

Supporting Information: Primary Photodynamics of Water Solubilized 2-Dimensional CdSe Nanoribbons

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1. Transient Dynamics

Spectral Evolution of CdSe nanoribbons (NRs) in H₂O under 460 nm excitation is depicted in Figure SII. As when excited with 400-nm light, the characteristic stimulated emission for $\lambda > 460$ nm, induced absorption for $\lambda < 445$ nm, and $1_B - 1_e / 1_A - 1_e$ bleaches at 455 nm / 428 nm respectively are clearly observed. The trapped carrier population resulting from exciton dissociation is also observed at later times as indicated by the induced absorption observed at 460 nm along with persistent bleach. The exciton / electron associated induced absorption is observed to decay back to zero at ~ 388 nm, which was not observed under 400 nm excitation do to scatter considerations. The two peaks observed at 503 nm and 550 nm in the 600 fs spectra roughly correlate to the stimulated Raman peaks of H₂O.

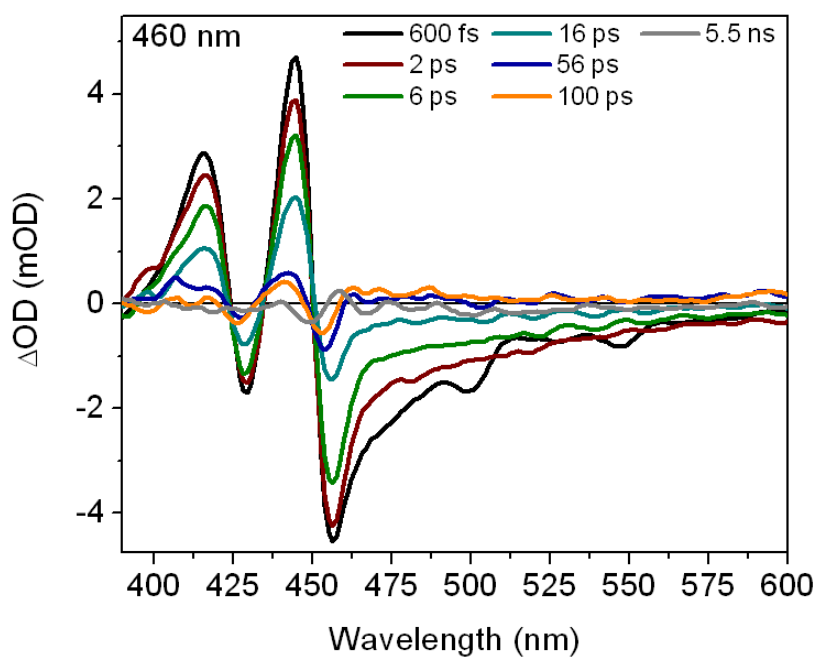


Figure SII: Transient spectral evolution observed for CdSe NRs excited at 460 nm in H₂O at a fluence of 6.2 μJ / pulse · mm².

The effect of increasing pulse energy on the rise time of the Stark (multiple-exciton) induced absorption in the blue region of the spectrum is shown in Figure SI2.

