ADVANCED MATERIALS

Supporting Information

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Stimulated Emission and Lasing from CdSe/CdS/ZnS Core-Multi-Shell Quantum Dots by Simultaneous Three-Photon Absorption

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Calculation of the average number of excitons per QD <N> based on one-, two- and three-photon pumping. The one- (1PA), two- (2PA) and three-photon (3PA) absorption cross-sections of CdSe/CdS/ZnS core-multi-shell QDs were determined in order to calculate the average number of excitons at threshold. The 1PA at 480 nm was determined, following previously reported method[1], through renormalization of extinction coefficient curves for CdSe QDs published by Yu *et al*.[2] during overcoating with CdS/ZnS multi-shell. According to the first exciton absorption peak wavelength of 603 nm, we derive the corresponding extinction coefficient to be 4.0×10^{5} L mol^{-1} cm^{-1}, which corresponds to the 1PA (σ_1) of 1.4 $\times10^{-15}$ cm^2 at 480 nm. The 2PA at 800 nm was determined by Z-scan measurements (see Experimental Section). Differently, Si biased detector was used at 800 nm, while Ge biased detector at 1300 nm. The 2PA (σ_2) and 3PA (σ_3) of CdSe/CdS/ZnS QDs were derived to be 13700 GM and 2.8×10^{-77} cm^6 s^2 photon^{-2}, respectively. Finally, the average number of excitons per QD were calculated by:

One-photon pumping: [1] $<N>= f\sigma_1/(\hbar\omega_1)$ (1)

Two-photon pumping: [1, 3] $<N>= f^2\sigma_2/\left(\tau(\hbar\omega_2)^2\right)$ (2)

Three-photon pumping: [3,4] $<N>=\pi^{1/2}\sigma_3 I^3\tau/\left(3^{3/2}(\hbar\omega_3)^3\right)$ (3)

where f is the pump fluence (J cm^{-2}), τ is the laser pulse-width (seconds), I is the pump intensity (W cm^{-2}), and $\hbar\omega_1$, $\hbar\omega_2$ and $\hbar\omega_3$ are the photon energies at 480 nm, 800 nm and 1300 nm, respectively. The relationship between f and I is given by:[3]

$$f=\pi^{1/2}I\tau/2 \quad (4)$$

The TEM statistical information on the size distribution of CdSe/CdS QDs and CdSe/CdS/ZnS QDs are shown in **Figure S1**a and S1b, respectively. The inhomogeneity of size distribution is found to increase after multi-shell coating from the fit with Gaussian curves (red lines).

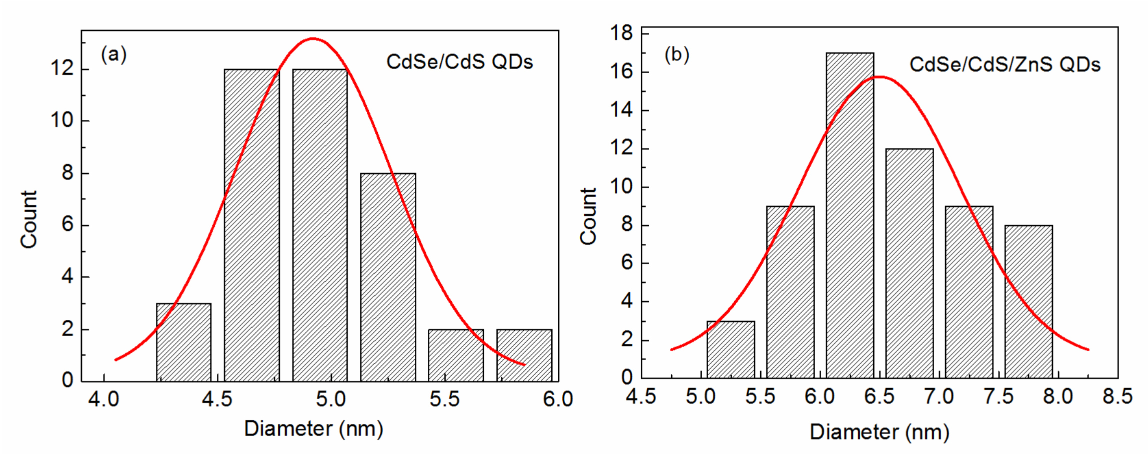

Figure S1. Size histograms for a) CdSe/CdS QDs and b) CdSe/CdS/ZnS QDs. The red lines are the fit with Gaussian curves.

