Single-dot Spectroscopy of Zinc-blende CdSe/CdS Core/Shell Nanocrystals: Non-blinking and Correlation with Ensemble Measurements

Haiyan Qin[1+*], Yuan Niu[1+], Renyang Meng[1], Xing Lin[2], Runchen Lai[1], Wei Fang[2*], Xiaogang Peng[1*]

[1] Center for Chemistry of Novel & High-Performance Materials, and Department of Chemistry, Zhejiang University, Hangzhou, 310027, P. R. China.

[2] State Key Laboratory of Modern Optical Instrumentation, Department of Optical Engineering, Zhejiang University, Hangzhou, 310027, P. R. China.

*Correspondence to: hattieqin@zju.edu.cn (HQ), wfang08@zju.edu.cn (WF) or xpeng@zju.edu.cn (XP).

[+]Haiyan Qin (optical measurements) and Yuan Niu (synthesis) made the same contribution to this work.

Methods

Determination of the threshold between 'on' and 'off' states:

A threshold between 'on' and 'off' states should be determined in calculating the 'on' time fraction and 'on' state bandwidth. For a PL intensity time trace for a single dot, e.g. traces in Figure 2a, we first fitted the histograms of the QD emission trace and the background intensity trace respectively by a Gaussian function. The valley of the sum of these two Gaussian functions was determined as the threshold between 'on' and 'off' states. Since the 'on' and 'off' states separate very clearly, the calculation results of 'on' fraction and 'on' state bandwidth are not sensitive to small changes of the threshold value.

Estimation of the corrected 'on' state intensity bandwidth:

As the fluctuation or standard deviation of signal detected is proportional to the square root of the average photon counts itself. Here we defined the corrected 'on' state intensity bandwidth as

$$W_{on} = \frac{SD_{on} / \sqrt{I_{on}}}{SD_{bg} / \sqrt{I_{bg}}}$$

where, SD_{on} and SD_{bg} are the standard deviation of the 'on' state and the background signal of the blinking traces. I_{on} and I_{bg} are the average intensities of the 'on' state and the background.

Estimation of the photons absorbed per lifetime cycle $\langle N \rangle$:

The calculation of absorption cross-section for CdSe/CdS core/shell QDs were referred to Ref 1. The diameter of CdSe core QDs was 3.1 nm and the thickness of each CdS monolayer shell was 0.34 nm.

The number of photons absorbed per lifetime cycle $\langle N \rangle$ can be estimated as

$$\langle N \rangle = \frac{C_{abs} \times P}{E(\lambda)} \cdot \tau$$

here C_{abs} is the absorption cross-section of CdSe/CdS core/shell QDs; P is the excitation power density; $E(\lambda)$ is the energy for a photon with the excitation wavelength of λ; τ is the lifetime of the QDs. In order to avoid multi-exciton process in blinking measurements in Figure 2a, the excitation power density was as low as $\langle N \rangle <$ 0.01 for all QDs with difference sizes. This excitation power level corresponding to a excitation rate between 2×10^4 and 3×10^5 s^{-1} was consistent with Ref 2, which using excitation rates of 2×10^5 and 3.4×10^5 s^{-1}.

It is notable that the thin shell QDs was also non-blinking under a 450 nm pulsed laser excitation with a high peak power density of 20 KW/cm^2, as long as the average exciton per pulse $\langle N \rangle$ is small (see Figure S2 in Supporting Information).

Determination of PL decay lifetime from the PL decay curves[3]:

In the multi-exponential decay model, the PL intensity is assumed to be the sum of individual single-exponential decay components:

$$I(t) = A + \sum_{i=1}^{n} B_i \exp\left(-t / \tau_i\right)$$

here A is the background signal, B_i are the amplitudes of the components at t = 0, τ_i are the decay lifetimes, and n is the total number of decay components.
The average lifetime $\bar{\tau}$ can be determined by

$$\bar{\tau} = \frac{\sum_{i=1}^{n} B_i \tau_i^2}{\sum_{i=1}^{n} B_i \tau_i} = \sum_{i=1}^{n} f_i \tau_i$$

