

Electronic Supplementary Information

Large Two-Photon Cross Sections and Low- Threshold Multiphoton Lasing of CdS/CdSe/CdS Quantum Shells

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Experimental Details

Materials. The following chemicals were used as received without further purification or modification: anhydrous acetone (99 %, Amresco), cadmium oxide (CdO, 99.95%, MilliporeSigma), Anhydrous ethanol (99%, BeanTown Chemical), hexane (ACS grade, Thermo Scientific), 1-octadecene (ODE, technical grade, 90%, MiliporeSigma), Octane (98%, MiliporeSigma), 1-octanethiol (97%, Alfa Aesar), oleic acid (OA, technical grade, 90%, MiliporeSigma), oleylamine (OLAM, technical grade, 70%, MiliporeSigma), Dioctylamine(DOA, 97%, MiliporeSigma), selenium powder (Se, 99.5%, 200 mesh, Thermo Scientific), sulfur powder (S, 99.999%, Thermo Scientific), toluene (99.8%, MiliporeSigma), and tri-n-octylphosphine (TOP, 97%, Strem Chemical).

Synthesis. *Synthesis of 6-9-nm, bulk-size CdS nanocrystals.* CdS “bulk” NCs were synthesized according to a previously published coalescence-based growth procedure.¹ In brief, 8 mL OLAM and 42 mg CdCl₂ were loaded into a 25 mL flask and put under an argon atmosphere (maintained using a Schlenk line) and heated to 240 °C. Once the temperature stabilized, 540 nmols of small CdS seed NCs (2-4 nm diameter) were swiftly injected into the flask and left to coalesce for 60 minutes. The flask was then removed from the heating mantle and quenched in a water bath. The NCs were cleaned via precipitation with toluene/ethanol mixture, twice. The NCs were then dissolved in a mixture of 5 mL of ODE and 8 mL of OA and loaded into a 25 mL flask. The flask was again put under the argon atmosphere and heated to 150 °C for 60 minutes and then cooled to room temperature and precipitated as before. The final NCs were suspended in hexane and stored under ambient conditions. This produces NCs with a (medium) diameter of 6-9 nm. NCs with a (large) 10-12 nm diameter were synthesized with an identical procedure except the temperature was raised to 270 °C and 1080 nmols of small CdS seeds were injected.

Synthesis of CdS_{bulk}-CdSe core-shell NCs. The formation of the CdSe emitting shell layer onto CdS core NCs was done by injection of two precursors (0.1 M Cd-oleate and 0.1 M TOP-Se, not mixed) *via* a syringe pump. The Cd-oleate precursor was prepared by adding 412 mg CdO, 8 mL OA, and 5 mL ODE into a 50 mL flask and heating to 260 °C under argon until a clear and nearly colorless solution was obtained. At which point an additional 19 mL of ODE was injected into the flask. The Se precursor was made by combining 141 mg Se powder and 3 mL TOP into a 25 mL flask and heating to 140 C under argon until all the selenium powder had reacted, then 14 mL of ODE was added to the flask to dilute the solution. To begin, bulk size 4-9 nm CdS nanocrystals were loaded into a 100 mL flask with 2 mL of dioctylamine (DOA) and 2 mL ODE. The temperature was set to 110 °C and the flask was degassed until bubbling had ceased. The flask was then placed under argon (*via* a Schlenk line) and the temperature was set to 315 °C. At 270 °C the Cadmium and Selenium precursors began to be injected into the flask at a rate of 3 mL/hr. The injection was allowed to continue until the emission had reached the desired wavelength (usually anywhere from 630 nm to 680 nm). The total injection time was greater for the large NCs (~90-100 min) than for the medium NCs (~70 min). Once the injection was stopped, the reaction was removed from the heating mantle and cooled to room temperature. The solution was cleaned by precipitation with toluene and 1:2 ethanol acetone mixture. The final NCs were suspended in hexane.