The optical images of close-packed colloidal QDs solids are shown in **Figure S2**a-d. It is found that QDs solution can spread very well on the glass slides and optically smooth surfaces are formed at room temperature. However, a pretty rough surface was obtained by drying the QDs suspension drop-casted onto hydrophobic glass slides at a relatively high temperature (50 ~ 60 ^{o}C).

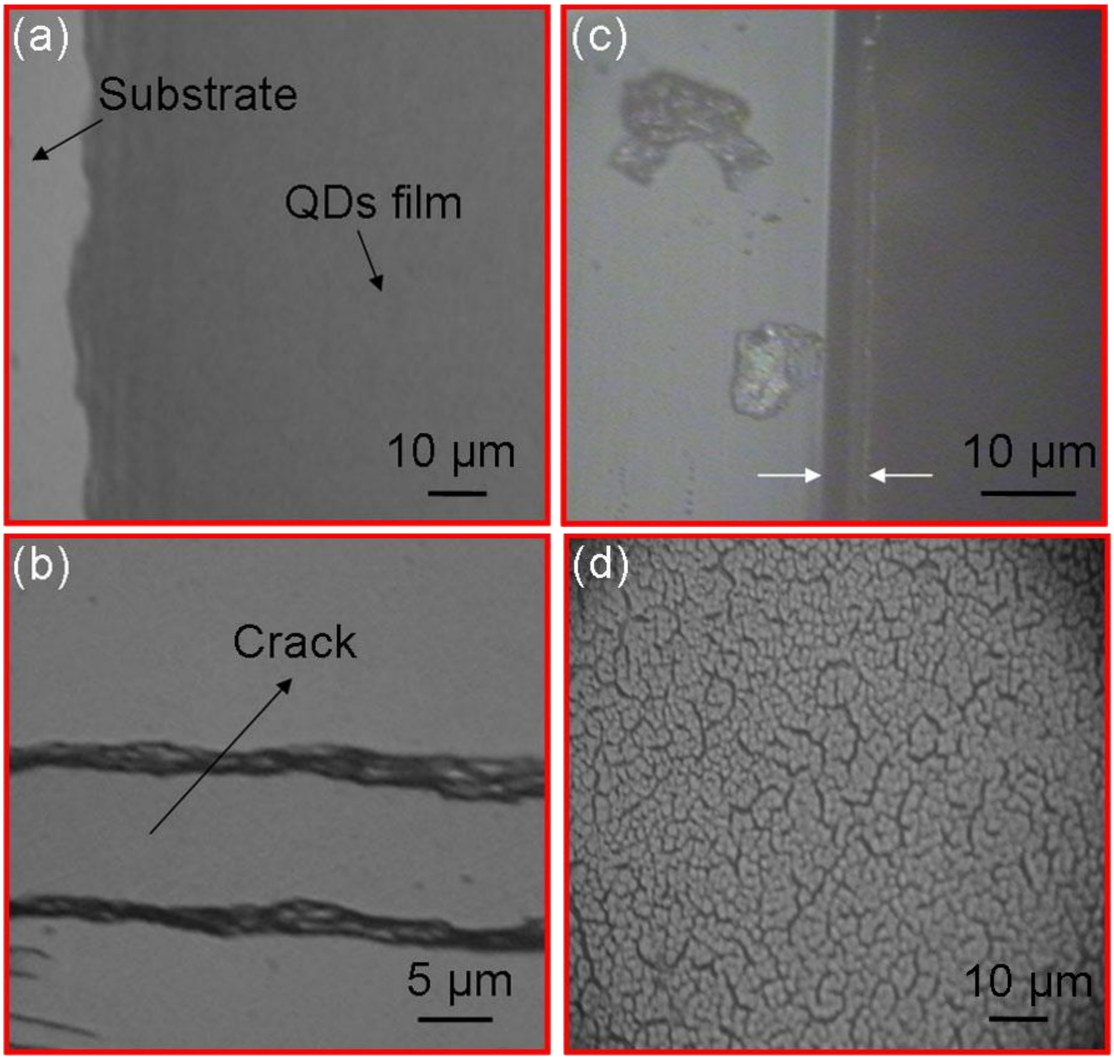

Figure S2. a) Smooth CdSe/CdS/ZnS core-multi-shell QDs film. b) Well-defined cracking formed in the sample during solvent evaporation. c) Film thickness characterization. (d) Self-assembled CdSe/CdS/ZnS core-multi-shell QDs aggregations.

