Supporting Information

Testing the Fate of Nascent Holes in CdSe Nanocrystals with Sub 10 fs Pump-Probe Spectroscopy

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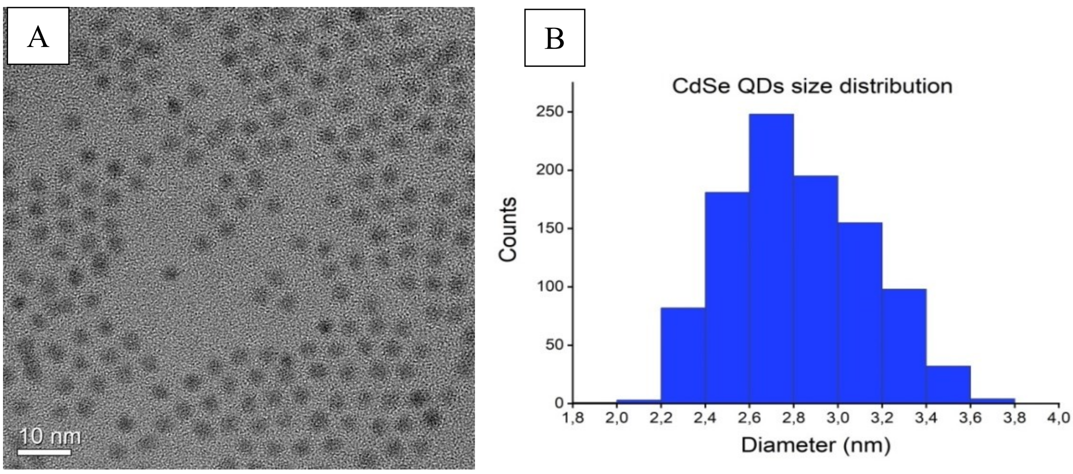
1. Characterization of CdSe nanocrystals.