Synthesis of CdS_{bulk}-CdSe-CdS core-shell-shell NCs. Previously prepared CdS/CdSe were loaded into a 100 mL flask with 2 mL DOA and 2 mL ODE. The flask was degassed at 120 °C, then placed under argon and heated to 315 °C. In separate syringe pumps, 0.1M Cd-oleate and 0.12M octanethiol-ODE prepared by mixing 0.34 mL of octanethiol with 11.66 ml of ODE were injected at a rate of 3 mL/hr beginning at 270 °C. The reaction for both the medium and large NCs was stopped once the desired shell thickness was reached (360 minutes for the 6.0-nm Core and 220

minutes for 8.2-nm Core). Once the injection was finished, the solution was left to anneal at 315 °C for 45 minutes before being removed from the heat and allowed to cool to room temperature. NCs were then cleaned by precipitation with toluene and a 1:2 ethanol acetone mixture *via* centrifugation. The final NCs were dispersed in hexane.

Structural Characterization. X-ray diffraction was performed using a Bruker D2-phaser with samples drop-cast on to a miscut silicon sample holder with copper k-alpha X-rays. Transmission electron microscopy (TEM) was performed using a JEOL 2100F or using a Spectra 200. The core, total sample size, and thickness of the CdSe layer was determined by TEM. The thickness of the CdSe layers of the samples, which was evaluated using electron microscopy, was 1.9 nm, 1.4 nm, and 1.7 nm for the 4.5 nm, 6.0 nm, and 8.5 nm CdS cores.

Steady-state Spectroscopy. Absorption spectra of the samples were recorded using a Perkin-Elmer Lambda 950. Photoluminescence was collected using a lamp excitation on a Horbia Jobin-Yvon Fluorolog spectrometer. Power-dependent photoluminescence spectra were collected under 1.55 eV (800 nm) excitation and 3.10 eV (400 nm, by frequency doubling of the amplified Ti:sapphire fundamental). The geometry of the measurement was the same for both samples (front face) in cuvettes, with power measured in front of the sample. Photoluminescence was collected into a fiber and spectrally dispersed on to a CCD. The acquisition conditions were kept fixed in terms of wavelength, integration time, and acquisitions, but the repetition rate of the laser was adjusted (from 2 kHz to 20 Hz) to ensure that the CCD was not saturated. For stripe excitation measurements the 1.55 eV fundamental of the Ti:sapphire laser was pulsed at 200 Hz and focused on to thin films coated of QDs coated on to glass, with emitted light collected in the sample plane (normal to excitation). For lasing cavity measurements, a laser cavity was made using two color-

filtering mirrors (Thorlabs): one was coated with polymethylmethacrylate to provide a small spacer and the other with QS samples. The pair of mirrors was sandwiched together and positioned at 45° with respect to an 1.55 eV pump beam which was focused on to the active layer of the cavity. Emitted light was collected normal to the surface. In both stripe and cavity measurements, power was measured just before the sample.

Extinction Coefficient Measurements. Extinction coefficients are estimated in this work by taking the absorption spectra of well-washed samples (to remove any additional ligand or unbound cadmium carboxylate), digesting the sample with aqua regia (high purity nitric and hydrochloric acid), and measuring the concentration of cadmium in the solution at defined dilutions using ICP-OES (Agilent). Measurements were performed in triplicate, then the cadmium concentration was used to estimate the concentration of QS based upon the size observed from TEM.

Time-resolved photoluminescence. The configuration of time-resolved photoluminescence was the same as power-dependent photoluminescence measurements, but instead of focusing the output photoluminescence into a fiber, it was directed into a streak camera (Hamamatsu). At higher fluence excitation, the photoluminescence was attenuated using a broadband neutral density filter wheel placed in front of the streak camera, to ensure single photon sensitivity.