The fractional contribution f_i of each decay component is given by

$$f_i = \frac{B_i \tau_i}{\sum_{i=1}^{n} B_i \tau_i}, \text{ and } \sum f_i = 1.$$

Fitting measured time series of PL intensity $I(t_k)$ by the multi-exponential decay function, one can obtained the calculated PL intensity $I_c(t_k)$. The goodness-of-fit, reduced-χ^2, is given by

$$\chi_R^2 = \frac{1}{m} \sum_{k=1}^{m} \frac{\left[I(t_k) - I_c(t_k) \right]^2}{I(t_k)}$$

here, m is the total number of data points for $I(t_k)$.

Table S1. *Representative PL decay lifetimes obtained at single-dot and ensemble levels by fitting the PL decay curves.*

	Single-dot level						Ensemble level					
	τ_1	f_1	τ_2	f_2	$\bar{\tau}$	χ_R^2	τ_1	f_1	τ_2	f_2	$\bar{\tau}$	χ_R^2
CdSe/4CdS	19.0	100%	-	-	19.0	1.13	17.4	100%	-	-	17.4	1.13
CdSe/8CdS	20.7	53%	35.6	47%	27.6	1.10	19.9	69%	31.0	31%	23.4	0.93
CdSe/12CdS	28.6	56%	44.3	44%	35.6	1.09	25.8	62%	44.8	38%	33.0	0.95
CdSe/16CdS	31.0	27%	59.7	73%	52.1	1.18	32.7	65%	68.6	36%	45.4	0.97

* $\bar{\tau}$ was calculated by accounting the contributions of all channels found in a specific measurement of PL decay curves for both single-dot and ensemble levels. All lifetime values, τ_1, τ_2 and $\bar{\tau}$, are in unit of ns.

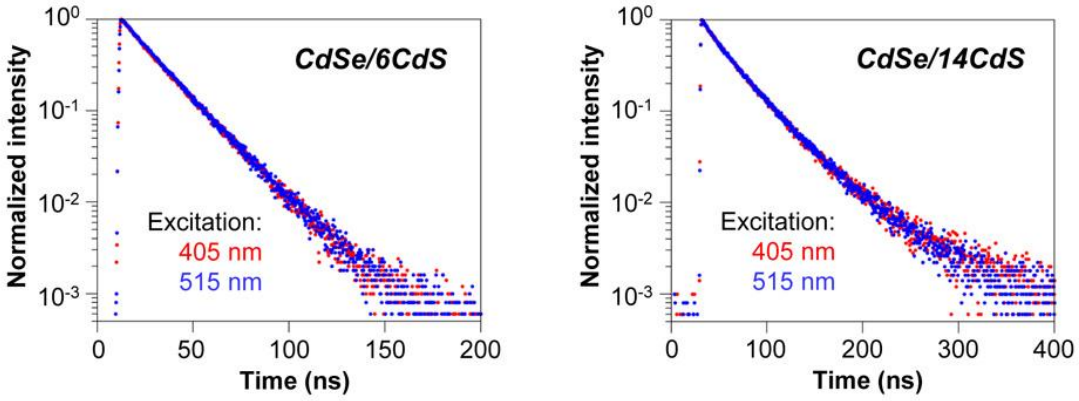

Figure S1. Transient PL decays of ensemble CdSe/CdS core/shell QDs with different excitation wavelengths. 405 nm (red) and 515 nm (blue) picosecond pulsed diode lasers were respectively used as excitation light sources for the PL decay measurement of ensemble CdSe/6CdS (left panel) and CdSe/14CdS (right panel). For both thin- and thick-shell QDs, the PL decay curves were identical with different excitation wavelengths.