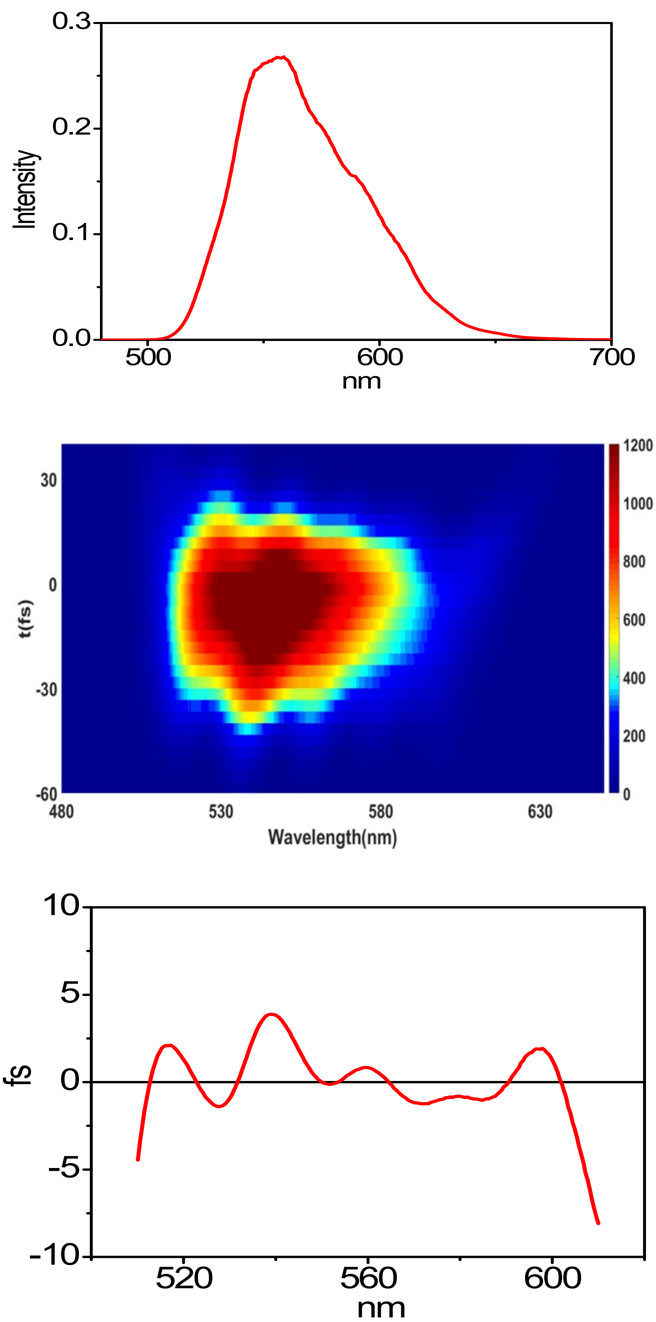


SI Figure 1. A. TEM images of CdSe nanocrystals dispersed in n-hexane solvent. **B.** Size distribution of the CdSe NCs based on 1000 particles from TEM images. The average particle's size of CdSe NCs is 2.7(±0.1) nm.

2. Photoluminescence Quantum Yield (QY) Measurement. The photoluminescence quantum yields (PL QY) of CdSe NCs dissolved in hexane was determined in relative to a

Rhodamine 6G reference sample (where the PLQY of Rhodamine 6G in ethanol is 95%). The determined PL QY is ~23% which is closely matches with the earlier literature.

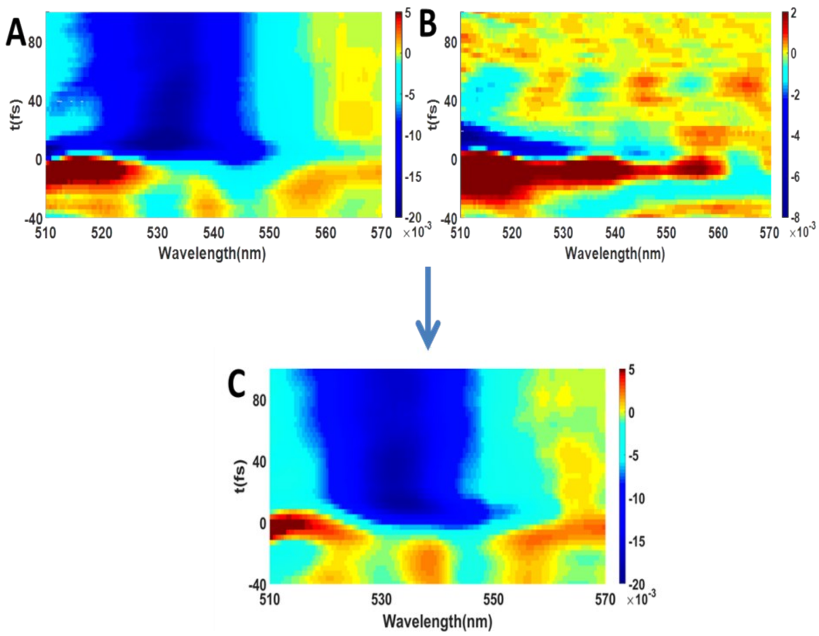
3. NOPA Pulse Characterization: To characterize the NOPA pulse we did a cross correlation FROG measurement, showing below with the group delay (GD) as a function of wavelength of the pulses. It confirms the perfect compression of the NOPA pulse.



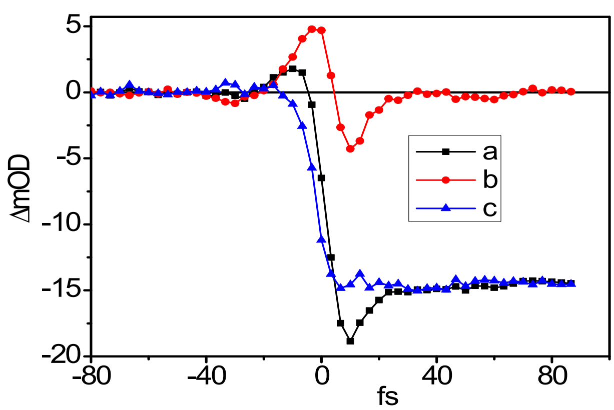
SI Figure 2. Upper Panel; NOPA intensity spectrum, **Middle Panel;** 2-D contour map of FROG, and **Lower panel;** GD as a function of wavelength.

