

# Supporting information for Ultrafast Exciton Dynamics in CdTe Nanocrystals and Core/Shell CdTe/CdS Nanocrystals

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## EXPERIMENTAL

**Chemicals.** *n*-Tetradecylphosphonic acid (TDPA) was purchased from PCI Synthesis. Oleic acid (OA; 99%) was purchased from Alfa Aesar. Cadmium oxide (CdO; 99 %) was purchased from Fluka. Sulfur (99.999%) was obtained from Strem Chemicals. 1-Octadecene (ODE; tech. 90%), tributylphosphine (TBP; 97%), tellurium (200 mesh, 99.8%), and thioglycolic acid (TGA, 98%) were purchased from Aldrich. Chloroform (CHCl<sub>3</sub>) and Dulbecco's phosphate buffered saline (PBS) (without calcium & magnesium salts, sterile filtered) were purchased from VWR. Methanol (MeOH) was obtained from J.T. Baker. Atomic spectroscopy standards, such as Cd (2% HNO<sub>3</sub>, 1000 mg/L), Te (5% HNO<sub>3</sub>, 1000 mg/L), and S (H<sub>2</sub>O, 1000mg/L), were obtained from PerkinElmer Pure. All reagents were used as received.

**Nanocrystal synthesis.** Synthesis of CdTe cores followed the procedure previously reported by Peng and coworkers.<sup>1,2</sup> Standard Schlenk-link or inert glovebox procedures were used to exclude air and water from the reactions.

CdO (0.0256 g, 0.20 mmol) and TDPA (0.114 g, 0.41 mmol) were added to 7.8 g ODE, and the mixture was heated to 300 °C with vigorous stirring under a flowing argon atmosphere. At this temperature, the solution was clear and colorless. A solution of tellurium (0.0125 g, 0.1 mmol) dissolved in 0.475 g of TBP and 1.500 g of ODE in was prepared in an argon-filled

glovebox and loaded into an airtight syringe. The syringe was removed from the glovebox, and the tellurium mixture was injected very rapidly into the cadmium-containing mixture. The temperature of the reaction was set at 260 °C for growth of the NCs, and the size of the NC cores was controlled by reaction time. For the samples described in detail in this paper, the cores were grown for approximately 2 minutes (small cores) and 30 minutes (large cores).

A CdS shell was deposited onto the CdTe cores by gradually injecting a solution containing Cd and S precursors into the crude CdTe mixture using a syringe pump (NE-300, New Era Pump Systems, Inc.).<sup>3</sup> The shell precursor solution was prepared as follows. A mixture of CdO (0.0417 g, 0.33 mmol), OA (0.8 mL, 2.5 mmol), and ODE (3.6 mL) was heated to 260 °C under argon to produce a 0.08 M solution of cadmium oleate. In a separate flask, sulfur (0.0154 g, 0.48 mmol) was dissolved in ODE (4 mL) by heating to 200 °C under argon. These two precursor solutions were allowed to cool to room temperature and then mixed together. A portion of the crude reaction mixture containing CdTe cores (5 mL, containing approximately 50 nmol cores, as determined by UV-visible absorption measurements)<sup>1</sup> was diluted with rigorously deoxygenated ODE (3 mL) and extra TBP (0.5 mL) and then heated to 250 °C under argon. The CdS precursors were then loaded into a syringe and injected into the CdTe mixture at a rate of 0.1 mL/min. After injection of the entire CdS precursor mixture, the heat was removed from the system. The crude product solutions of the core and core/shell NCs were kept under argon and stored in an argon-filled glovebox to prevent degradation by oxygen, which is known to occur with the CdTe cores.

Except for the case of the aqueous core/shell samples, the samples were kept under argon for absorption, PL, and TA spectroscopic measurements. The samples were prepared by diluting the

crude NC samples in argon-saturated  $\text{CHCl}_3$ . These solutions were then loaded into an airtight cuvette and removed from the glovebox.

Absorption spectra were measured using an HP 8453 diode array spectrometer.

Photoluminescence spectra were obtained using a model C-60 spectrofluorometer from Photon Technology International (PTI). Light from a 75 W xenon arc lamp was sent through a monochromator to produce the excitation beam. Luminescence from the sample was collected and focused through a double grating monochromator and then detected with a PMT (Hamamatsu R928) in photon counting mode. Emission spectra were corrected for the wavelength-dependent instrument response.

