in figure 2. The red curve is an optimal fit using equation {1} and the parameters in table 1 the residual of which is shown below. The Inset shows bleach signal rise on an expanded time scale.

	Value	Standard Error
Y_0 (OD)	-0.0128	1E-4
T_1 (fs)	680	50
T_2 (fs)	840	100
Φ (Rad)	-0.92	0.08
ω (Rad / fs)	0.038	2E-4
A (OD)	-0.0016	1-4
B (OD)	-4.9E-4	4.E-5

Table 1. Best fitted parameters for the bleach dynamics shown in Figure 3.

two which is the time interval of interest here. In order to look for a ~30% decay in bleach amplitude as reported in reference 10, which would be anticipated for rapid hole trapping or population redistribution, figure3 presents a spectral cut obtained by averaging data between the markers in the colour maps of figure 2. This regions coincides with the peak of the 1Se-1Sh bleach, and integration over the half width of the bleach serves to average out this structure and any other spectral shifts related to pump-probe overlap in order to cleanly observe changes in the transient dipole strength.[26]

Following a sudden rise in the bleach signal, ~10 fs in duration, there is a mild rise over the first ~100 fs, and definitely no sign of a rapid decay in the bleach. When observing the full 2.5 ps of delay this slow rise can be assigned to the onset of spectral modulations due to impulsively induced coherent phonons as demonstrated in literature.[28,29] The appearance of this feature has been reported by Kambhampati and coworkers for X1 photoexcitation with short laser pulses.[29] Aside from this modulation, figure 3 shows the absence of any sub 100fs decay signal which would be expected for rapid trapping of nascent holes assuming that they contribute to the bleach signal as previously suggested, and dismissing the ultrafast trapping or population redistribution scenarios.[10,21] This is demonstrated by fitting the bleach evolution in Figure3 with equation {1}:

$$\{1\} \qquad y = Y_0 + Ae^{-t/T_1} + Be^{-t/T_2}\sin(\omega t + \Phi)$$

Parameters which produce the optimal fit are summarized in Table 1. The dephasing time of the coherent modulations of just under 1ps can be assigned to the ~205 cm^{-1} optic phonons in CdSe. Thus aside from a shallow and slow bleach decay typical to core only samples,[30] previously assigned to a mild and gradual component of electron trapping, the signal is perfectly fit by a step function superimposed by an exponentially decaying harmonic oscillation. These observations can't result from limitations in time resolution since our methods can record all decay processes contributing to the homogeneous line width of the X1 transition. This is demonstrated by the spectra in figure 1 and the evidence for pulse Compression in figure 2. However, the lack of an ultrafast initial decay in itself does not prove the absence of stimulated emission. For that we need to quantify the initial bleach per exciton and compare it to the well characterized absorption cross section of these CdSe NCs,[31] further verified here by bleach saturation methods. As detailed in the SIO, the density of absorbed pump photons was compared with the initial bleach signal and from it a bleach cross section per exciton of 4.8×10^{-16} cm^2 was obtained. Within our estimated 5% error margin, this is precisely half of the peak 1Se1Sh absorption cross section, σ_{BE}, and matches the expected impact on the TA of filling one of the two 1S electron states, without contributions from holes.[31] Accordingly not only is there no sign of rapid hole-trapping or population redistribution, the amplitude of the initial bleach already matches a scenario where stimulated emission plays no role. Yet another consistency test is presented by measuring the saturation bleach possible when exciting the sample intensely well above the band-gap. Results of this test are presented in figure 4, showing that presence of ≥2 relaxed excitons per NC will at most bleach the BE transition completely. In fact, due to an imperfect separation of time scales between exciton cooling (~1 ps) and Auger recombination (~14 ps), the bleach is limited even at saturation just below 90% of the sample absorption. After taking this into account, the absence of net gain demonstrates the absence of hole contributions from ~1 ps and onwards. Earlier times are covered by the data in figure 3.