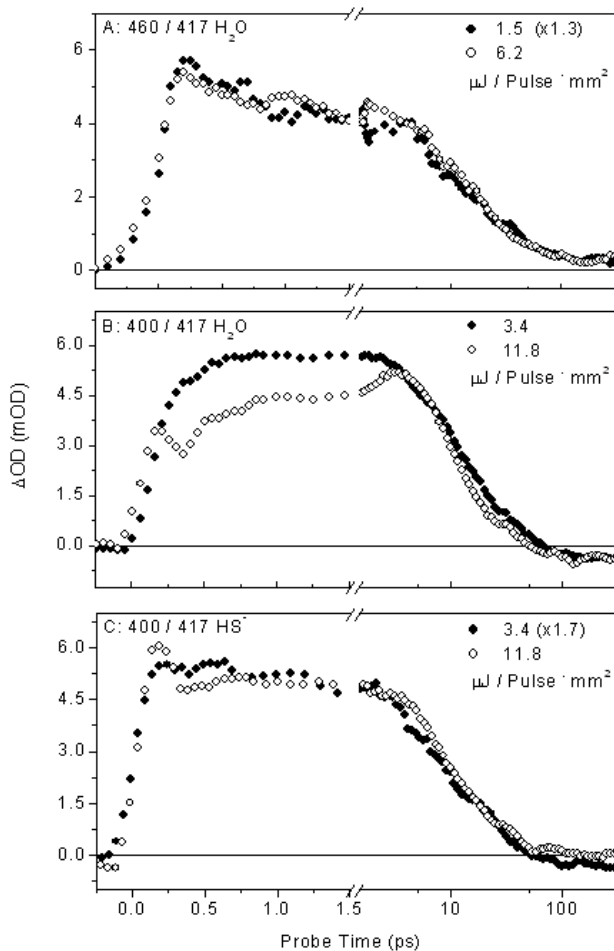


Figure SI2: Power dependent transient kinetics observed for CdSe NRs excited at (A) 460 nm in H_2O , (B) 400 nm in H_2O and (C) 400-nm in HS^- probed at 417 nm.

This data demonstrates that the variation in 460 nm flux attainable in this study has a negligible effect on charge carrier dynamics (Figure SI2A), in contrast to the dynamics observed under 400 nm excitation (Figure SI2B). Addition of HS^- eliminates the rise time fluence dependence observed upon 400 nm excitation yielding an early time response that seems to be somewhere between that observed in panels A and B (Figure SI2C).

The lack of observed variation in long time kinetics with increasing flux also verifies that Auger recombination is not a dominant interaction in CdSe NRs.

2. Global Analysis

Four compartment sequential analysis (Scheme SI1) can adequately describe the NR data in H_2O or $\text{H}_2\text{O} / \text{HS}^-$ over the entire spectral range at all probe delays, however it does not accurately account for the bimolecular (non-exponential) dissociation of excitons at trap sites known to occur (Figure 6). In this model, EADS and concentration profiles for the four populations (Figure SI3 and SI4) are still interpreted the same as in the target analysis and represent: $^h\text{Exciton}$, $^c\text{Exciton}_1$, $^c\text{Exciton}_2$, and $^t\text{Carrier}$. Where $^h\text{Exciton}$ represents unrelaxed Excitons (hot excitons) and $^c\text{Exciton}_1$ represents relaxed band-edge (cool excitons). $^c\text{Exciton}_2$ population is a superposition of $^c\text{Exciton}_1$ and $^t\text{Carrier}$ populations, which is required to account for non-exponential dynamics. The $^t\text{Carrier}$ population represents either trapped electron or hole carriers resulting from trap site dissociation. Regardless of the model used to describe the data the same general trends are observed: band edge excitation results in a reduction of hot exciton, as flux is increased, the hot exciton relaxation is delayed, and HS^- results in a delay of the final trapped carrier population decay.