Photoluminescence decay measurements were made using the time-correlated single photon counting method. A mode-locked, diode-pumped Ti:sapphire laser (Mai Tai, Spectra-Physics) produced a train of 120 fs pulses with a wavelength of 795 nm and repetition rate of 40 MHz. The repetition rate was decreased using an electro-optic pulse picker (Quantum Technology, Inc.), and the pulse train was focused into a BBO crystal to generate 398 nm photons, which were used for sample excitation. A small monochromator was used to select the emission wavelength, and a fast PMT was used as the detector. A Becker & Hickl SPC-430 single photon counting module was used for data collection.

Transient absorption measurements were performed using a commercially available transient absorption spectrometer (HELIOS, Ultrafast Systems). An amplified Ti:sapphire laser (Solstice, Newport/Spectra-Physics) was used for sample excitation. The Solstice provides 3 mJ, 150 fs pulses at a repetition rate of 1 kHz and 795 nm wavelength. This beam was split to produce separate pump and probe pulse trains. The pump pulses were produced by directing one-half of the Solstice output into an optical parametric amplifier (TOPAS-C, Light Conversion) to

generate pulses with widely tunable wavelength and pulse energies in the 5-500  $\mu\text{J}$  range. The probe beam was generated by focusing approximately 5% of the Solstice output onto a sapphire crystal to generate a white light continuum extending from approximately 400–800 nm. Neutral density filters were used to reduce the pump intensity well below the threshold for biexciton production. Pumping was typically achieved using a wavelength of 400 nm and pulse energy of 50 nJ. The pump beam was focused down to a spot size of approximately 1 mm diameter, and the sample pathlength was 2 mm. Pump fluence was kept low to avoid biexciton formation and photodegradation as explained in the main text.

TA data analysis was performed using Surface Explorer Pro software (Ultrafast Systems). This software includes a chirp correction algorithm that is based on measurement of the wavelength-dependent pump-probe time delay observed via the nonresonant optical Kerr effect in a solvent blank (chloroform for most of the experiments reported here).<sup>4</sup> The non-resonant optical Kerr effect data were also used to estimate the instrument response function. The pump-probe cross-correlation was measured as the full-width-at-half-maximum of the Kerr response peak of the solvent at ten different probe wavelengths. The instrument response function was determined by this method to be 190 fs.

Small angle x-ray scattering (SAXS), transmission electron microscopy (TEM), powder x-ray diffraction (XRD), and inductively-coupled plasma optical emission spectrometry (ICP-OES) measurements were performed on purified, air-exposed NC samples as described below.

For elemental analysis, the CdTe/CdS NCs were removed from the glovebox and purified in air by precipitating with  $\text{CHCl}_3$  and MeOH (volume ratio = 1:1). The sample was centrifuged, the clear supernatant was discarded, and then the NCs were re-dissolved in  $\text{CHCl}_3$ . This process was repeated twice more, but after the final precipitation, the NCs were dissolved in 5%  $\text{HNO}_3$ . The

atomic spectroscopy calibration standards (Cd, Te, and S) were diluted in deionized water at several concentrations (1ppm, 5ppm, 10ppm, 20ppm, and 25ppm) to produce a calibration curve. The amounts of Cd, Te and S in the NCs were measured using a CCD-based, inductively-coupled-plasma optical emission spectrometer (Varian Vista-MPX).

For XRD measurements, the crude core and core/shell NCs were removed from the glovebox and purified in air by precipitating three times as described above. After the third precipitation, the NCs were allowed to dry thoroughly on a planar glass substrate. Powder diffraction measurements were made on a Rigaku Miniflex diffractometer using a Cu K- $\alpha$  rotating anode source operating at 30 kV and 15 mA.

For TEM measurements, the samples were precipitated three times as above and a very small amount was dissolved in toluene. A drop of the toluene suspension was deposited onto a carbon-coated copper TEM grid (Electron Microscopy Sciences) and allowed to air-dry overnight. Transmission electron micrographs were collected on a JEOL JEM-1010 operating at an accelerating voltage of 100 kV and at 100,000 $\times$  direct magnification.