Figure S3a shows the single exciton decay of close-packed CdSe/CdS/ZnS QDs solids with a lifetime of 16.5 ns at low pumping intensity of 5.4 mJ cm^{-2}. The decreased lifetime compared to that of dilute solution of CdSe/CdS/ZnS QDs was mostly due to the dipole-dipole interaction between adjacent QDs.[5] Figure S2b-d depicts the time resolved PL spectrograms of PL dynamics with varied pumping intensities.

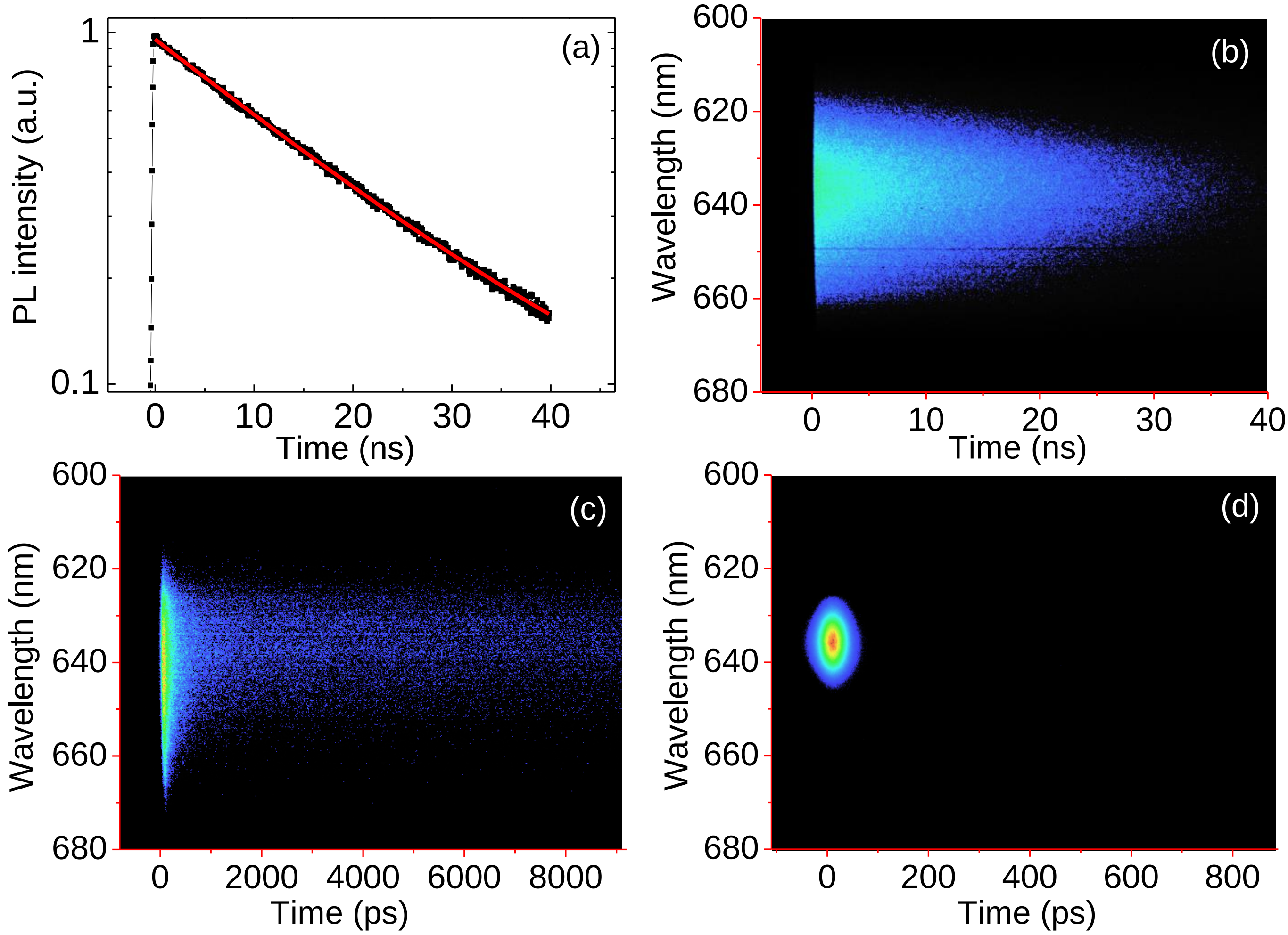

Figure S3. a) Single exciton decay of close-packed CdSe/CdS/ZnS QDs solids with a lifetime of 16.5 ns at low pumping intensity of 5.4 mJ cm^{-2}. b)-d) Time resolved PL spectrograms of PL dynamics of close-packed CdSe/CdS/ZnS QDs solids at excitation intensities of 5.4 mJ cm^{-2}, 14.0 mJ cm^{-2} and 16.0 mJ cm^{-2}, respectively.