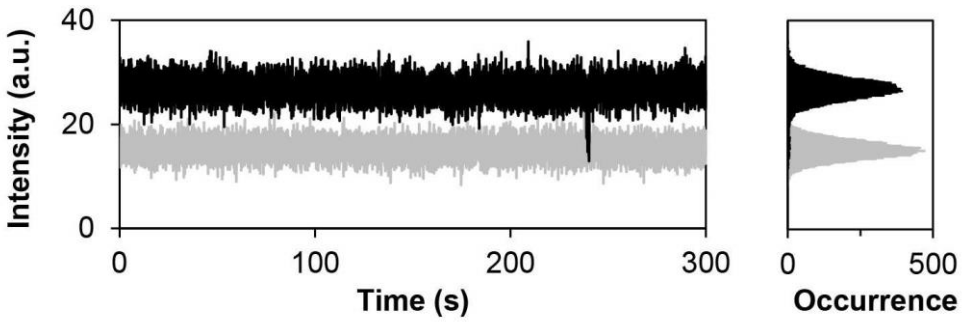

Figure S2. PL intensity time trace of CdSe/4CdS QDs under pulsed laser excitation. A representative PL intensity time trace and corresponding histogram of CdSe QDs with 4 monolayers of shell excited by a 450 nm pulsed laser with 1 MHz repetition rate and 50 ps pulse duration. The peak power density was 20 KW/cm^2. Average exciton per pulse $\langle N \rangle$=0.02, which was still within the linear window range described above. This result indicates that the peak power density of a pulsed laser is not sufficient for judging the linear window as long as the repetition rate is significantly low in comparison to the PL decay rate. Under such conditions, there would be no more than one excitation pulse within one single-exciton lifetime period.

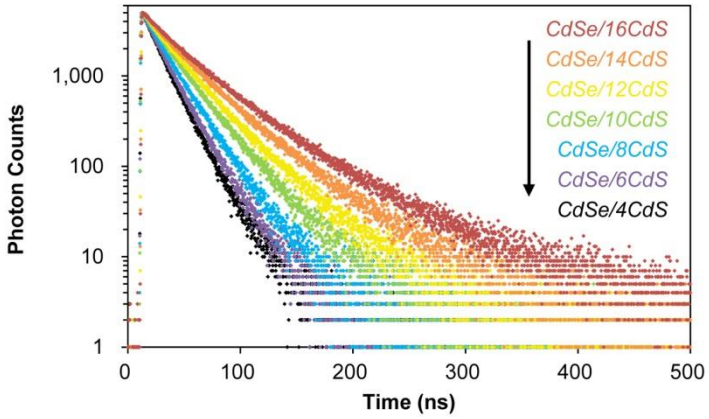

Figure S3. PL decay dynamics of ensemble CdSe/CdS core/shell QDs with different shell thicknesses. Evidently, the decay curves for the QDs with 4 and 6 monolayers of CdS shell could be well fitted into single exponential decay, and the curves for 8-16 monolayers of CdS shell could be fitted as double-channel decay. To ensure reliability and reproducibility, the peak photon counts were set at 5000 photons for each measurement, and multiple measurements for the same shell thickness from different batches were repeated. The excitation pulse peak power was varied between 1 and 0.1 W/cm^2. To exclude possible energy transfer for the samples with multiple decay channels, the optical density for the solution samples was set to be significantly below 0.1 at the first absorption peak. The goodness-of-fit (χ_R^2) was set not greater than 1.30 for obtaining the lifetime values shown in Table 1 in the text and Table S1 in Supporting Information.