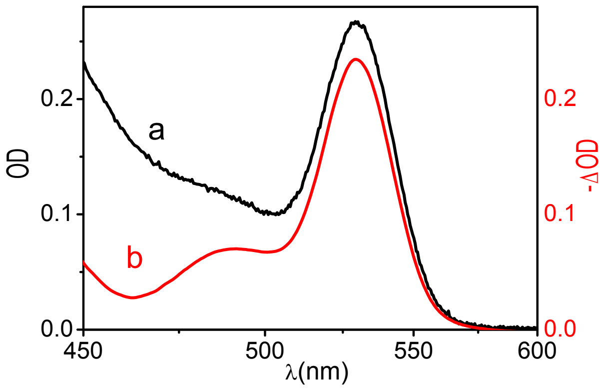

Figure 4. Comparison of steady state absorbance spectrum of the CdSe NCs (a) with a saturated TA bleach difference spectrum obtained by high intensity 400 nm photoexcitation at a pump-probe delay of 1.5 ps (b).

These results are compatible with earlier reports of BE pump-probe experiments conducted on CdSe samples. Using tuneable pump and probe, Kambhampati and co-workers investigated the effects of pumping in X1 or X2 on the BE bleach and demonstrated the absence of obvious hole contributions with a time resolution of ~50 fs defined by their requirement of pump state selectivity.[6] Other experiments which used sources in the sub 10 fs range have also been brought to bear on this system, but mainly in the context of 2D electronic spectroscopy.[32–34] In some of these cryogenic cooling was used to reduce homogeneous line widths of the samples, bringing out the appearance of phonon side bands in the spectral maps.[34] The appearance of a phonon side band both above and below the main diagonal would suggest an involvement of stimulated emission along with electron state filling.[33] However at room temperature these signatures are washed out by rapid dephasing,[34,35] so direct connection with the present investigation is difficult. A rapid albeit delayed build-up of band edge bleaching after excitation to the 1Σe2Σh state in CdSe nano-rods was observed recently using 2D spectroscopy, but it is again not clear whether this response is specific to systems confined in 2 dimensions.[36] Thus the current study reports the first extreme time resolution pump-probe experiment dedicated to the dynamics of bleaching at the BE following selective X1 band pumping. Here this is conducted with coherent pulse duration shorter than the homogeneous dephasing time of the X1 transition dipole. Thus no physically important dissipation processes will go undetected due to limitations of time resolution.

Results presented here dispel ultrafast hole-trapping as the mechanism behind the absence of stimulated emission contributions to the X1 bleach in conventional CdSe core NCs. This is consistent with the timescales of Auger cooling in the conduction band by transfer of energy to hole states in the valence manifold. They still do not identify the cause of this curious behaviour. This needs consideration in terms of both suggested mechanisms for its explanation. If the access of trap states is so fast that it can't be resolved in time at all, it must represent the fastest relaxation process of the transition dipole and define the homogeneous width of the samples' absorption band. However the room temperature BE transition width, proven to be dominated by homogeneous dephasing using single particle spectroscopy,[37] is not significantly affected by particle capping which should curtail trapping. As for the suggestion that redistribution of the initially excited bright exciton states into dark one should also take significantly longer than the earliest delay accessed here. Furthermore the unusual perfect cancellation of residual stimulated emission and "excited state absorption" would require both redistribution and thermalization,[21] providing a significant period for the detection of hole state filling to the bleach band. Thus, neither interpretation of hole occupation contributions is consistent with our results, or in light of them able to point in the direction of an alternative explanation.