4. Nonlinear Artefacts Correction.

To subtract the non-linear artefacts from the signal, we measured the artefacts of same solvent (hexane) in same optical cell at the same condition and subtracted from our real data, showing below.

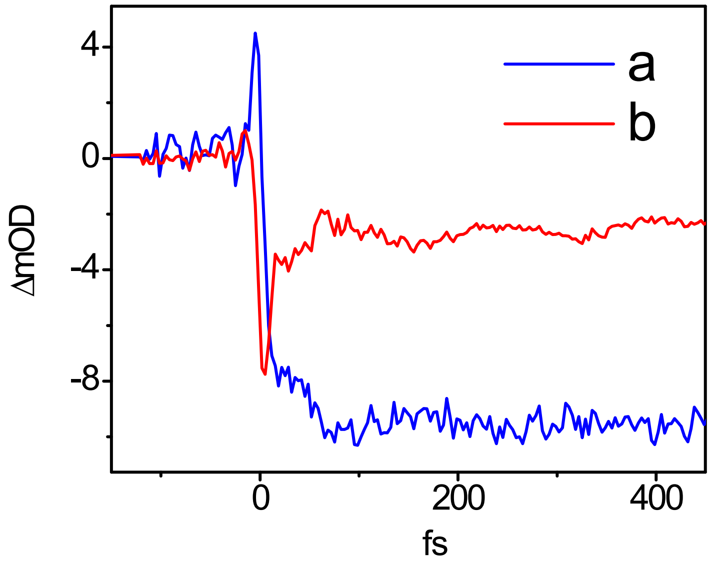


SI Figure. 3. 2D contour map of A. before artefacts correction, B. Artefacts and, C. after artefacts correction.



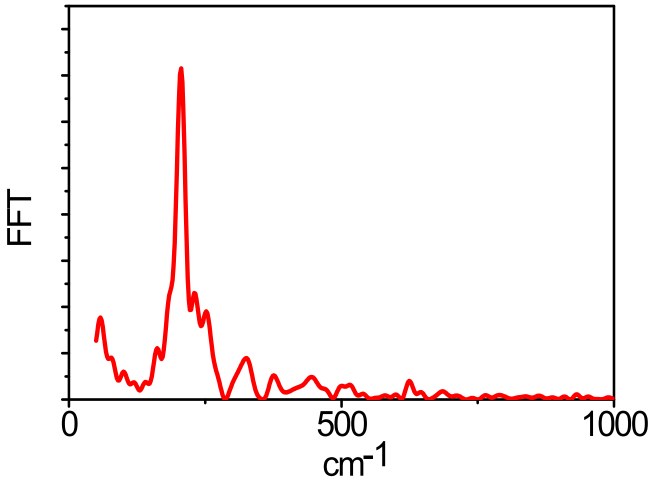
SI Figure 4: Integrated (mentioned in main text) (a) bleach dynamics of CdSe NCs, (b) Non-linear artefacts of hexane solvent in thin quartz optical cell. C. Bleach dynamics of CdSe after subtraction of artefacts.

5. Phase shift in Bleach: Coherent artifacts related to pump-probe overlap includes some self-phase modulation which introduces spectral shifting of the probe and gives rise to spectrally periodic intensity changes. These average to zero and therefore do not change probe transmission changes once the TA is averaged over such ranges. To show the rapid spectral phase shift in the band edge bleach, we are showing the spectral cuts at the blue region (integrate over 515-520nm) and red region (integrate over 545-550nm) in a single graph below.



