Electronic Supplementary Material (ESI) for Nanoscale.

Supporting Information

Dissecting Charge Relaxation Pathways in CdSe/CdS Nanocrystals Using Femtosecond Two-Dimensional Electronic Spectroscopy

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S1. Experimental Setup for Two-Dimensional Electronic Spectroscopy

Figure S1 depicts the experimental setup for two-dimensional electronic spectroscopy (2DES) measurements in the visible. The optical layout and procedure for acquiring femtosecond 2DES data has been previously described in detail.[1] The Translating-Wedge-Based Identical Pulses eNcoding System (TWINS)[1, 2] is used to generate a time-delayed (t_1), phase-locked excitation pulse pair that is used to create the pump frequency axis. The t_1 calibration and phasing procedures used to generate the 2DES maps in the main text have been described previously.[1]

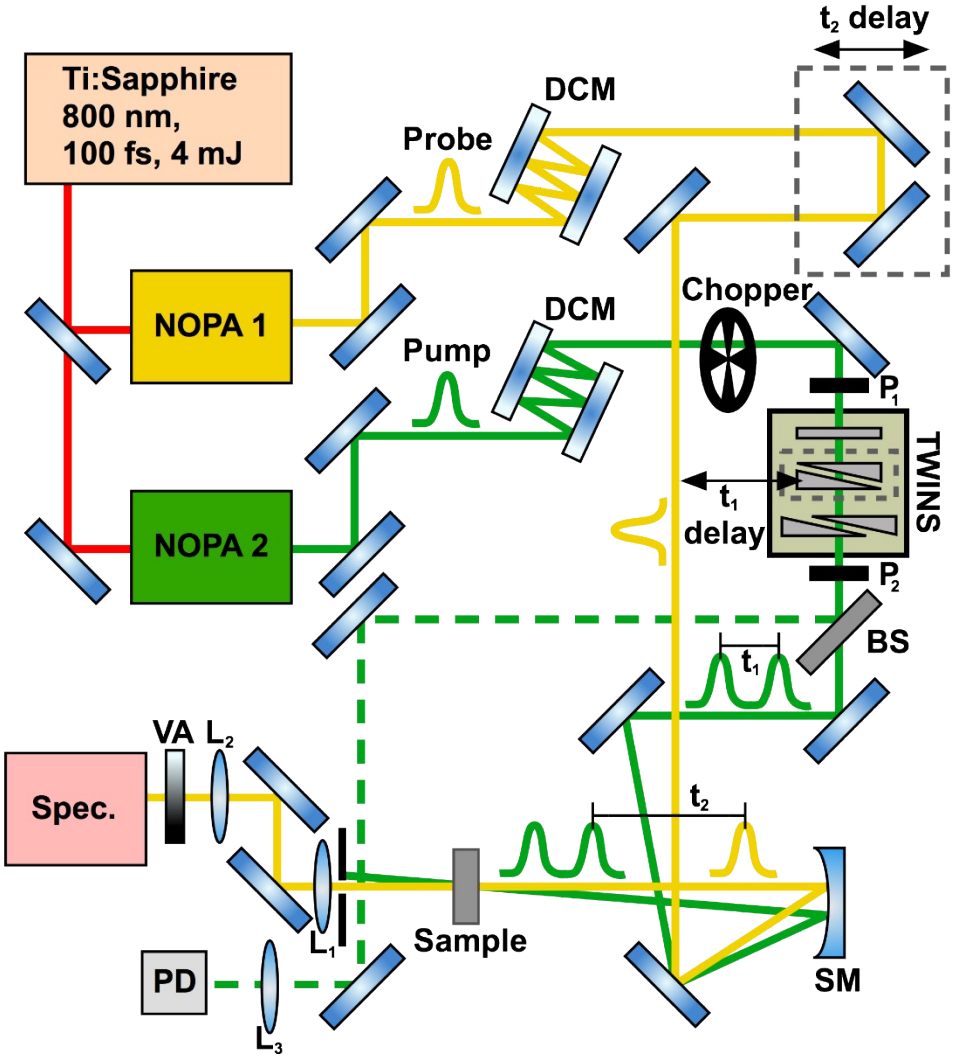

Figure S1. Optical layout for femtosecond time-resolved 2DES. Components include: NOPA: Noncollinear Optical Parametric Amplifier; DCM: Double Chirped Mirror; TWINS: Translating Wedge-based Identical Pulses eNcoding System; P_N: Linear Polarizer; BS: Beam Splitter; SM:

Spherical Mirror, f = 125 mm; L_N: Converging Lens; VA: Variable Attenuator; Spec.: spectrometer