Transient Absorption. Transient absorption was performed by splitting the fundamental output of a 35 fs Ti: sapphire laser into pump and probe branches. The temporal response (FWHM) of the 1.55 eV pump beam passing through the thin film samples used in this work was found to be 79 fs (Figure S1). The pump branch was chopped to 1 kHz; the probe branch was focused through a 2 mm sapphire plate to generate a supercontinuum white light. The pump and probe are spatially overlapped at the sample position and pump-probe delay is adjusted using a delay stage. To

ascertain the gain spectrum, the change in absorption measured in transient absorption is added to the static absorption.

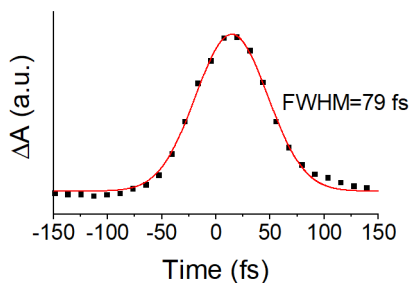


Figure S1. Measurement of the temporal response of transient absorption with 1.55 eV photon excitation. The FWHM of the observed feature is 79 fs, which is understood as the interaction time for calculating the number of electron-hole pairs generated under two-photon excitation.

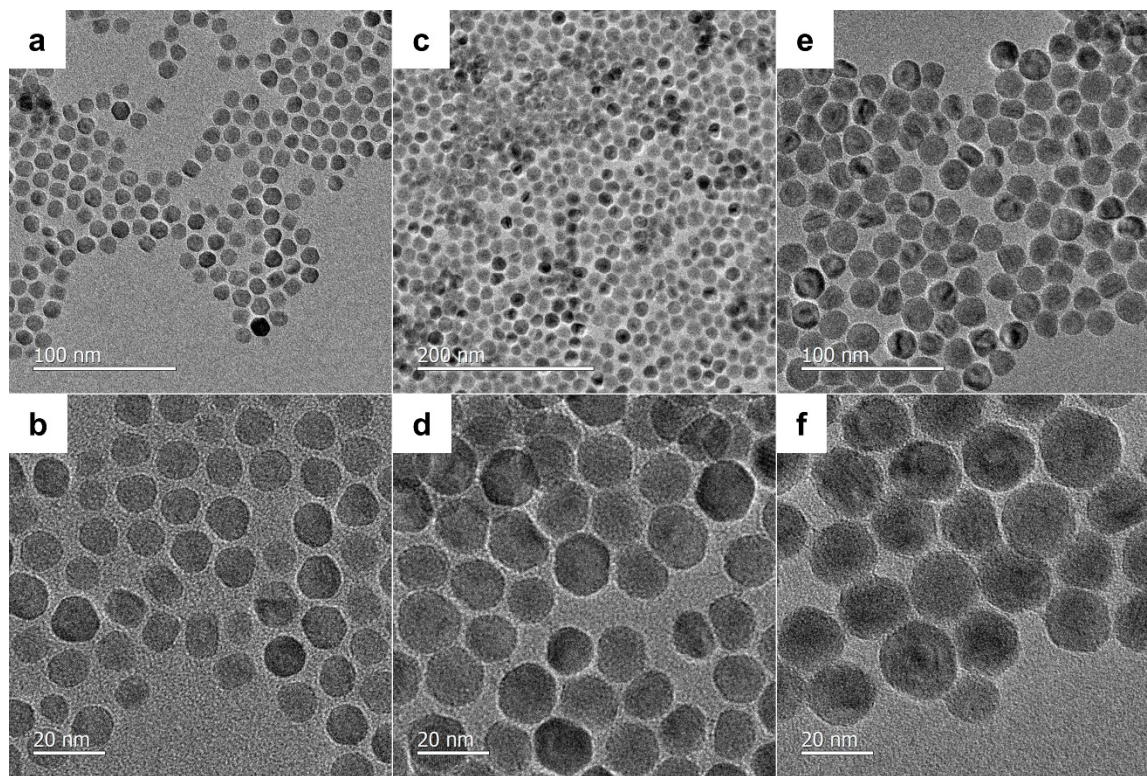


Figure S2. Transmission electron micrographs of (a, b) 6.0 nm core QDs, (c, d) 4.5 nm core QDs, and (e, f) 8.2 nm core QDs.