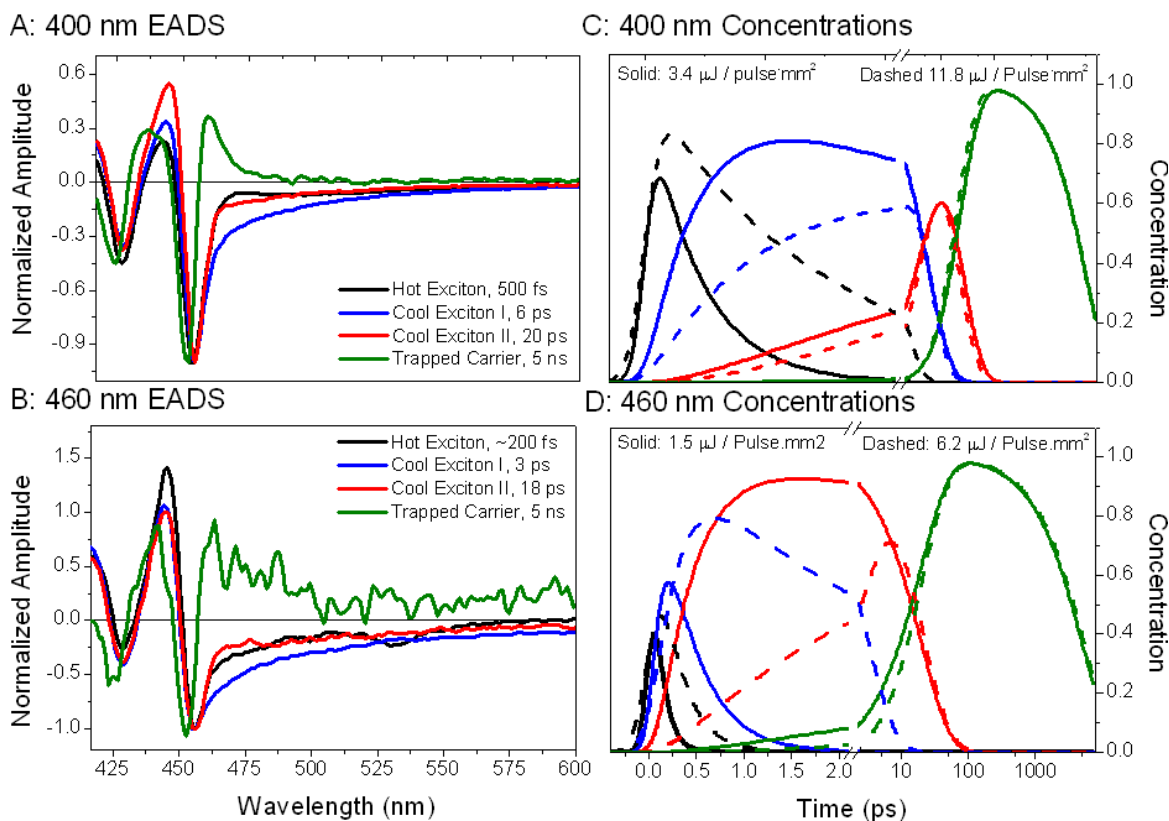


Figure SI3: Normalized EADS and concentration profiles of CdSe nanoribbons in H₂O resulting from 400-nm (A and C) and 460-nm (B and D) excitation calculated by fitting the raw data via equation 1.

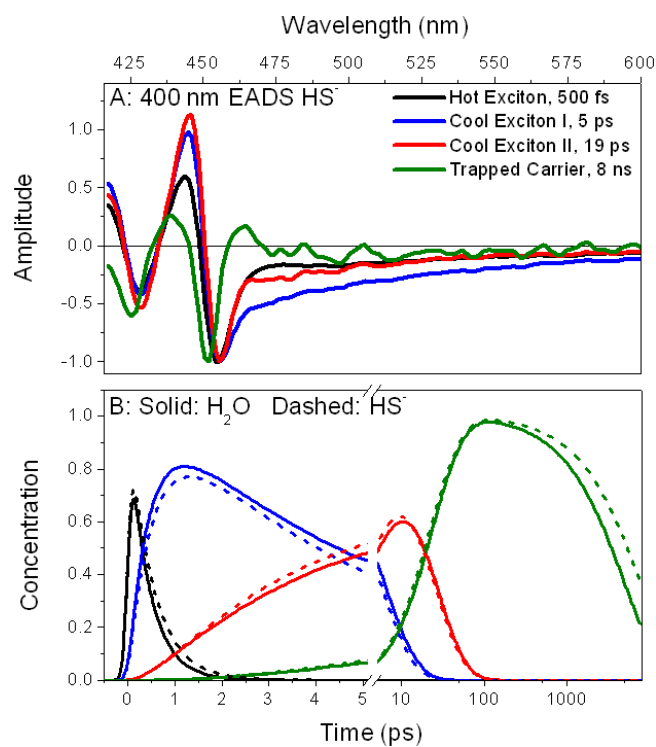


Figure SI4: (A) Normalized EADS of CdSe nanoribbons in H_2O / HS^- normalized at the 455 nm bleach. (B) Concentration profiles of CdSe nanoribbons in H_2O (solid curves) and H_2O / HS^- (dashed curves) after 400-nm pulsed excitation. Flux = $3.4 \mu\text{J} / \text{Pulse} \cdot \text{mm}^2$.

The non-normalized SADS for Figures 6A, 6B, and 7A are presented below (Figure SI5) for reference.