SI Figure 5: The spectral cuts at the (a) blue region (integrate over 515-520nm) and (b) red region (integrate over 545-550nm).

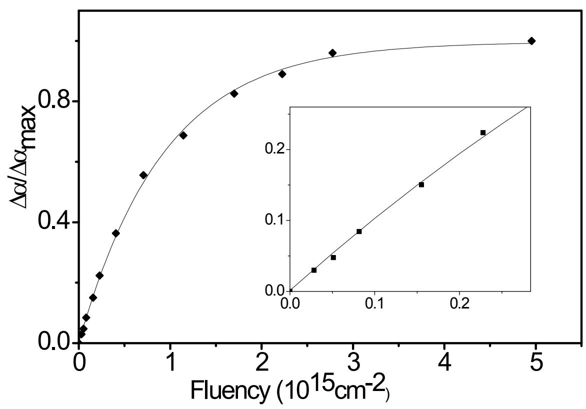
6. Fast Fourier Transform (FFT) of the Bleach Oscillation: FFT of the bleach dynamics was done after background correction to elucidate the frequency of coherent oscillation of the optical phonon,



SI Figure 6. FFT for the vibrational dynamics.

The frequency of the coherent oscillation is ~205 cm^{-1}.

7. Calculation of Absorption Cross Section at 400 nm andbleach cross sectio Per Exciton from Transient Absorption.



SI Figure 7: Fractional absorbance change Vs fluency after 400 nm excitation. From this graph we calculated the absorption cross section of the CdSe NCs at 400 nm.

The calculated absorption cross section from this saturation curve at 400 nm=$1.1*10^{-15}$ cm^2

At Band edge=$0.99*10^{-15}$ cm^2

To calculate the bleach cross section per exciton, we consider the bleach intensity at the BE after BE Excitaion.

To calculate the bleach cross section for per exciton we used the formulae,

$$10^{-A} = e^{-\sigma\rho}$$

Where, A= Change of Absorbance , σ=aborption cross section, ρ=photon flux (number of absorbed photon per unit area)

$\Delta A = 0.0154$, $\rho=7.29*10^{13}$ cm^{-2}

So, calculated σ at BE for single exciton =$4.87*10^{-16}$ cm^2

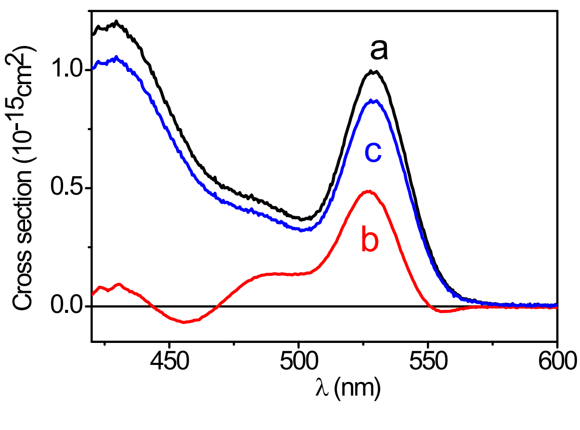
From SI reference 1, The reported σ at BE =$8.7*10^{-16}$ cm^2

From literature, the ratio for single and double = 0.55

The calculated absorption cross section from this saturation curve at BE=$9.9*10^{-16}$ cm^2

From saturation curve, the ratio for single and double = 0.49

Measurement was done after considering ±5% error.



SI Figure 8: Absorption cross section graph from (a) saturation curve and (b) literature (SI Ref 2). (c) Bleach cross section per exciton.

SI References.

1. Karel Čapek, R.; Moreels, I.; Lambert, K.; De Muynck, D.; Zhao, Q.; Van Tomme, A.; Vanhaecke, F.; Hens, Z. Optical Properties of Zincblende Cadmium Selenide Quantum Dots. J. Phys. Chem. C 2010, 114 (14), 6371–6376. https://doi.org/10.1021/jp1001989.