Supporting Information for:

Low-threshold Laser Medium Utilizing Semiconductor Nanoshell Quantum Dots.

Dmitry Porotnikov, [1,2] Benjamin T. Diroll, [6] Dulanjan Harankahage, [1,2] Laura Obloy, [1,3] Mingrui Yang, [1,2] James Cassidy, [1,2] Cole Ellison, [1,2] Emily Miller, [1,2] Spencer Rogers, [5] Alexander N. Tarnovsky, [1,3] Richard D. Schaller [4,6], Mikhail Zamkov [1,2]

The Center for Photochemical Sciences[1], Department of Physics[2] and Department of Chemistry[3], Bowling Green State University, Bowling Green, Ohio 43403. Department of Chemistry[4], Northwestern University, Evanston, Illinois 60208. Department of Physics and Astronomy[5], University of Rochester, Rochester, New York 14627. Center for Nanoscale Materials[6], Argonne National Laboratory, Lemont, Illinois 60439.

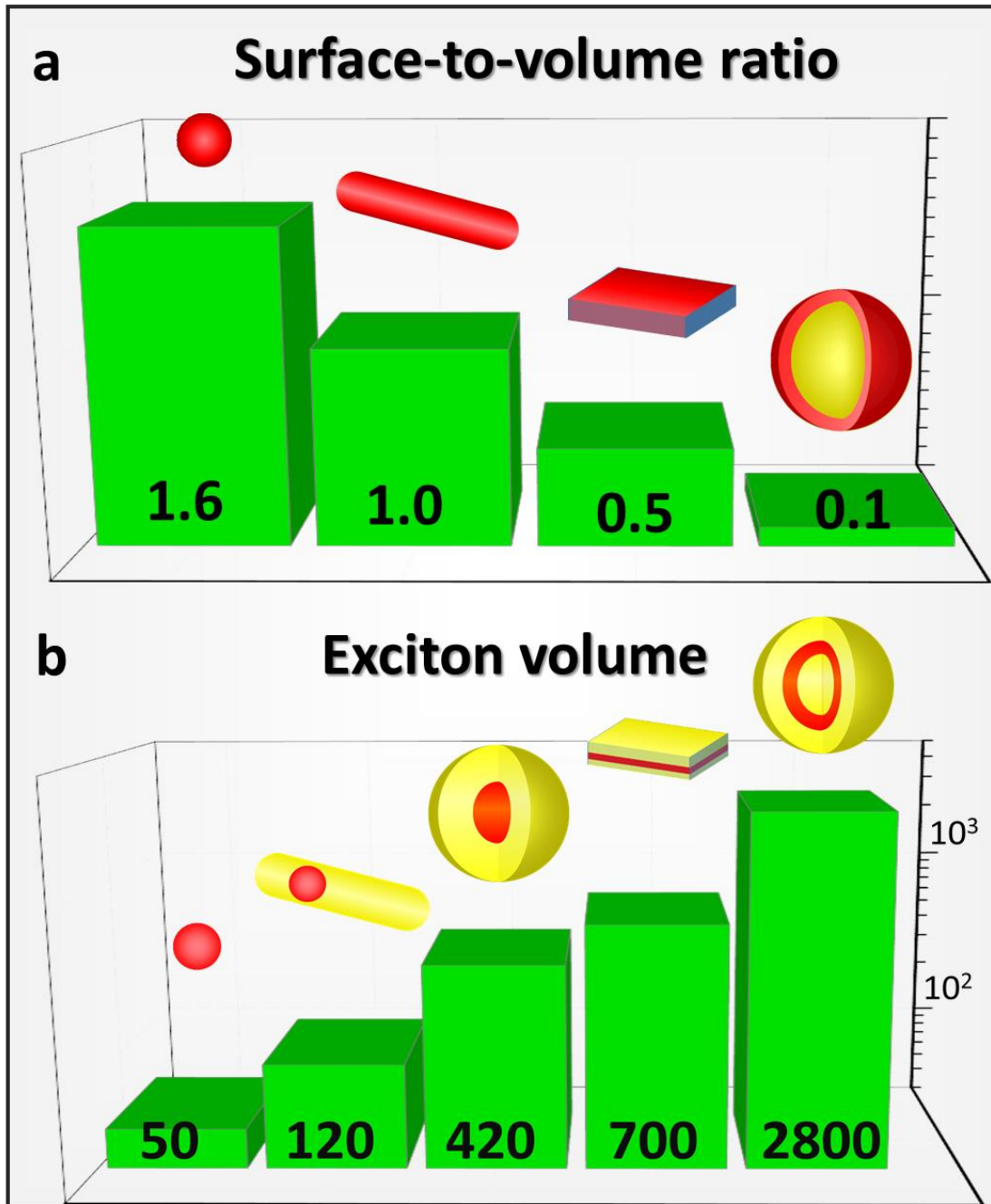Corresponding author: zamkovm@bgsu.edu; Tel: 419-372-0264; Fax: 419-372-9938