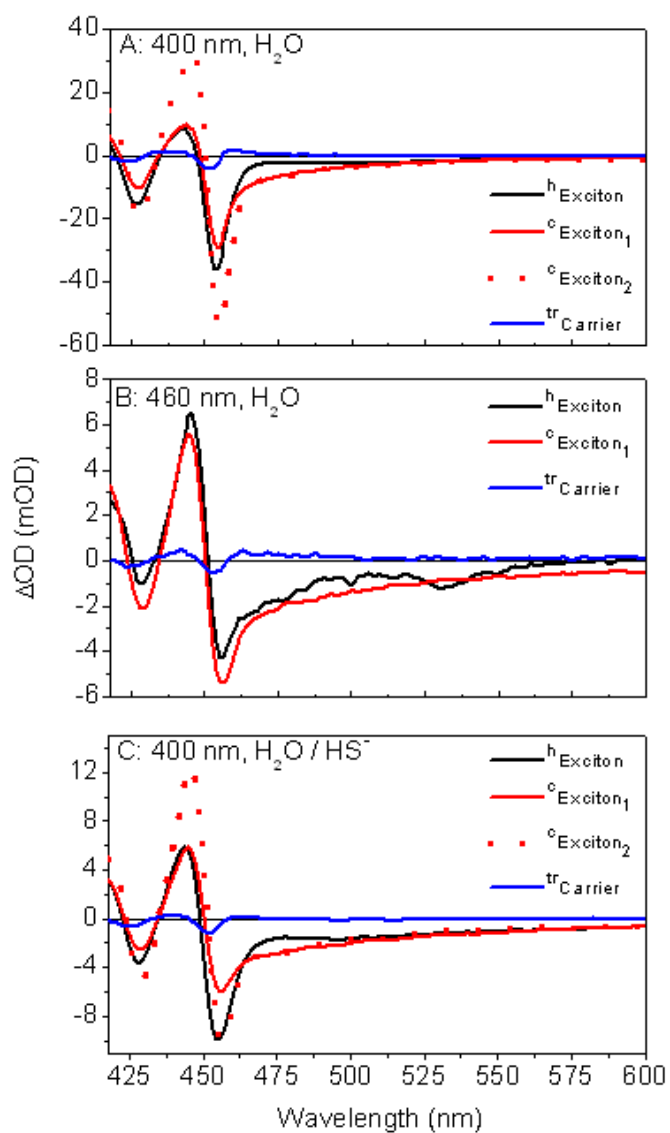


Figure SI5: Non-normalized SADS for NRs under (A) 400 nm excitation in H_2O (B) 460 nm excitation in H_2O and (C) 400 nm excitation in $\text{H}_2\text{O} / \text{HS}^-$. Flux = $3.4 \mu\text{J} / \text{Pulse} \cdot \text{mm}^2$ for 400 nm data, and $6.2 \mu\text{J} / \text{Pulse} \cdot \text{mm}^2$ for 460 nm data.

3. Power Dependence

Power dependent decomposition of NRs in H₂O / HS⁻ are presented in Figure SI6. At 1.6 ps, increasing pulse energy increases the ^hExciton population and ^{tr}Carrier population, while ^cExciton₁ population increases up until a certain threshold (28.5 μJ / Pulse · mm²) before beginning to plateau. The growth of the ^{tr}Carrier population is also delayed compared the results in H₂O (Figure SI5A and 9A) requiring higher fluxes before it begins to be observed. These results indicate HS⁻ passivates deep trap sites resulting in a reduction of observable ^{tr}Carrier population and an increase of ^cExciton₁ population, and is consistent with the persistence of stimulated emission observed in the power dependent spectra (Figure 8C) and the proposed mechanism of bimolecular trap site recombination (Scheme 2). At 32 ps, the ^{tr}Carrier population undergoes a linear increase as fluence is raised, indicating it becomes the dominant population and provides an alternative pathway for relaxation to the “hot-phonon bottleneck” (Figure SI5B).