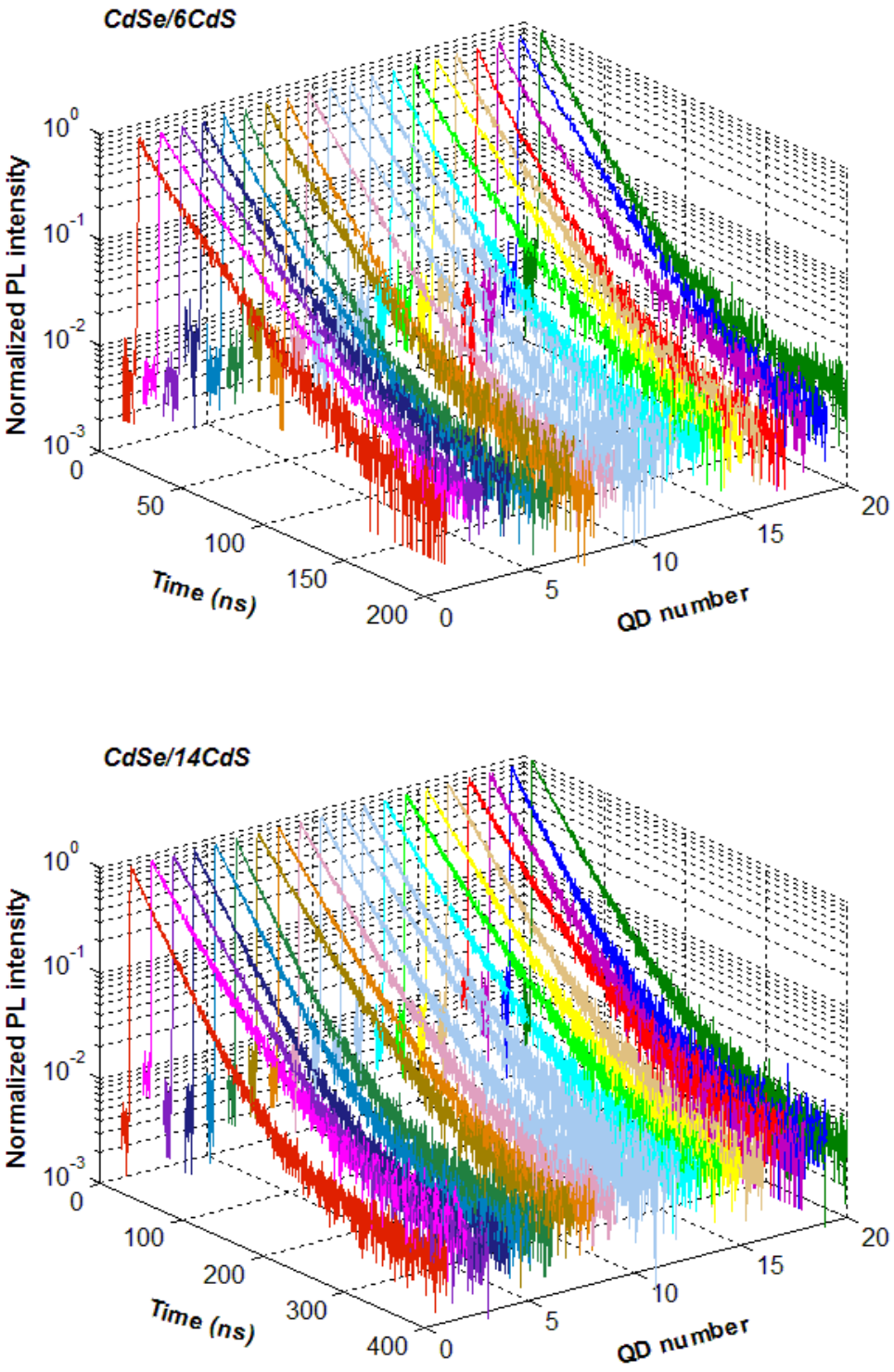

Figure S4. PL decay dynamics of single CdSe/CdS core/shell QDs. PL decay curves of 20 randomly selected single dots for zinc-blende CdSe/CdS core/shell QDs with 6 (upper panel) and 14 (lower panel) monolayers of shell.