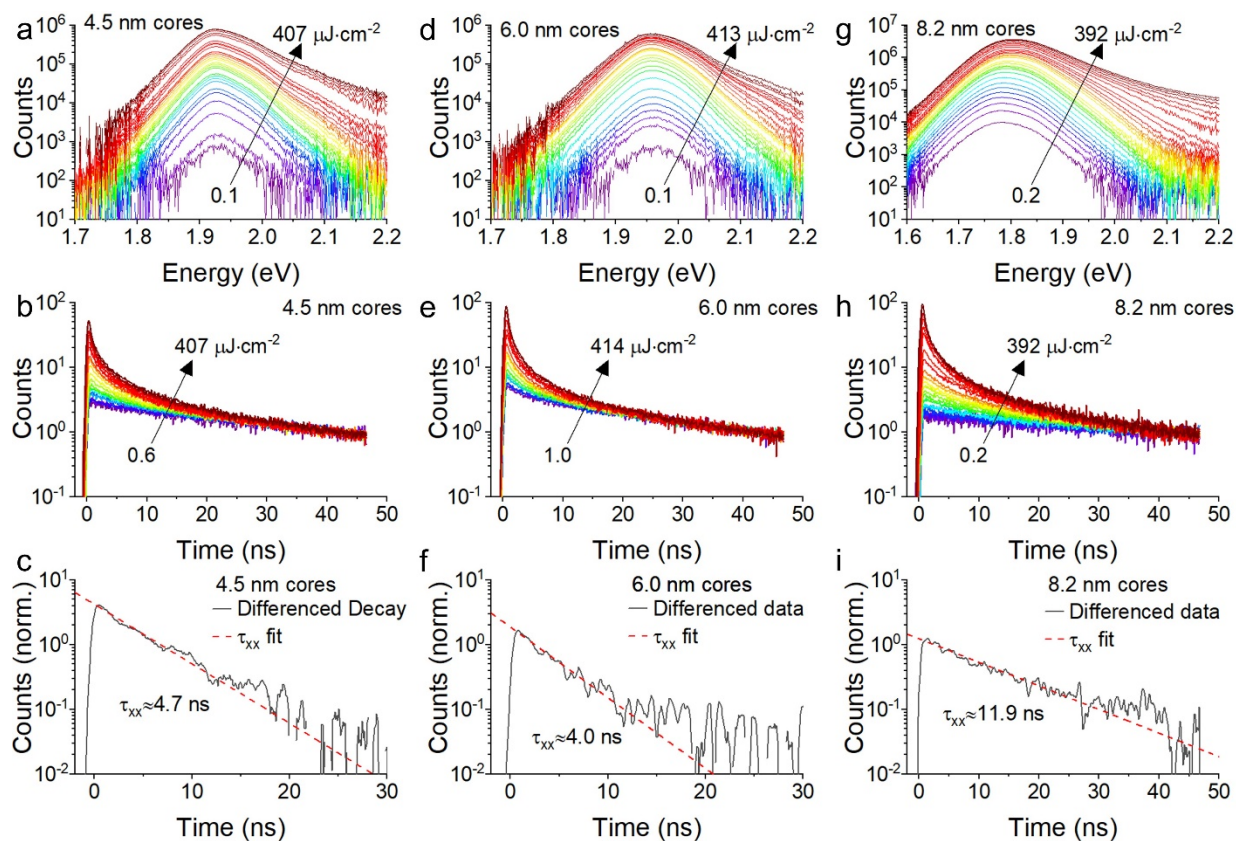


Figure S3. (a) Fluence-dependent photoluminescence spectra of 4.5 nm core QDs with 3.10 eV pump. (b) Time-resolved photoluminescence of 4.5 nm QDs with 3.10 eV pump. (c) Differenced data from (b) and monoexponential decay fit to extract biexciton lifetime. (d-f) Analogous data from 6.0 nm core QDs and (g-i) 8.2 nm core QDs.