Figure SF1. (a). A comparison of the surface-to-volume ratios and (b) - exciton volumes corresponding to several quantum dot geometries. In (b) - from left to right: spherical CdSe quantum dots (diameter = 4 nm), CdSe/CdS dot-in-a-rod (dot diameter = 4 nm, rod length = 30 nm), CdSe/CdS core/shell (core radius = 2 nm, shell radius = 10 nm), CdSe/CdS nanosheets (20 nm × 20 nm × 2nm), QW nanoshells, reported

here (CdSe shell radius = 6 nm, shell thickness = 2 nm, total radius = 10 nm). Part (b) was adapted with permission from the permission of Ref. 1. Copyright 2016 American Chemical Society.
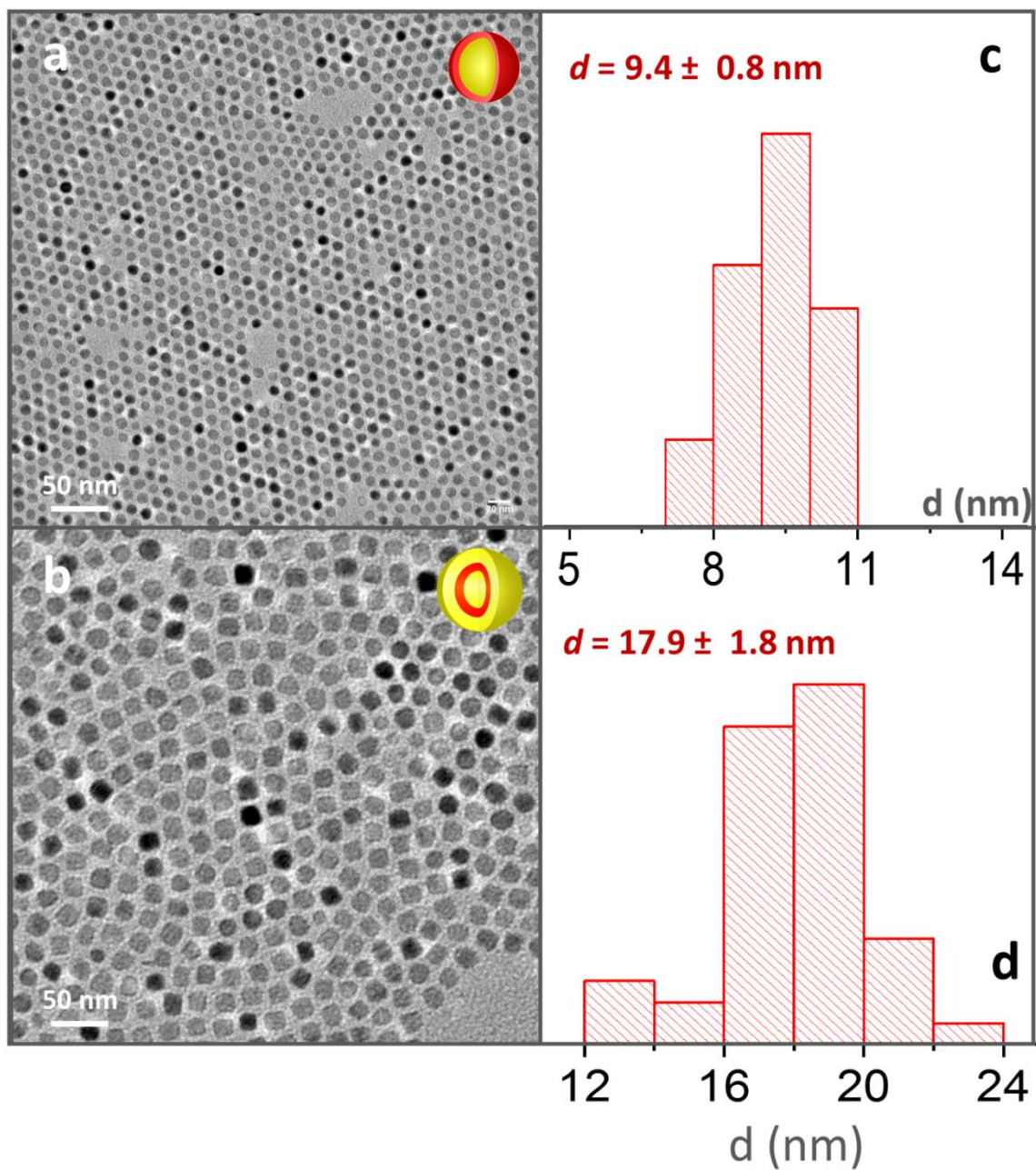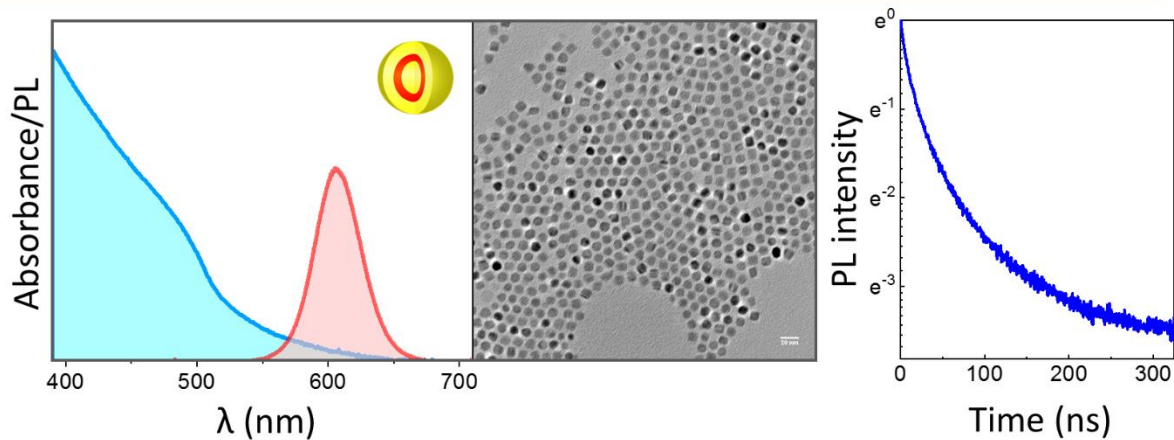

Figure SF2. Statistical analysis of particle size distributions corresponding to Fig. 3 (main text). (a,c). 9.4-nm CdS_{bulk}/CdSe NCs used for seeding the growth of quantum-well nanoshells, CdS_{bulk}/CdSe/CdS_{shell}. (b,d). 17.9-nm CdS_{bulk}/CdSe/CdS_{shell} nanoshell QDs.

