Improving Optical Gain Performance in Semiconductor Quantum Dots via Coupled Quantum Shells

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Supporting Information

Materials and Methods

CdSe nanocrystals cores were prepared using the alternate precursor method developed by Peng and co-workers.[1] The CdSe nanocrystals were capped with trioctylphosphine oxide (TOPO) and octadecylamine (ODA). The layered CdSe/ZnS/CdSe systems were prepared using the modified successive ionic layer adsorption and reaction (SILAR) method developed by Peng and co-workers.[1-3] This synthesis was recently reproduced by our group and Rogach et al.[4-6] For this study two monolayers of ZnS were added, followed by two monolayers of CdSe. For the spectroscopic measurements the nanocrystals were dissolved in spectral grade toluene.

CdSe nanoncrystal samples used for the spectroscopic studies were purchased from NN Labs. The primary ligand was octadecylamine.

Steady-state absorption measurements were performed on a Varian Cary 5000 UV/Visible spectrophotometer. Linear absorption measurements were preformed before and after the fluence dependent gain experiments in order confirm the absence of photo-degradation. The photoluminescence (PL) were measured on a Spex Fluromax-2 spectrofluorometer. The TEM images were taken on a Philips CM200 operating at 200 kV.

The nonlinear spectroscopic measurements were made using an amplified Ti:sapphire laser system (800 nm, 70 fs, 1 kHz, 2.5 mJ; Coherent) in the pump/probe configuration. The probe pulses were derived from single filament white light continuum generated in a 2 mm sapphire crystal. The pump pulses were created via optical parametric amplifiers (OPA). The OPA derived pulses were ~ 40 – 50 fs at all wavelengths used, and were tuned to the initial excitonic states specified in the manuscript. The continuum and OPA pulses were dispersion compensated by fused silica prism pairs, resulting in instrument response functions of approximately 70 - 80 fs over all wavelength combinations. The pulse durations and instrument response functions were measured by autocorrelation and cross correlation in 30µm BBO crystals at the sample position.

The chirp-free transient absorption (TA) spectra were obtained using a scanning monochromater.[7] The chirp across the continuum was also determined by cross correlation at the sample position and used to calibrate transient spectra in a chirp free manner. Here, the probe pulses are split into a signal and reference beam in which the signal beam is focused through the photo-excited sample using reflective optics. The two beams were transmitted through a holographic notch filter (Kaiser Optical) to reject the 800 nm residual light from the continuum, and then dispersed in a 0.14 m monochromater (Horiba Jobin-Yvon). The chirp-free TA spectra are obtained by scanning the monochromater and simultaneously adjusting the relative pump-probe delay according to the calibrated chirp. The timing uncertainty was ~ 10 fs across the probed spectrum. The dispersed beams were detected with matched large area Si photodiodes

coupled to current preamplifiers which were then digitized at 18 bits. Probe ratiometry was performed after spectral selection in order to minimize continuum noise.

Spot sizes were approximately 250 – 400 μm for the pump pulses and 75 μm for the probe pulses with a crossing angle of 5 degrees. The time delay between the pulses was set by a computer controlled delay stage with 0.1 μm precision (Newport PM500). For the pump/probe experiments, the sample consisted of quantum dots dispersed in toluene in a1 mm path length quartz flow cell. Experiments were performed simultaneously at two pump wavelengths in order to maximize reproducibility of the results. Two different pump colors were specified for a given experiment and simultaneously chopped at 333 Hz with a phase shift to enable alternating collection of transients on a shot-by-shot level.

Fluence Dependence of Band Edge Fractional Bleach

The fractional bleach at band edge (590 nm) is the magnitude of the TA spectral signal divided by the magnitude of the absorption at 590 nm. To calculate the expected fluence required to achieve a given fractional bleach, we assume that the magnitude of the fractional bleach is proportional to the fluence times the absorption cross section at the pump wavelength. All values are normalized to 1 for the 590 nm pump.