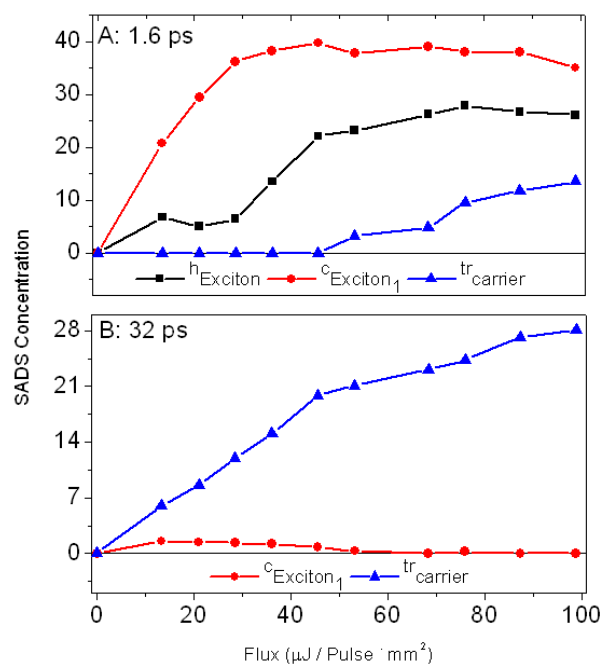


Figure SI6: Power dependent decomposition of CdSe nanoribbons at (A) 1.6 ps and (B) 32 ps in $\text{H}_2\text{O} / \text{HS}^-$. The spectra collected at each time point and power were fit using EADS as a basis set to determine what percentage of each component was present at each intensity.

Representative power dependent spectra (black) and their associated decomposed fits (red) are depicted in Figure SI6. The fits were derived by using SADS (Figure 6A and 7A) as a basis set and allowing variation at each power probed until the most accurate linear combination representing the spectra at that power was found. The basis set for the 1.6 ps spectra included $^h\text{Exciton}$, $^c\text{Exciton}_1$, and $^{\text{tr}}\text{Carrier}$ SADS, while the 32 ps spectra only included $^c\text{Exciton}_1$ and $^{\text{tr}}\text{Carrier}$ SADS.