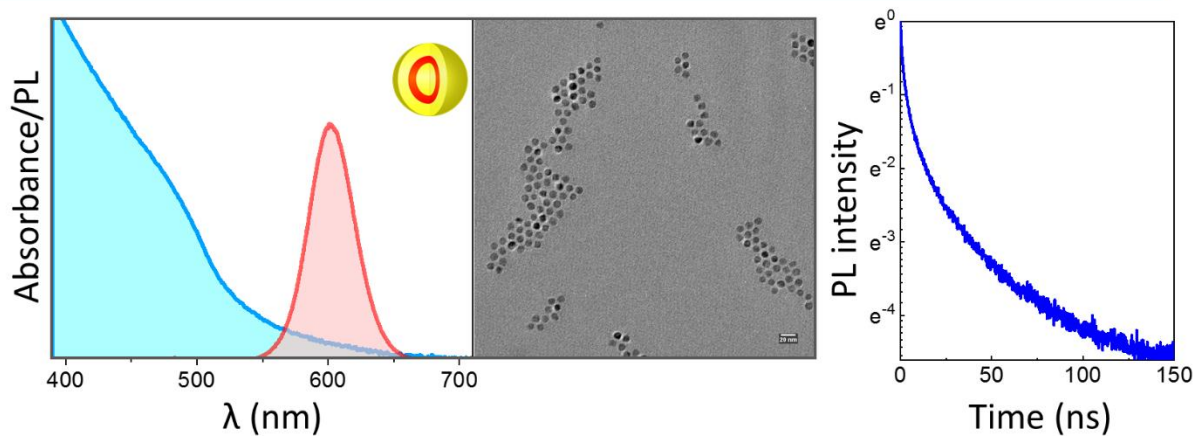**Sample 2:   QY = 17%, ASE threshold 140 µJ/cm²**