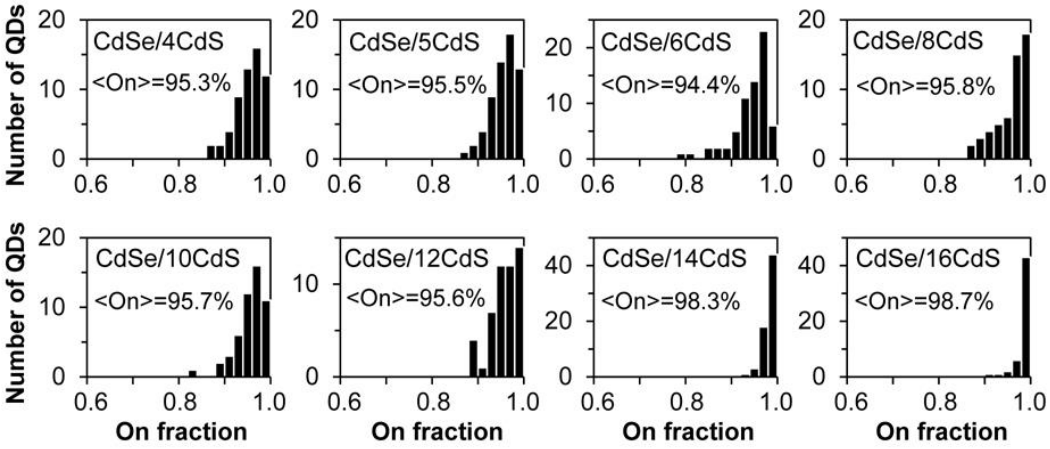

Figure S5. 'On' fraction statistics. Histogram of the blinking 'on' time fraction for CdSe/CdS core/shell QDs with different shell thicknesses.

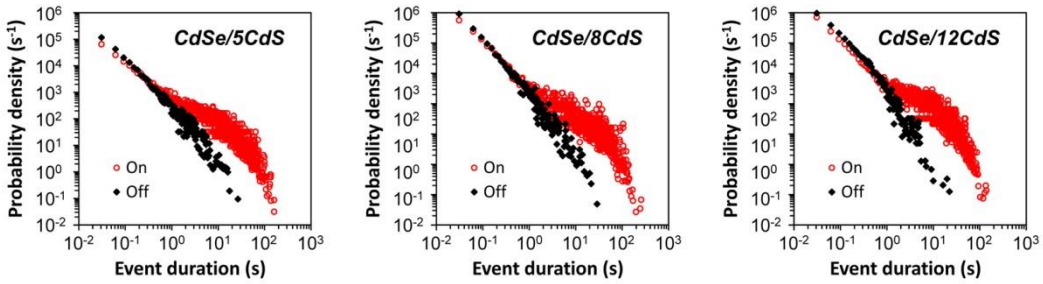

Figure S6. Probability densities of 'on' and 'off' times. Log-log plot of the probability densities of 'on' and 'off' times for QDs with 5, 8 and 12 monolayers of shell. In all plots, the 'on' and 'off' probability distributions are similar to those shown in Figure 8 but different from the conventional ones reported in literature (e.g. see Ref 4).

Movie 1: A 60 s microscope video of non-blinking CdSe/5CdS QDs. The QDs were excited by a 405 nm CW laser with a power density of 0.9 W/cm^2. The fluorescence images were recorded by an EMCCD with 30 ms exposure time per frame.

Movie 2: A 60 s microscope video of non-blinking CdSe/14CdS QDs. The QDs were excited by a 405 nm CW laser with a power density of 0.3 W/cm^2. The fluorescence images were recorded by an EMCCD with 30 ms exposure time per frame.

References:

(1) Park, Y. S.; Malko, A. V.; Vela, J.; Chen, Y.; Ghosh, Y.; Garcia-Santamaria, F.; Hollingsworth, J. A.; Klimov, V. I.; Htoon, H. *Phys. Rev. Lett.* **2011**, *106*, 187401.

(2) Greytak, A. B.; Allen, P. M.; Liu, W. H.; Zhao, J.; Young, E. R.; Popovic, Z.; Walker, B. J.; Nocera, D. G.; Bawendi, M. G. *Chem. Sci.* **2012**, *3*, 2028.

(3) Lakowicz, J. R. *Principles of Fluorescence Spectroscopy*; 3 ed.; Springer: Baltimore, 2006.

(4) Kuno, M.; Fromm, D. P.; Hamann, H. F.; Gallagher, A.; Nesbitt, D. J. *J. Chem. Phys.* **2001**, *115*, 1028.