Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Nearly Suppressed Photoluminescence Blinking of Small Sized, Blue-Green-Orange-Red Emitting Single CdSe Based Core/Gradient Alloy Shell/Shell Quantum Dots: Correlation between Truncation Time and Photoluminescence Quantum Yield

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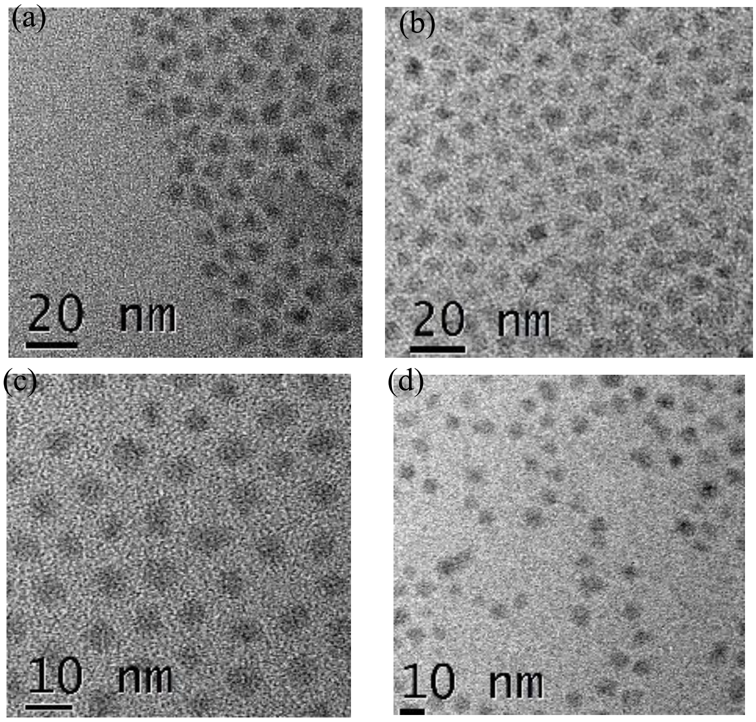
S1: Synthesis of CGASS QDs.

GASS QDs with chemical composition gradient were synthesized in a single pot following conventional 'Hot Injection' approach. The emission wavelength of the QDs were tuned by varying the initial precursor ratios. Aliquots were withdrawn from reaction mixture at different intervals of time to characterize the shell growth. In this one pot synthesis after very rapid initial nucleation of CdSe core, shells of wider band gap materials namely CdS, ZnSe and ZnS were grown over the core epitaxially in accordance of their reactivity. Synthesis of different color emitting QDs have been performed following literature procedure.[1-2] Details of the synthesis of individual CGASS QDs have been mentioned in details in a recent report by our group.[3]

S2: Transmission Electron Microscopy (TEM). The TEM images of the CGASS QDs were obtained using a JEOL JEM-2100 operating at an acceleration voltage of 200 kV. The QDs were deposited from dilute toluene solutions onto copper grids with carbon support by slowly evaporating the sample overnight in air at room temperature.



TEM images of the isolated QDs of different CGASS QDs; blue (a), green (b), orange (c), red (d)

S3: Experimental details for ensemble spectroscopic measurements.

Steady State Measurements.

Steady state absorption spectra have been recorded in CARY Bio 300 UV-Visible Spectrophotometer. Corrected PL emission and excitation spectra have been recorded with Fluoromax-3, Horiba Jobin Yvon spectrofluorimeter. PLQY for all the samples have been calculated using the following equation,

$$Q = Q_{\mathrm{R}} \frac{OD_R}{OD} \frac{I}{I_R} \frac{n_R^2}{n^2}$$

where, Q, OD, I and n stands for quantum yield, optical density, integrated intensity, refractive index of solvents respectively. Subscript R refers to the reference.

S4: Experimental details for single particle experiments.