In retrospect it is worthwhile to reflect on the full effects of thick shell coating on the photo physics of CdSe NCs. It appears that the over-layers in extensively capping NCs may do more than just efficiently passivate the core surface and eliminate carrier trapping.[10,38] In a number of recent studies, the intricate effects of shell thickness on bi-exciton recombination rates and on the related observation of net optical gain in highly excited samples has been addressed experimentally[39–42] and theoretically.[40,43,44] First and foremost is the finding that indeed in CdSe/CdS quasi type II NCs positive optical gain is achieved for NX>1.[42] Since simple passivation is not responsible, other ways in which the shell effects the carrier dynamics may be active, particularly in view of the way such structures often selectively confine only one band to the core volume.[44,45]

Alternatively, it was proposed theoretically[46,47] and experimentally[40] that suppression of Auger recombination is induced in cases including alloying composition at the core-shell interface, when a soft boundary precludes high-frequency Fourier components that otherwise enable a charge ejection from core levels. From a chemical perspective, alloying may be formed intentionally by a pre-designed capping procedure, or unintentionally via annealing during the shell growth. An alloyed interface is of particular importance in the case of wide shells where compressing and tangential strains become strong beyond a few (2-3) monolayers. Thus, the lack of stimulated emission can sensitively depend on the architecture of the examined NCs, which has been the source of contradictory reports.[40] We stress here that the Auger recombination time scales are orders of magnitude longer than the brief window in time opened by our experiments here. Furthermore, we are not dealing here with observables directly related to multi-exciton states, and suppression of Auger recombination in giant core/shells is not relevant to our findings directly but only through their common dependence on hole state occupation effects. None the less a comprehensive analysis of the factors which allows the development of gain in heavily capped CdSe cores may provide insights into its absence in samples such as that investigated here.

Conclusions:

In an effort to clarify why conduction band state filling alone controls the bleach amplitude of the $1S_e1S_h$ absorption in CdSe nanocrystal TA, here we have resolved the appearance of that signal following band edge photoexciting with sub 10 fs pulses. Detailed analysis demonstrates that precisely half of the $1S_e1S_h$ band absorption is erased at a rate limited by our experimental resolution. It is not accompanied by any initial component of stimulated emission due to short lived state filling of the bright valence band edge states responsible for the $1S_e1S_h$ transition dipole. This proves that the absence of hole-state filling contributions to band edge bleaching is attributable neither to ultrafast hole-trapping nor rapid redistribution of the nascent hole over the dark valence band states. Given the impact of this phenomenon on applications of such NCs where stimulated emission is of essence, this calls for a renewed effort for its correct assignment.

Conflicts of interest

There are no conflicts to declare.

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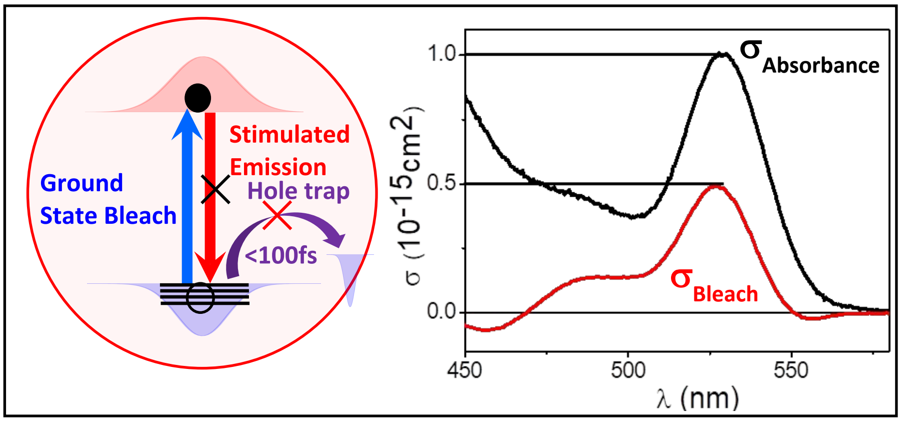
Ground
State Bleach
Stimulated
Emission
Hole trap
<100fs
σ_{Absorbance}
σ_{Bleach}
σ (10-15cm2)
1.0
0.5
0.0
450
500
550
λ (nm)