Sample 3:   QY = 14%, ASE threshold 133 µJ/cm²

Figure SF3. The summary of optical and structural characteristics for $CdS_{bulk}/CdSe/CdS_{shell}$ nanoshell QDs corresponding to other synthetic batches (PL QY = 11-17%), as discussed in the main text.
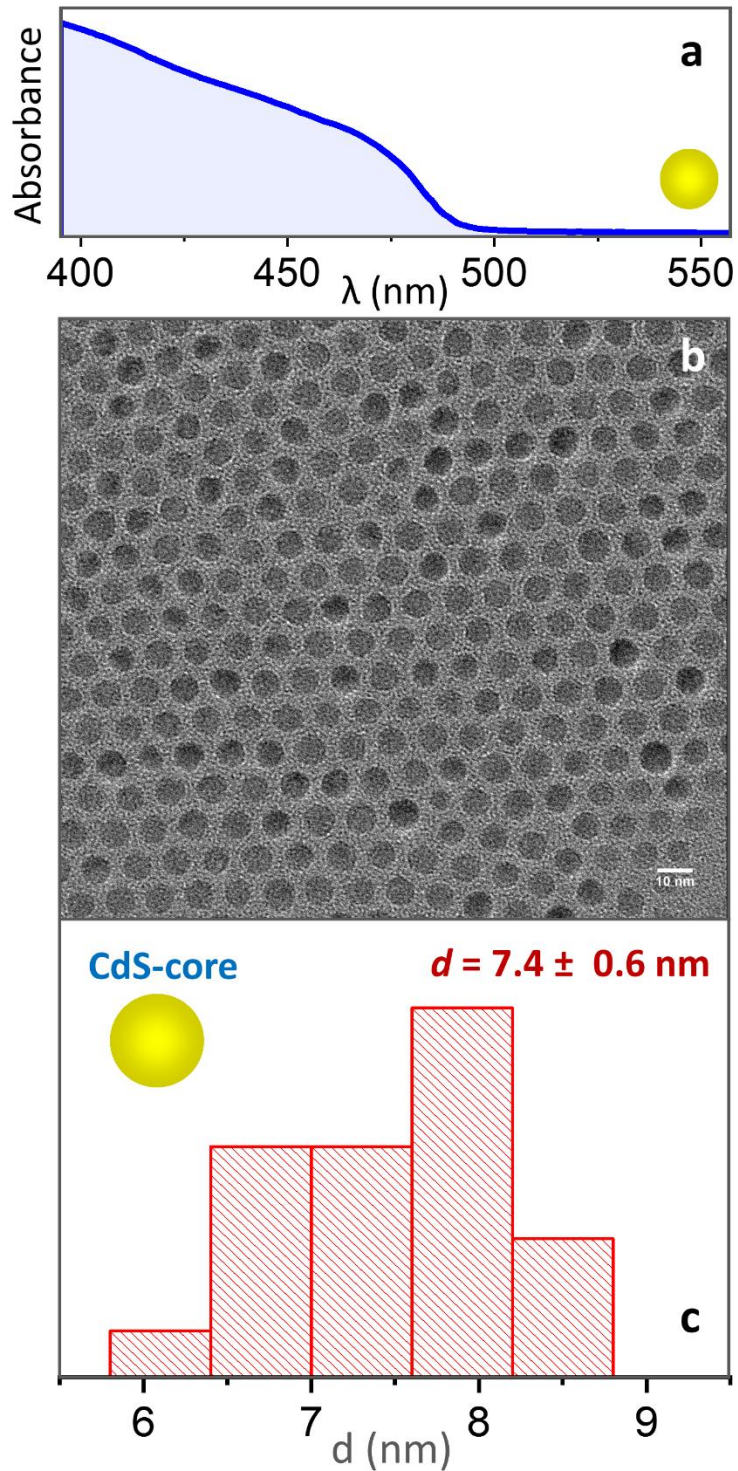
Figure SF4. (a). Absorption profile of the CdS_{bulk} "core" NCs