To quantitatively elucidate blinking microscopy techniques along with statistical analysis methods has been adopted. QDs were embedded in Poly (methyl methacrylate) (PMMA) matrix and spin coated on cleaned glass coverslip of 0.17 mm thickness. These single QDs have been probed using a home-build Total Internal Reflection Fluorescence (TIRF) microscope. Excitation of the QDs has been achieved through an oil-immersion objective (Zeiss, PlanApo, 100x, NA 1.46) using 405 nm laser (COHERENT CUBE). PL signal has been detected with an EMCCD camera (ANDOR iXON3) with 100 msec integration time and a suitable EM gain. We have investigated at least 100 single CGASS QDs for each set of QDs. Widely separated single spots ensures measurement from single particles. The total intensity from each single particle has been obtained choosing a suitable region of interest and intensity – time trace has been obtained from each single particle. Blinking behavior has been observed from each single QDs and analyzed using a home-build software written in MATLAB. Histogram of the intensity of each time trace yielded a well separated bimodal distribution of intensities. Hence it was quite convenient to put a well-defined threshold to separate high intensity PL signal from low intensity signals. The threshold has been assigned as five times the standard deviation above average low intensity signal. Anything above the threshold is considered to be ON and below threshold is considered to be OFF. Upon thresholding the PL intensity time trace is converted into a sequence of ON- and OFF-events of given time durations. Using this thresholding-histogramming technique a distribution of ON- and OFF-event durations have been generated. From this ON- and OFF-event duration distributions probability densities of these events as a function of its event duration (ON- and OFF- event) have been calculated. The probability of event durations has been weighted by the average time duration between the two nearest neighbor (one less and one more) event durations. The estimation of this kind of time weighted probability density distribution improves sampling statistics at longer event durations.[4]

S5: Literature comparison of ON-fraction, size and emission maximum

Literature	QD	Diameter (nm)	PL maxima (nm)	PL QY	Average ON-fraction	Synthesis Method
Nature Materials, 2008, 7, 659	CdSe/CdS	~ 13	620	~0.70	Non-blinking (68% of the QDs)	SILAR, multistep, multi-pot
J. Am. Chem. Soc., 2008, 130, 5026	CdSe/CdS	~ 15.5	638	-	>0.80 (40% of the QDs; >99.9 (20% of the QDs)	SILAR, multistep, multi-pot
Nature Materials, 2013, 12, 445	CdSe/CdS	~ 9.2	625	0.97	0.94	SILAR, multistep, multi-pot
J. Mater. Chem. C, 2014, 2, 3439	CdSe/CdS	~23.6	~670	-	Non-blinking	SILAR, multistep, multi-pot
Nano. Lett., 2014, 14, 396	CdSe/CdS, CdSeS	14	635 650	~0.50	>0.95	SILAR, multistep, multi-pot
J. Phys. Chem. B, 2014, 118, 14140	CdSe/CdZnSe/ZnSe	~10	~625	~0.50	0.92 >0.99 (25% of the QDs)	SILAR, multistep, multi-pot
J. Am. Chem. Soc., 2014, 136, 179	CdSe/CdS	5.8-14	>600	-	>0.95	SILAR, multistep, multi-pot
Nanoscale, 2016, 8, 14109	CdSe/CdS/ZnS	~9.6	~530	~0.80	0.78	SILAR, multistep, multi-pot
ACS Nano, 2016, 10, 4072	CdSe/CdS, CdSe/CdS/ZnS	~5.6 ~6.2 ~7.5	~585 ~600 ~615	~0.45 ~0.60 ~0.45	~0.20 ~0.20 ~0.50	SILAR, multistep, multi-pot
J. Phys. Chem. C, 2016, 120, 20547	CdSeS	~6.5	~630	~0.45	>0.70 (76% of the QDs)	One pot
J. Phys. Chem. C, 2016, 120, 5257	CdSe/ZnSe	~4.5 ~4.9	~530 ~555	~0.60	>0.90 (83% of the QDs) >0.90 (80% of the QDs)	One pot
Our result	CdSe/CdZnSeS/ZnS	6.86 6.19 5.74 6.76	510 532 591 619	0.47 0.59 0.96 0.71	0.75 (>0.70, 55% QD) 0.75 (>0.70, 45% QD) 0.80 (>0.70, 45% QD) 0.85 (>0.70, 70% QD)	One pot