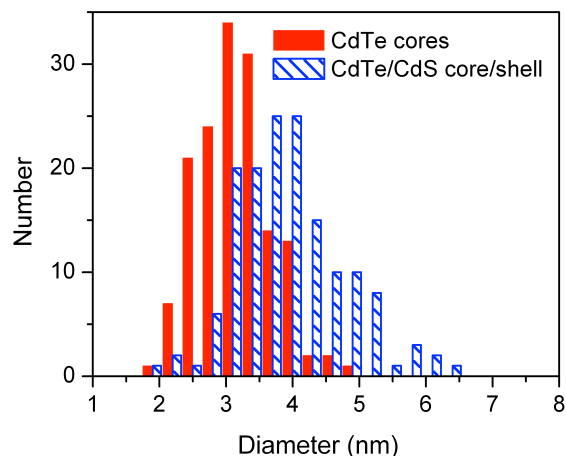
For small angle x-ray scattering (SAXS) measurements, the crude core and core/shell NCs were removed from the glovebox and purified in air by precipitating (one time only) as described above. Approximately 50 nmol of NCs were purified and dissolved in 1 mL toluene for each measurement. SAXS measurements were made using a bench-top instrument (SAXSess, Anton Paar GmbH). A Cu K- $\alpha$  x-ray line source was used as the probe. The particles were measured using a flow-through sample cell in transmission mode. The scattered x-rays were first recorded by a two-dimensional (2D) detector, and these 2D patterns were converted into 1D patterns after subtracting background and desmearing. The 1D SAXS patterns were analyzed using the Irena package.<sup>5</sup> Size distributions of the particles were derived by fitting the SAXS patterns using a

total non-negative least squares method.<sup>5</sup> For the CdTe quantum dots, a spheroid shape model was applied, while for the CdTe/CdS core-shell particles, a core-shell shape model was used for the fitting.

**Transfer to aqueous solution.** CdTe/CdS NCs were precipitated one time as described above in preparation for transfer to PBS. Approximately 5 nmol of the purified CdTe/CdS nanocrystals were dissolved in 2 mL CHCl<sub>3</sub> and then mixed with a large excess (600  $\mu$ L) of TGA. The NCs began to precipitate immediately upon addition of the TGA. The mixture was placed in a bath sonicator for 1 hour after which the sample was centrifuged. The supernatant was removed, and the CdTe/CdS NCs were washed once with CHCl<sub>3</sub> to remove excess TGA. After drying, these NCs dissolved easily in PBS.

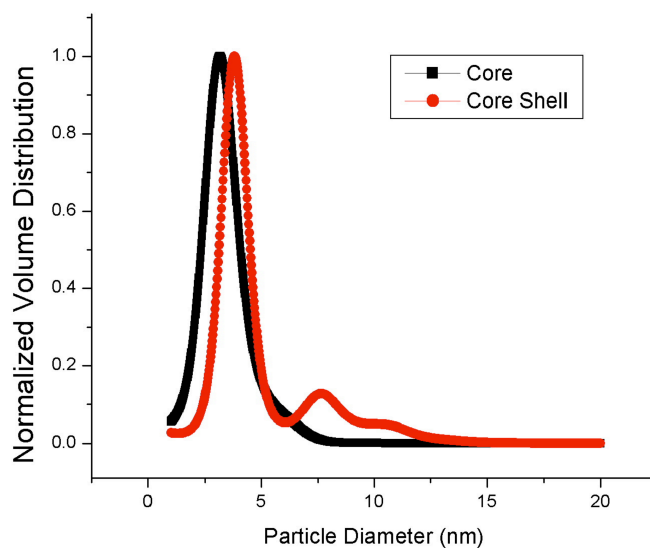
## **PARTICLE SIZE MEASUREMENTS**

**TEM.** A particle size histogram derived from measurements of particles in TEM images is shown below in Figure S1 for the small cores and small core/shell NCs described in the text. The data give a mean particle size of 3.17  $\pm$  0.05 nm for the cores, with a standard deviation of 0.55 nm, or 17%. For the core/shell particles, the mean particle size estimated from the TEM data is 3.94  $\pm$  0.07 nm, and the standard deviation of the particle sizes is 0.81 nm, or 20% of the mean. In each case, the statistics represent measurements of 150 individual particles.



**Figure S1.** Particle size distribution histogram obtained from TEM measurements on core and core/shell particles. Mean sizes of the core and core/shell particles are  $3.17 \pm 0.05$  nm and  $3.94 \pm 0.07$  nm, respectively. The estimated mean shell thickness from these measurements is  $3.9 \pm 0.9$  Å.

**SAXS.** Figure S2 shows the normalized (to unit peak height) volume distribution of CdTe and CdTe/CdS NCs versus particle diameter. This data was obtained from SAXS measurements on small CdTe cores and CdTe/CdS core/shell NCs prepared from those cores. The peaks in the size distribution are 3.16 nm for the cores and 3.80 nm for the core/shell particles. The core/shell sample shows some evidence for formation of small aggregates.



**Figure S2.** Normalized volume distribution of CdTe cores and CdTe/CdS core/shell NCs. Data were obtained via small-angle x-ray scattering measurements as explained above.

## REFERENCES

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