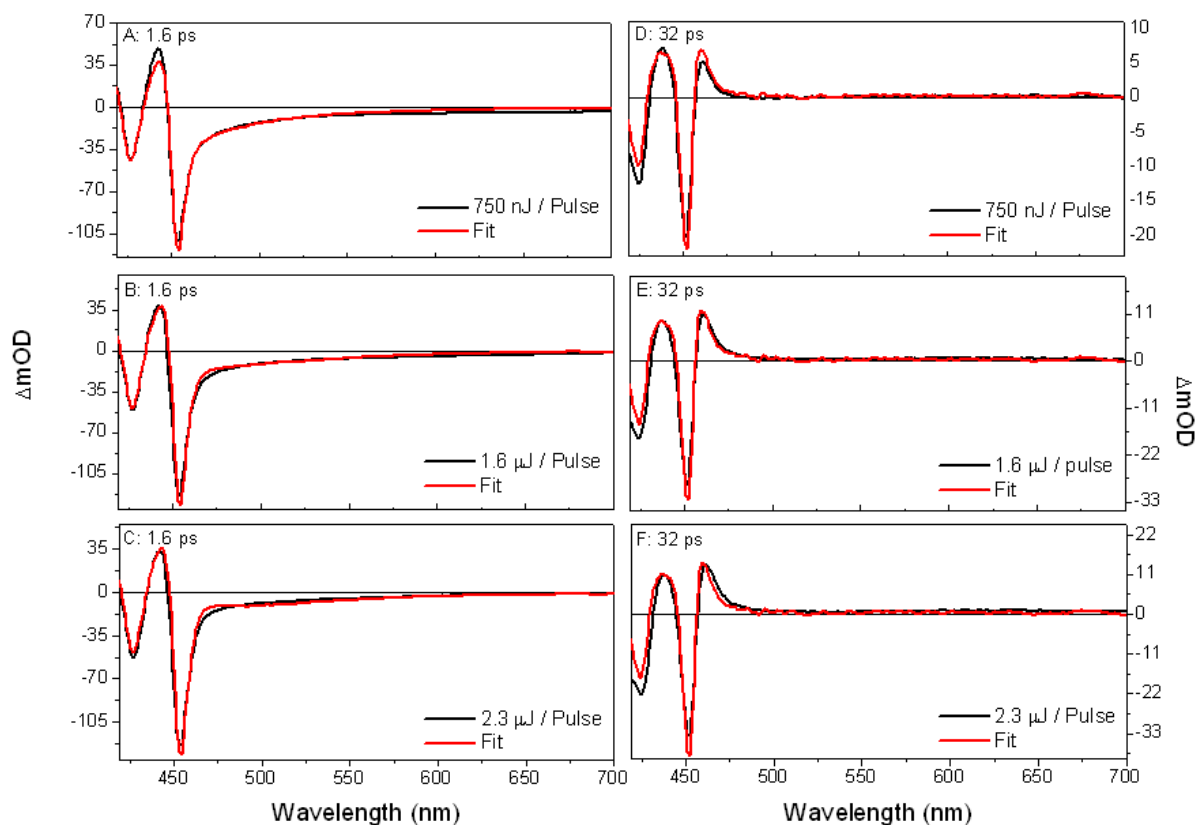


Figure SI7: Power dependent spectra (black) of NRs in H₂O at (A - C) 1.6 ps and (D - F) 32 ps. The associated fits (red) were derived using SADS (Figure 6A) as a basis set.

4. Long-Time Kinetics

When CdSe NRs are excited under high fluences an induced absorption is observed in the red region of the transient spectrum that is obscured under lower fluencies by the experimental noise (Figure SI8). To analyze the nature of this induced absorption under high fluencies long-time kinetics associated with samples of CdSe NRs suspended in H₂O and H₂O/HS⁻ were measured using an electronically gated pump-probe setup. The setup utilized the fourth harmonic (266 nm) of an Nd:YAG laser (Polaris II New Wave Research) operating at 18 Hz as the pump source, which yielded a fluence of 318 $\mu\text{J}/\text{Pulse} \cdot \text{mm}^2$. A temperature / current regulated 657 nm continuous wave diode (TCLDM9 Thor Labs) served as the probe, which was isolated using long pass ($\lambda > 560$ nm OC14) and bandpass ($280 \text{ nm} < \lambda < 900 \text{ nm}$ C3C24) filters. Probe light was detected using a high-speed photodiode (DET10A Thor Labs). The signal was then amplified one-hundred times by a DC-coupled wide band preamplifier (BX-31A NF Electronic Instruments) before being downloaded via a 1 GHz oscilloscope (TDS 784A Tektronix) and transferred to a computer for analysis. The associated instrument response function was 6.5 ns. The results show that the induced absorption observed under high fluence is significantly extended in the presence of HS⁻ (Figure SI9). This is likely a result of sacrificial electrons scavenging holes and extending the lifetime of their electron counterparts.