An amplified Ti:sapphire laser system (Libra, Coherent) delivering 4-mJ, 100-fs pulses centered at 800 nm at a 1-kHz repetition rate was used to seed two synchronized non-collinear optical amplifiers (NOPAs), each one pumped with 300 μJ of energy, which served as the pump and probe arms of the 2DES setup. One NOPA delivered visible pump pulses spanning 1.8 eV to 2.4 eV, while the other delivered visible probe pulses spanning 1.7 eV to 2.3 eV. The outputs from both NOPAs were compressed to sub-20-fs duration by multiple reflections on custom-designed double-chirped mirrors (DCMs). The waiting time, t_2, between pump and probe lines was delayed using a conventional translation stage, and the time delay between the excitation pulse pair, t_1, was generated by the TWINS setup. Possible t_2 delays ranged from -150 fs to 10 ps, with step sizes as small as 10 fs. The t_1 delays can be set from ~10 as to 500 fs. A portion of the pump beam is directed from the pump propagation path to a photodiode to monitor the t_1 interferogram of the pump pulse pair, and this information is used to determine time zero and phase the 2DES spectra. The pump and probe pulses are non-collinearly focused into a 200-μm pathlength cuvette of sample with spot sizes of 110 μm and 100 μm, respectively, and the transmitted probe light was dispersed on a spectrometer. The t_1 time delays were rapidly scanned, which allowed for a typical 2DES map at a single t_2 delay to be acquired in less than 10 seconds. The measurement across all t_2 delay times was repeated multiple times and averaged until satisfactory data quality was achieved.

Dispersion introduced to the pump pulse replicas by the TWINS optics was compensated by a suitable number of reflections on a DCM pair, and spectral phase correction was verified using a Spatially Encoded Arrangement for Temporal Analysis by Dispersing a Pair Of Light E-fields (SEA-TADPOLE) setup.[3]

S2. Data Fitting Procedure

Dynamics traces were extracted from 2D maps at specified excitation-detection energies at each t_2 pump-probe delay. These data were fit with an in-house program that uses an iterative least-squares approach to fit the data with the following equation:

$$S(t) = g(t) \otimes \left(\sum_i A_i \exp(-t / \tau_i) + A_{\text{inf}} \right)$$

Where the symbol ⊗ stands for convolution and *g(t)* is the instrument response function (IRF), i.e. the cross-correlation of Gaussian pump and probe laser pulses, A_i is the amplitude coefficient of the i^{th} component, τ_i is the time constant of the i^{th} component, and A_{inf} is a non-decaying plateau function. Since the decay of the transient bleach in these semiconductor nanocrystals persists for much longer than the possible t_2 durations available, the dynamics data in this study were treated with a single exponential function (i = 1) to determine the growth component and a constant non-decaying plateau function.

S3. Additional Figures

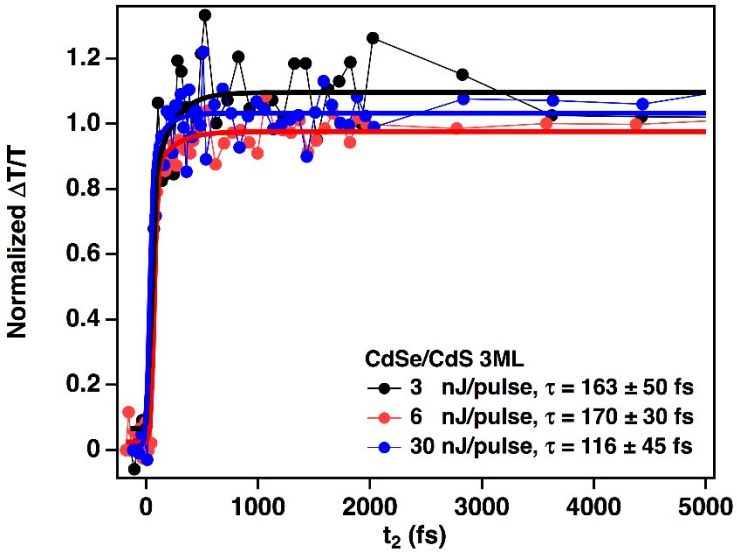

Figure S2. Extracted t_2 time-dependent signal amplitudes acquired from band-edge detection (Excitation Energy 2.26 eV, Detection Energy 2.08 eV) of CdSe/CdS core/shell nanocrystals with three monolayers of CdS at various excitation pulse energies. Data were fit to a single exponential growth with a time constant of ~150 fs, regardless of pulse energy.