used for seeding the growth of CdS_{bulk}/CdSe core/shell QDs. (b). A characteristic TEM image of CdS_{bulk} "core" NCs. (c). Statistical analysis of particle size distributions for CdS_{bulk} "core" NCs.
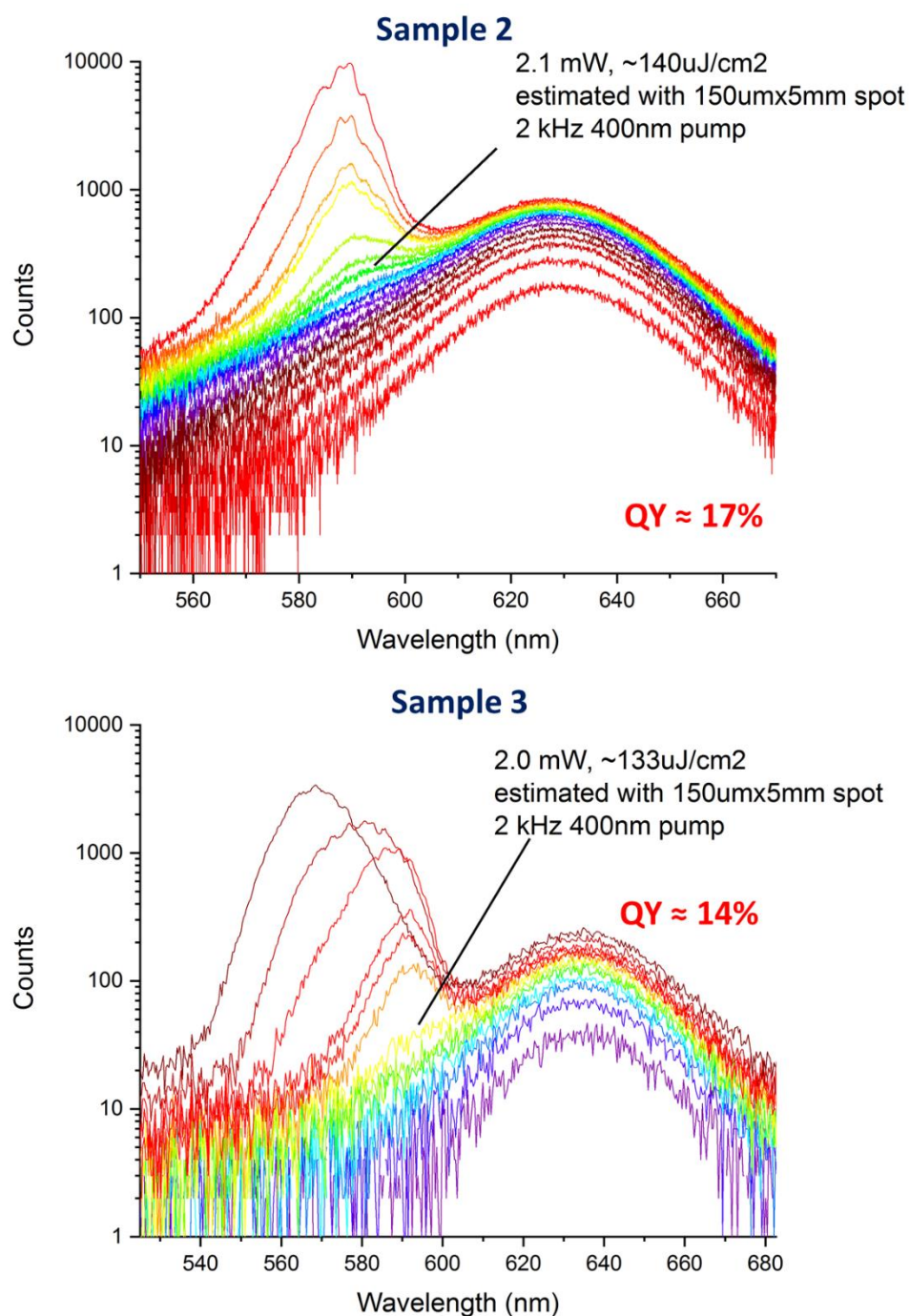
Figure SF5. Emission spectra versus different pump fluences observed for higher-threshold nanoshell QD