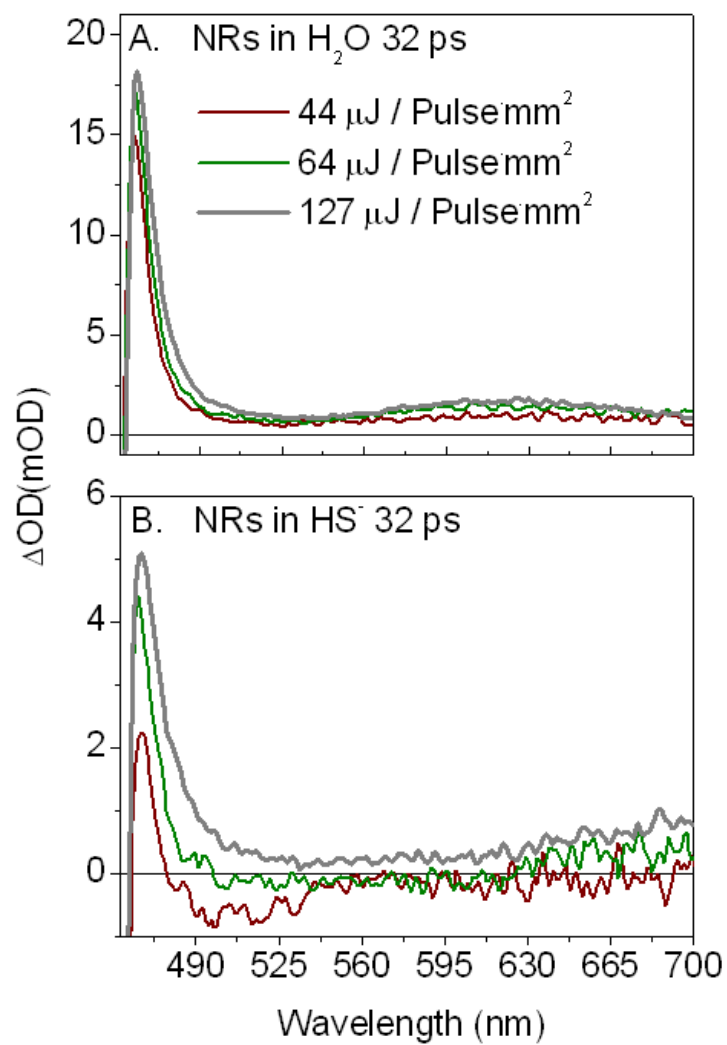


Figure SI8: Power dependent transient spectra of CdSe NRs at 32 ps in (A) H_2O and (B) $\text{H}_2\text{O}/\text{HS}^-$ illustrating the induced absorption observed in the red region of the spectra under high 400 nm fluxes. Data is normalized on the 1_A-1_e bleach (not shown here).

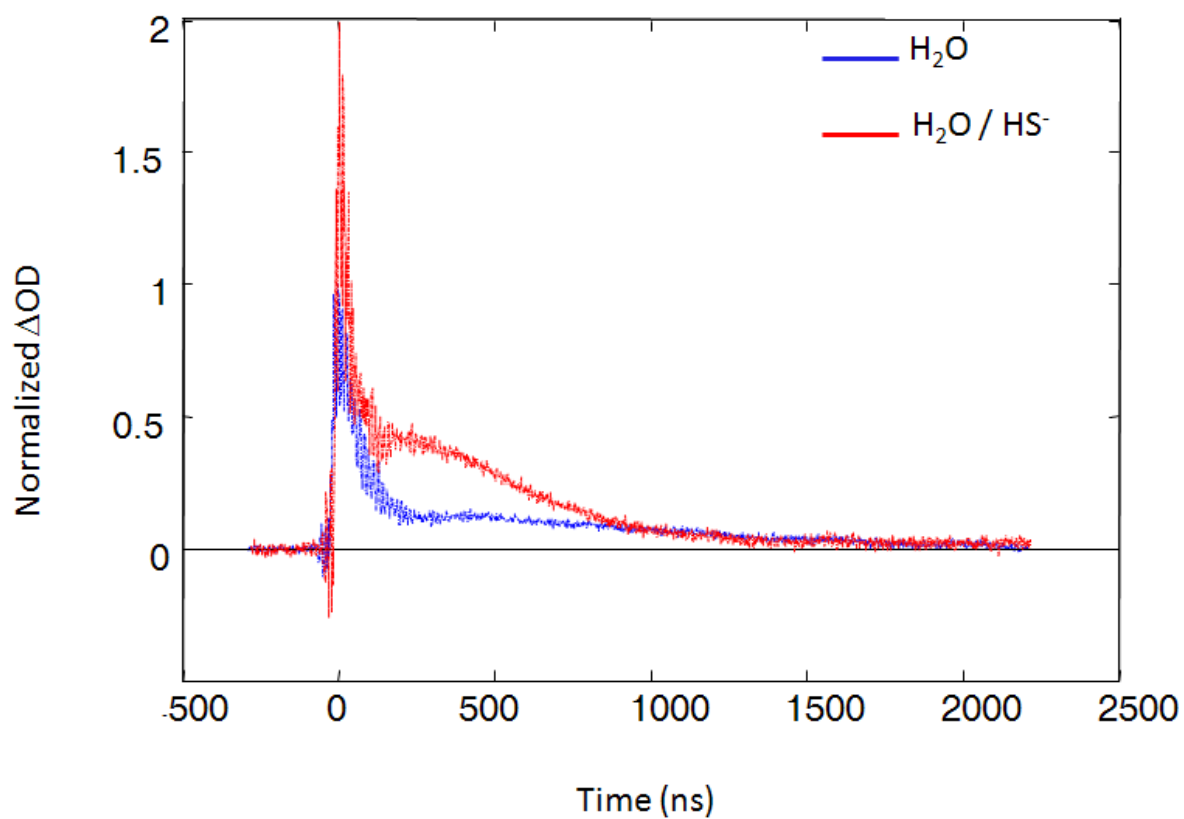


Figure SI9: Long time kinetics associated with the induced absorption observed in ultrafast transient absorption data of CdSe NRs in H_2O and H_2O/HS^- under high fluences (Figure SI8). Pump = 266 nm @ 318 $\mu J/Pulse \cdot mm^2$, CW Probe = 657 nm.