Figure S4 shows the schematic of Z-scan experimental setup used in this work. The laser beam was separated into two parts through a beam splitter. The reflected beam was recorded (Detector 1) in order to reduce the influence of pulse fluctuations. The transmitted beam was focused onto a 1 mm thick quartz cuvette containing the sample with radius of ~20 μm by a circular lens with a focus length of 20 cm, which moved along the laser beam axis, and finally detected by a Ge biased detector (Detector 2) using standard lock-in amplifier technique.

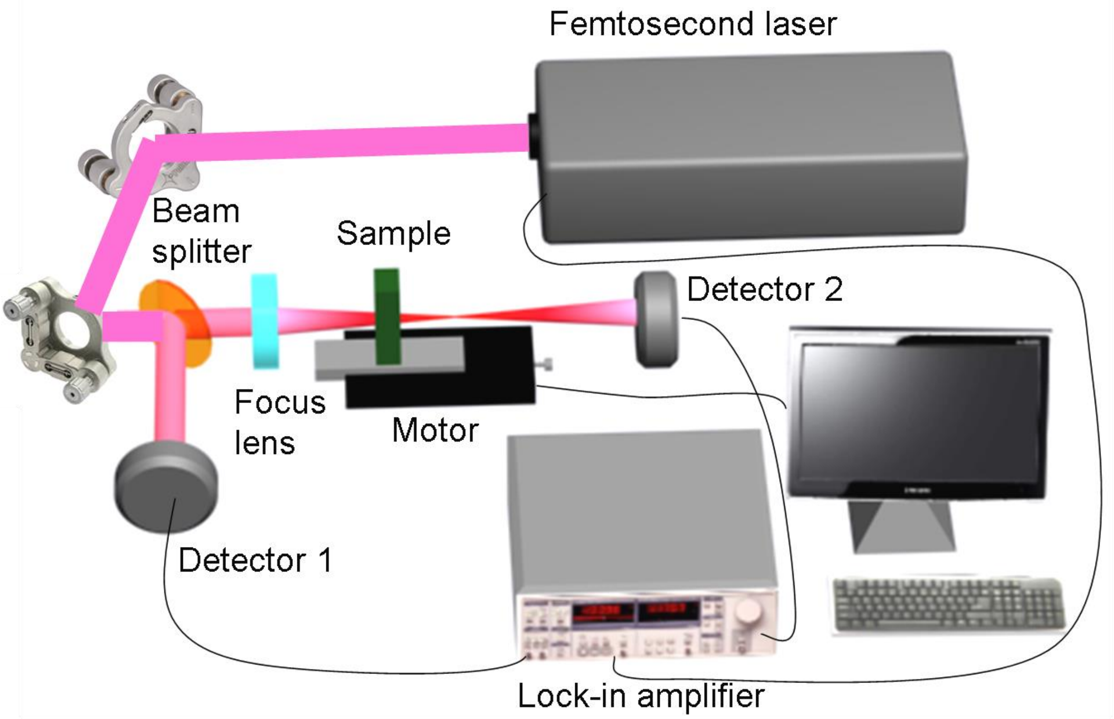

Figure S4. Schematic of Z-scan experimental setup.

Table S1. A summary of results in this work and data available in the literature about 3PA cross-sections of commonly used QDs and dye.

Samples	Diameters (nm)	Parameters of excitation pulse	3PA cross-sections (cm^6 s^2 $photon^{-2}$)
CdSe/CdS QDs[a]	4.95	100 fs,1300 nm	4.3×10^{-78}
CdSe/CdS/ZnS QDs[a]	6.57	100 fs,1300 nm	2.8×10^{-77}
CdSe QDs[6]	3.9	160 fs, 1300 nm	$\sim10^{-78}$
CdS QDs[7]	NA	100 fs, 1000 nm	$\sim10^{-79}$
ZnS QDs[8]	2.5	120 fs, 620-780 nm	$\sim10^{-78}$
Rhodamine 6G[9]	NA	150 fs, 1300 nm	6×10^{-81}

a: Experimental uncertainty: ±15%

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