samples 2 & 3 ($CdS_{bulk}/CdSe/CdS_{shell}$). ASE thresholds were determined to be 140 and 133 μJ/cm^2, respectively. The inferior quality of these films was most likely the reason for higher thresholds as any light scattering or haziness of films diminished the ability to see ASE.
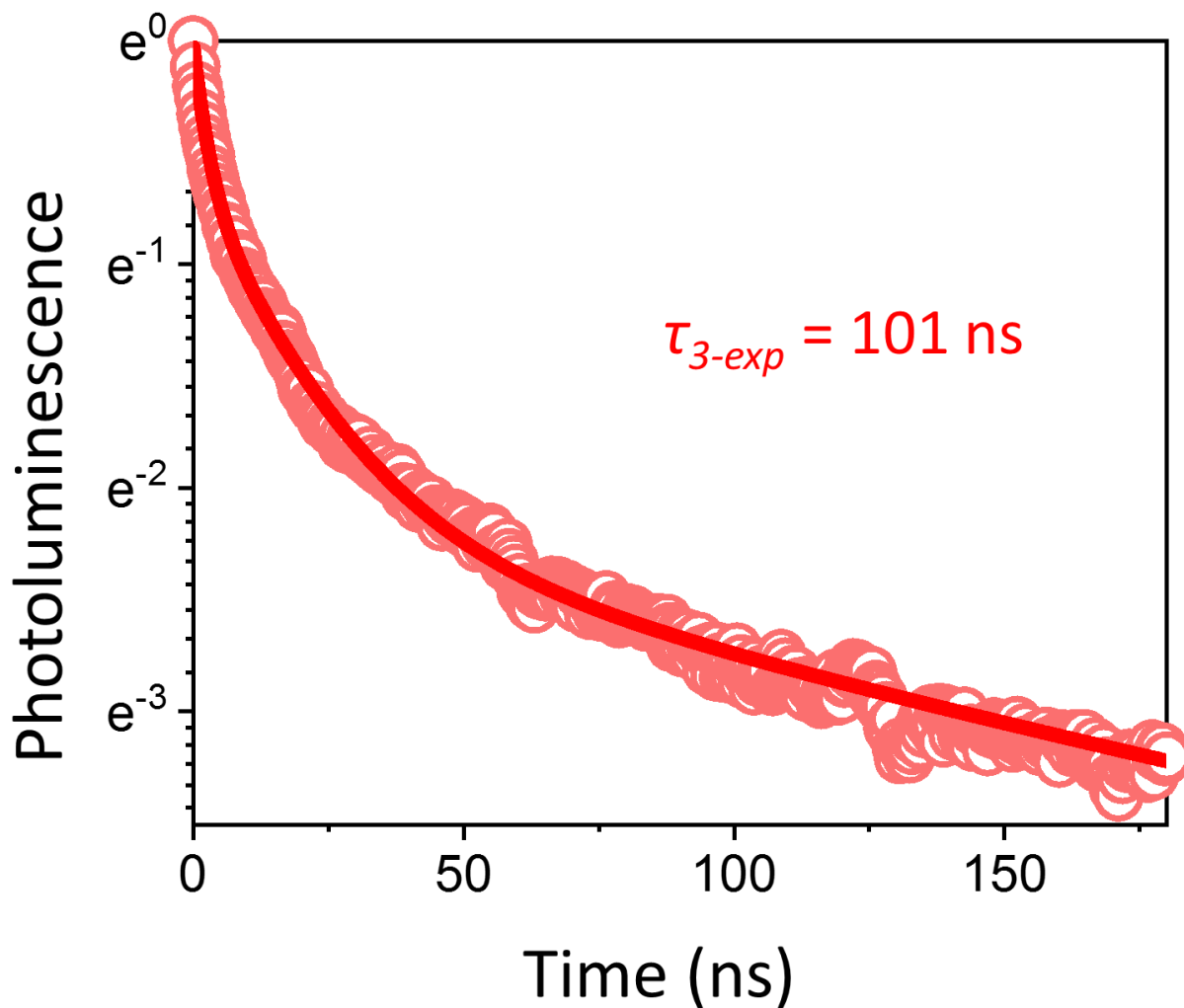
$\tau_{3\text{-}exp}$ = 101 ns