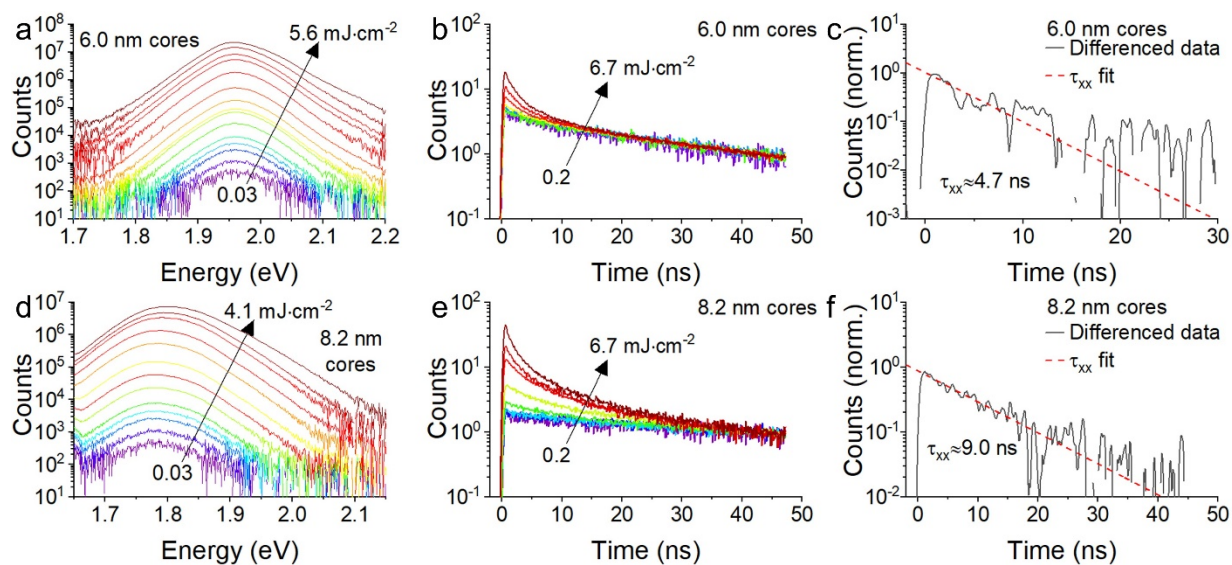


Figure S4. (a) Photoluminescence intensity with increasing pump 1.55 eV pump fluence for sample 6.0 nm core QDs. (b) Time-resolved photoluminescence of 6.0 nm core quantum shells normalized at ~ 50 ns delay for a series of increasing pump fluence. (c) Differenced data from (b) and monoexponential decay fit to extract biexciton lifetime. (d-f) analogous data from sample 8.2 nm core QDs.

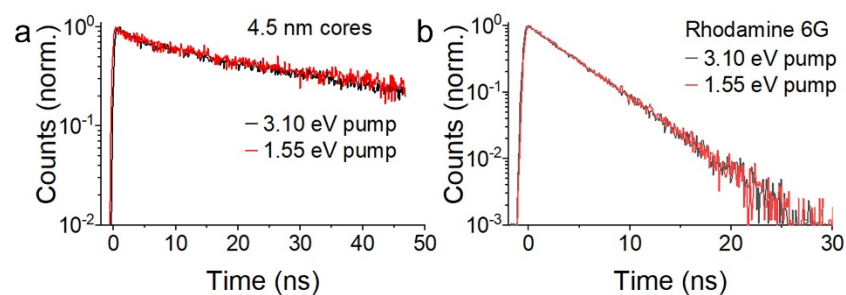


Figure S5. (a) Comparison of photoluminescence lifetime of 4.5 nm core quantum shell and (b) Rhodamine 6G dissolved in ethanol with 3.10 eV and 1.55 eV pump excitation.