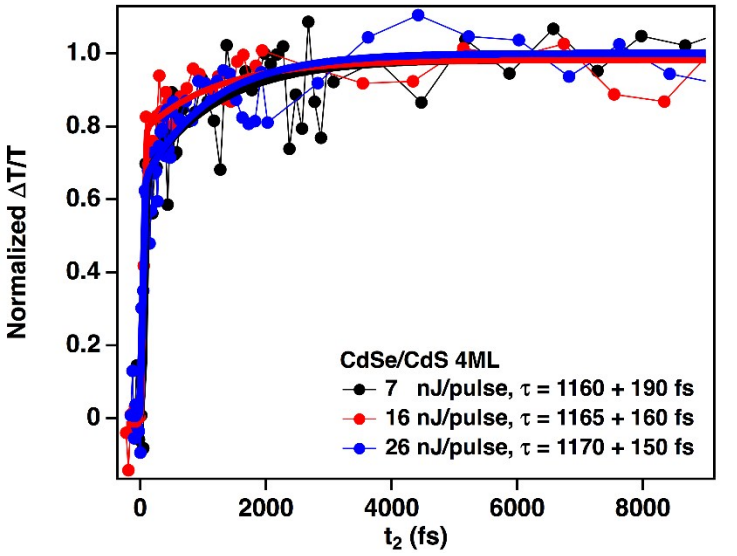

Figure S3. Extracted t_2 time-dependent signal amplitudes acquired from band-edge detection (Excitation Energy 2.26 eV, Detection Energy 2.08 eV) of CdSe/CdS core/shell nanocrystals with four monolayers of CdS at various excitation pulse energies. Data were fit to a single exponential growth with a time constant of ~1160 fs, regardless of pulse energy.

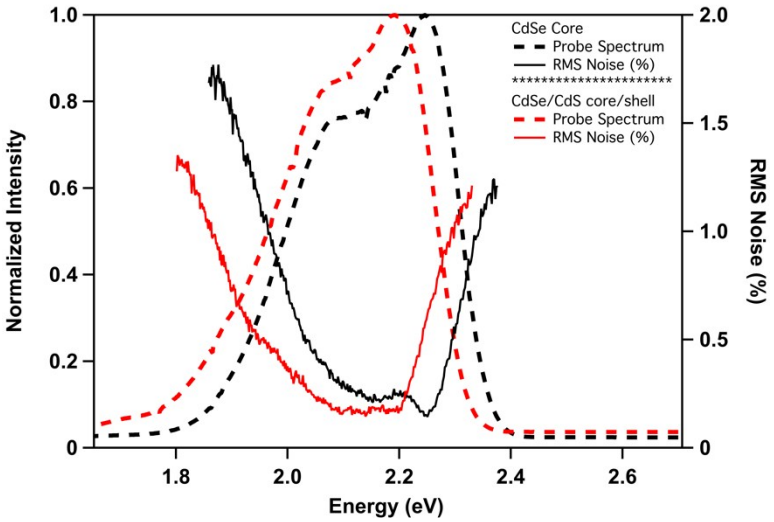

Figure S4. Probe laser spectra (dashed lines) and RMS noise (solid lines) used for 2DES on CdSe cores (black) and CdSe/CdS core/shell particles (red). The NOPA was tuned to lower energy for the core/shell particles in order to reduce noise at the red-shifted bandgap energy region.

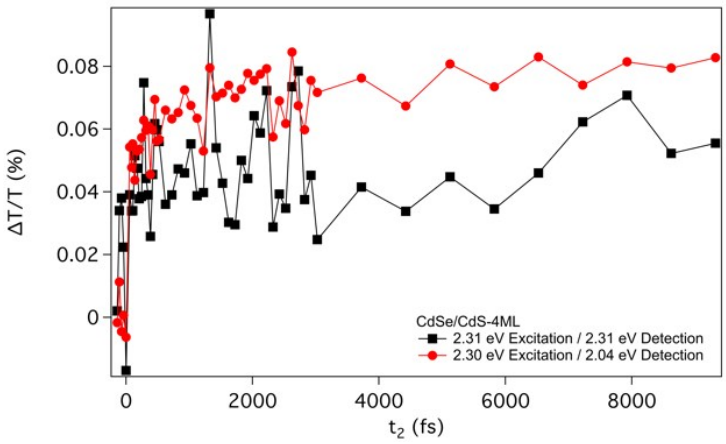

Figure S5. Extracted t_2 time-dependent signal amplitudes acquired from band-edge detection (red trace) and 2.31 eV/2.31 eV excitation/detection (black trace) of CdSe/CdS core/shell nanocrystals with four monolayers of CdS. Although there was non-decaying transient signal on the 2.31 eV diagonal, the noise level was very high because it falls at the high-energy range of the probe laser spectrum (see Figure S4).

References:

1. Rehault, J.; Maiuri, M.; Oriana, A.; Cerullo, G. *Rev. Sci. Instrum.* **2014,** 85, (12), 10.

2. Maiuri, M.; Rehault, J.; Carey, A. M.; Hacking, K.; Garavelli, M.; Luer, L.; Polli, D.; Cogdell, R. J.; Cerullo, G. *J. Chem. Phys.* **2015,** 142, (21), 10.

3. Bowlan, P.; Gabolde, P.; Shreenath, A.; McGresham, K.; Trebino, R.; Akturk, S. *Opt. Express* **2006,** 14, (24), 11892-11900.