Figure SF6. PL intensity decay of 17.9-nm CdS$_{bulk}$/CdSe/CdS$_{shell}$ nanoshell QDs. The PL lifetime was fitted using a triple exponential function to find average value using the following equation: $\tau_{av} = \sum_{i=1}^{3} A_i \tau_i / \sum_{i=1}^{3} A_i$ where A_i and τ_i represent the amplitude and the lifetime of each of the three exponents used in a triple exponential fit, respectively.
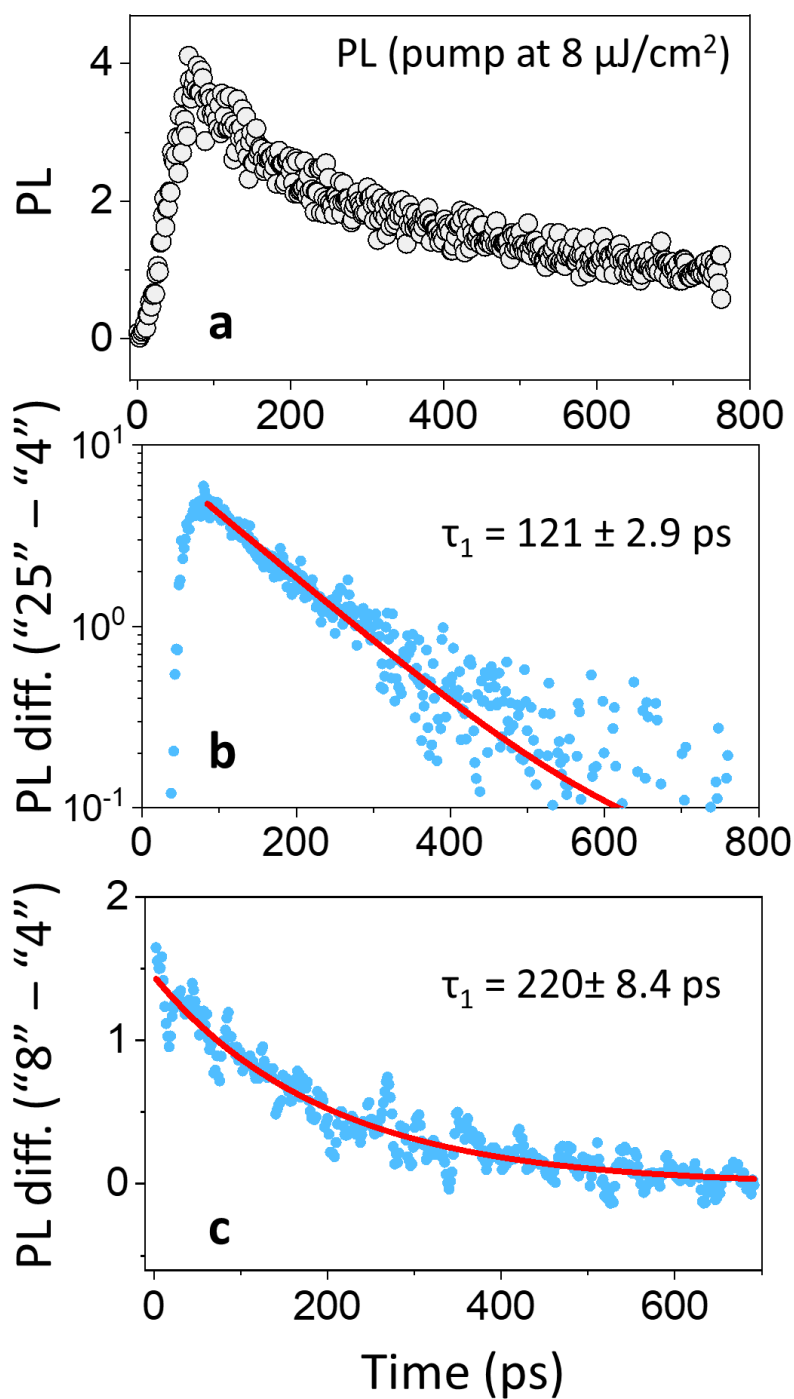
Figure SF7. (a). Time-resolved transient PL intensity for $CdS_{bulk}/CdSe/CdS_{shell}$ QDs measured at the 8 μJ/cm² pump excitation fluence. (b). The difference of PL spectra corresponding to 25 μJ/cm² and 4 μJ/cm² pump excitation fluences ("25" – "4"). The single exponential decay time constant is 121.2 ± 2.9 ps. (c). The difference of PL spectra corresponding to 8 μJ/cm² and 4 μJ/cm² pump excitation fluences ("8" – "4"). The single exponential decay time constant is 220 ± 8 ps.