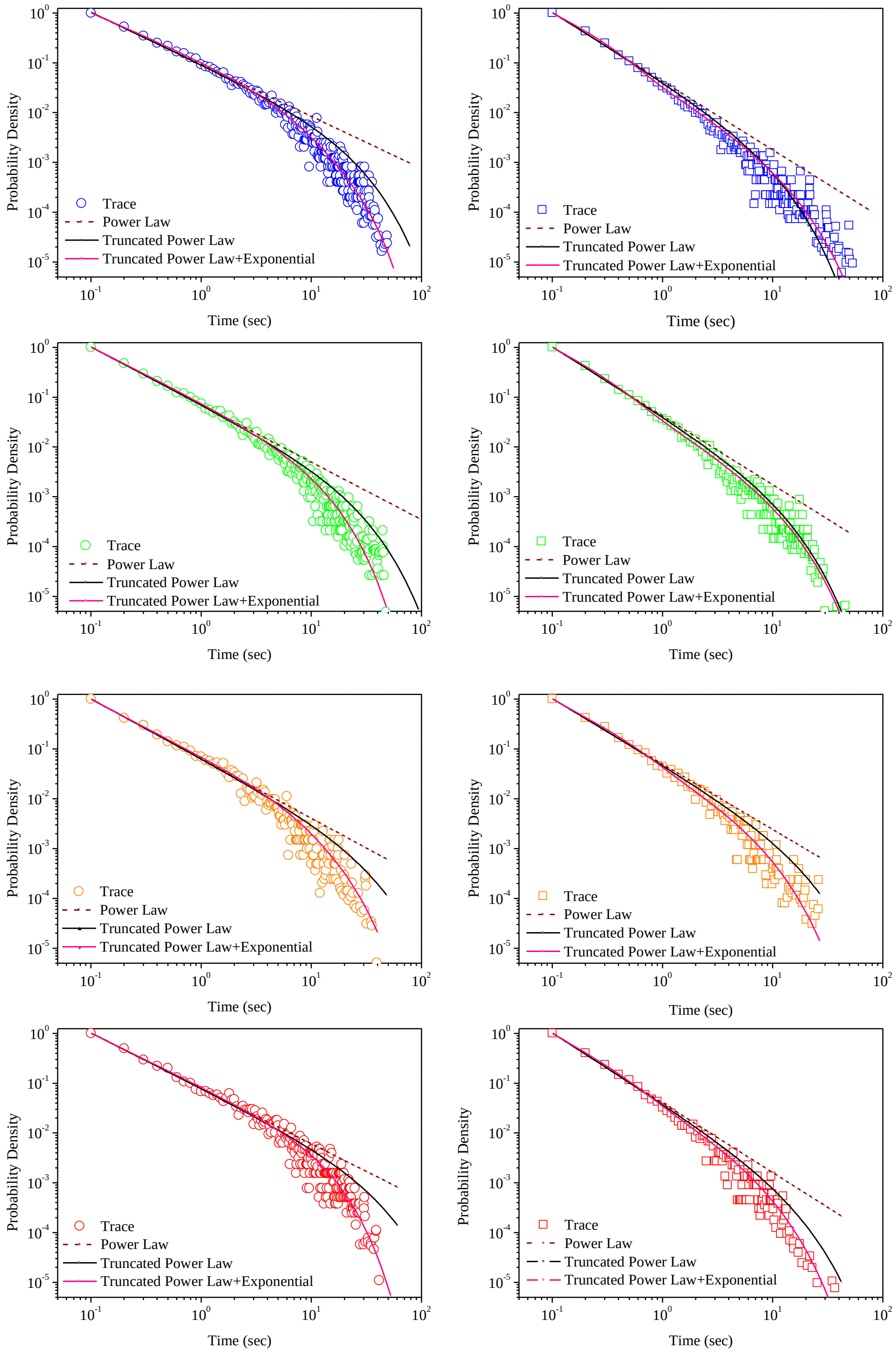
S6: Fitting comparison of probability density distribution of both ON- and OFF-event durations for all CGASS QDs.

The following three model equations have been used.

Inverse Power Law: $P_{event} = a.t_{event}{}^{-m}$

Inverse Truncated Power Law: $P_{event} = a.t_{event}{}^{-m}.e^{-k.t_{event}}$

Inverse Truncated Power law + Exponential: $P_{event} = a.t_{event}{}^{-m}.e^{-k.t_{event}} + b.e^{-j.t_{event}}$



The inverse truncated power law +exponential model equation yields the best fit.

S7: Complete table of best fitted parameters for all four differently emitting CGASS QDs.