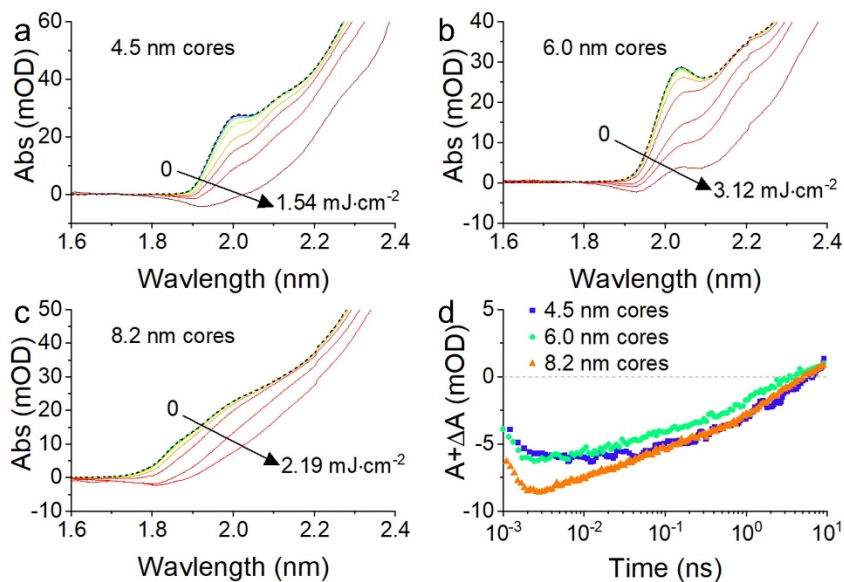


Figure S6. Gain spectra of (a) 4.5 nm core quantum shells, (b) 6.0 nm core quantum shells, and (c) 8.2 nm core quantum shells with 1.55 eV pumping. Dashed black lines show the absorption spectrum the sample without pump excitation. (d) Kinetics of gain at the energy of maximum gain for each sample at fluences of 1.54, 3.12, and 2.19 $\text{mJ}\cdot\text{cm}^{-2}$ respectively.

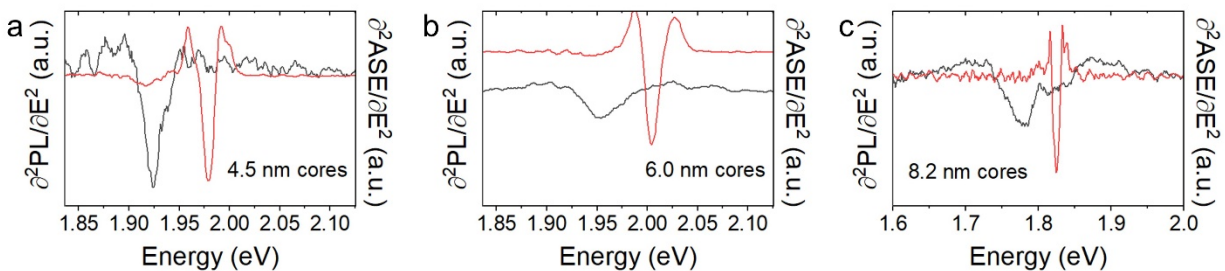


Figure S7. (a-c) Comparison of second derivatives of low-fluence photoluminescence spectra and ASE spectra (near threshold) for the samples with (a) 4.5 nm, (b) 6.0 nm, and (c) 8.2 nm cores.

Reference

- 1 J. Cassidy, C. Ellison, J. Bettinger, M. Yang, P. Moroz and M. Zamkov, *Chem. Mater.*, 2020, **32**, 7524–7534.