Determination of biexciton lifetimes from TA kinetics.

In order to extract biexciton lifetimes from the bleach recovery kinetics (Fig. 5d, main text), we have employed the coupled rate equation formalism,[2] which assumes: (*i*) - Poisson distribution of initial multi-exciton populations in a nanocrystal ensemble, and (*ii*) - statistical scaling of Auger lifetimes. Within this strategy, the average number of photons absorbed by a nanoparticle, <N>, is first estimated from the known excitation pulse power, spectral density, and the sample absorption profile.[3] The average number of absorbed photons per particle is subsequently used to create the statistical distribution of nanoparticle fractions in the sample that receive $n = 0,1,2 \ldots$ excitons, $P(n)$. To this end, the probability of a nanocrystal absorbing n photons, $f(n)$, is assumed to follow the Poisson distribution: $f(n) = \langle N \rangle^n \times e^{-n} / n!$. Under the assumption that multiple excitons in a given nanocrystal decay sequentially (*via* the Auger recombination), the temporal evolution of the n-exciton population in a particle, $P(n, t)$, can be determined by solving coupled rate equations:

$$\frac{dP(n,t)}{dt} = \frac{P(n+1, t)}{\tau_{n+1}} - \frac{P(n,t)}{\tau_n} \tag{SE1}$$

where, τ_n represents the lifetime of the n-exciton state. The resulting evolution of multi-exciton populations, $P(n,t)$, obtained by solving Eq. 1, depends on a single unknown parameter, τ_2, corresponding to the Auger-limited biexciton lifetime. The single exciton lifetime, τ_1, as well as multi-exciton lifetimes (τ_n; n>2) entering Eq. 1 can be determined *a priori*. To this end, τ_1 is either extracted from the long-time TA bleach recovery at low excitation powers or obtained from the PL intensity decay (Fig. SF7). The lifetimes of multi-exciton states, τ_n, are computed using a statistical scaling law: $\tau_n^{-1} = n^2(n-1)\tau_2^{-1}/4$.[4] Owing to relatively low excitation powers used in present experiments ($\langle N \rangle \sim 1$), we assume that the TA bleach, ΔA, is contributed by up to four excitons, such that the average number of excitons per nanocrystal becomes, $P(t) = 4 \times P(4,t) + 3 \times P(3,t) + 2 \times P(2,t) + P(1,t)$. The resulting parametric curve, $P(\tau_2, t)$, was used to fit the experimental measured TA bleach, $\Delta A(t)$, in order to determine the best fitting parameter, τ_2. We note that despite n = 2 being highest exciton occupation number for zero-

dimensional CdSe NCs, due to a continuous electron density in CdS/CdSe nanoshells, these colloids are likely to support a larger number of band-edge excitons.

References.

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