CdSe/ZnS/CdSe	590 nm Pump (Band Edge)	516 nm Pump
relative abs cross section	1	2.0
expected fluence required for same fractional bleach at 590 nm	1	0.5
observed fluence for same fractional bleach (at 2 ps)	1	1.8 (3x expected)

CdSe	591 nm Pump (1S)	500 nm Pump (1P)
relative abs cross section	1	1.4
expected fluence required for same fractional bleach at 590 nm	1	0.7
observed fluence for same fractional bleach (at 1 ps)	1	1.2 (1.7x expected)

Wavefunctions

The wavefunctions for CdSe/ZnS/CdSe were calculated using the effective mass approximation taking into account the dielectric boundary conditions,[8,9] with a CdSe core radius of 1.8 nm, ZnS layer thickness of 0.62 nm and CdSe layer thickness of 0.70 nm. Even for the lowest energy electron and hole wavefunctions ($1S_e$ and $1S_h$), the wavefunctions are slightly delocalized into the CdSe shell for this size of core and layer thickness.
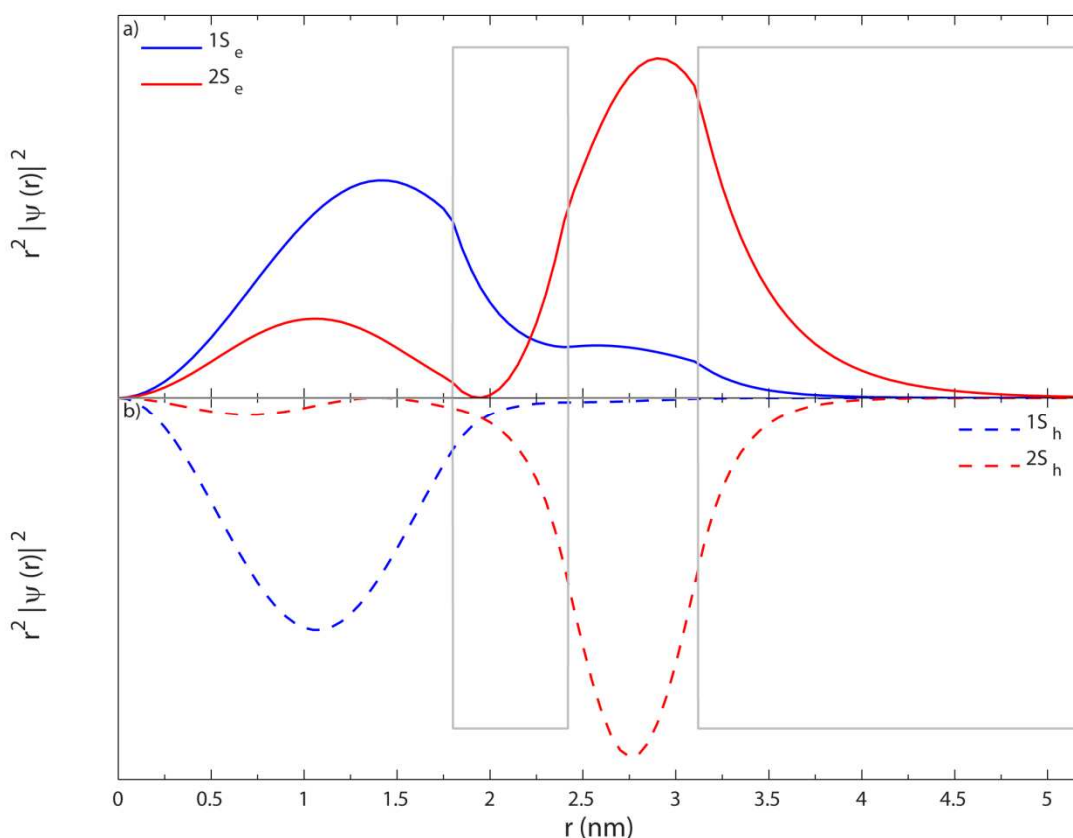
Figure S1: Electron and hole wavefunctions calculated for CdSe/ZnS/CdSe with a core radius of 1.8 nm, ZnS layer thickness of 0.62 nm and CdSe layer thickness of 0.70 nm.

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