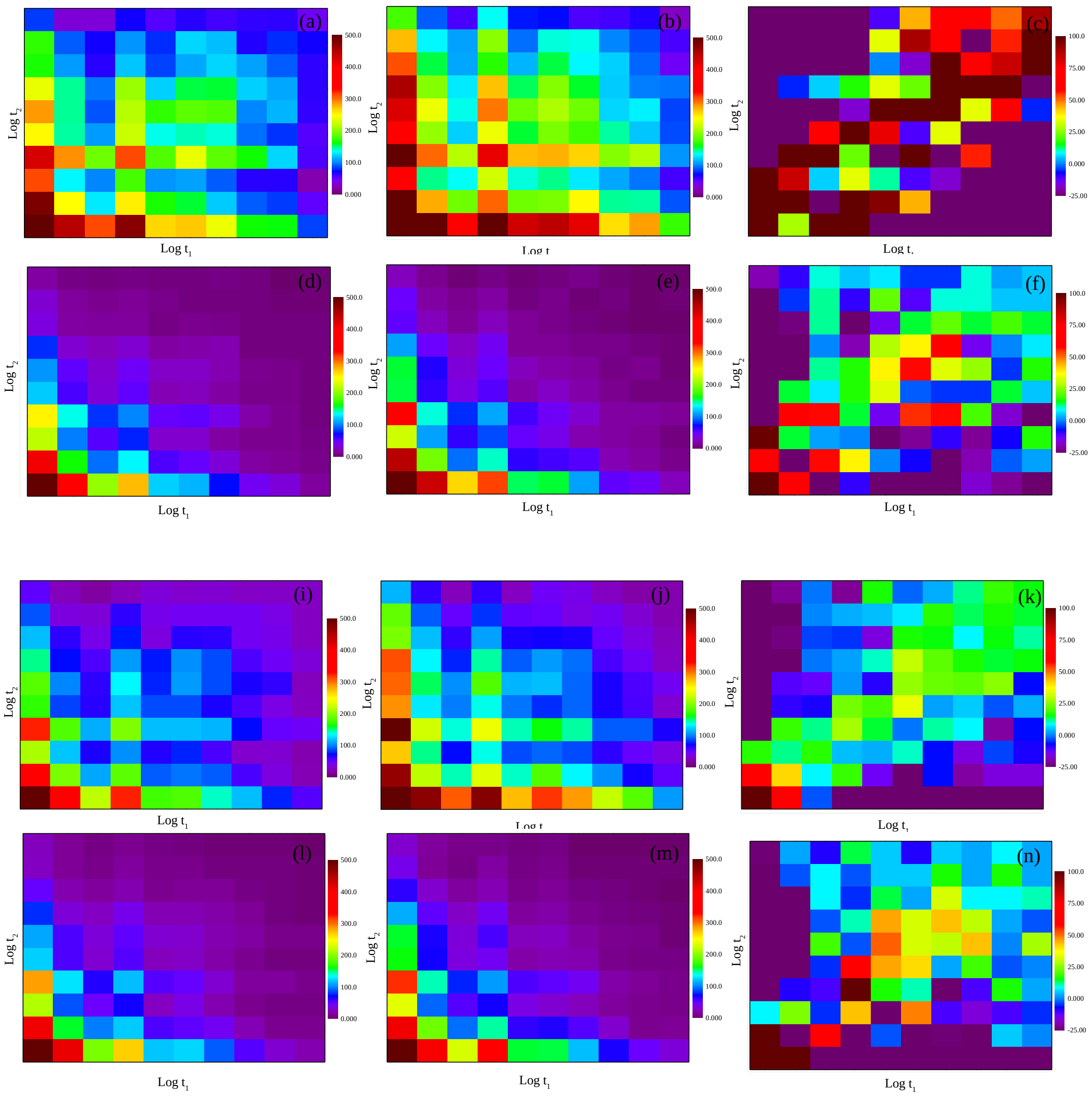
Sample	A_{rel}	m	k [sec^{-1}]	t_c (k^{-1}) [sec]	B	j [sec^{-1}]	t_D (j^{-1}) [sec]
Blue	94.37	0.95 ± 0.05	0.1956	5.11 ± 0.32	5.63	0.1125	8.89 ± 0.54
Green	95.25	1.09 ± 0.03	0.1588	6.30 ± 0.37	4.75	0.1343	7.45 ± 0.41
Red	95.95	1.07 ± 0.03	0.1097	9.12 ± 0.64	4.05	0.1534	6.52 ± 0.29
Orange	97.84	1.16 ± 0.02	0.0967	10.34 ± 0.64	2.16	0.4191	2.39 ± 0.53

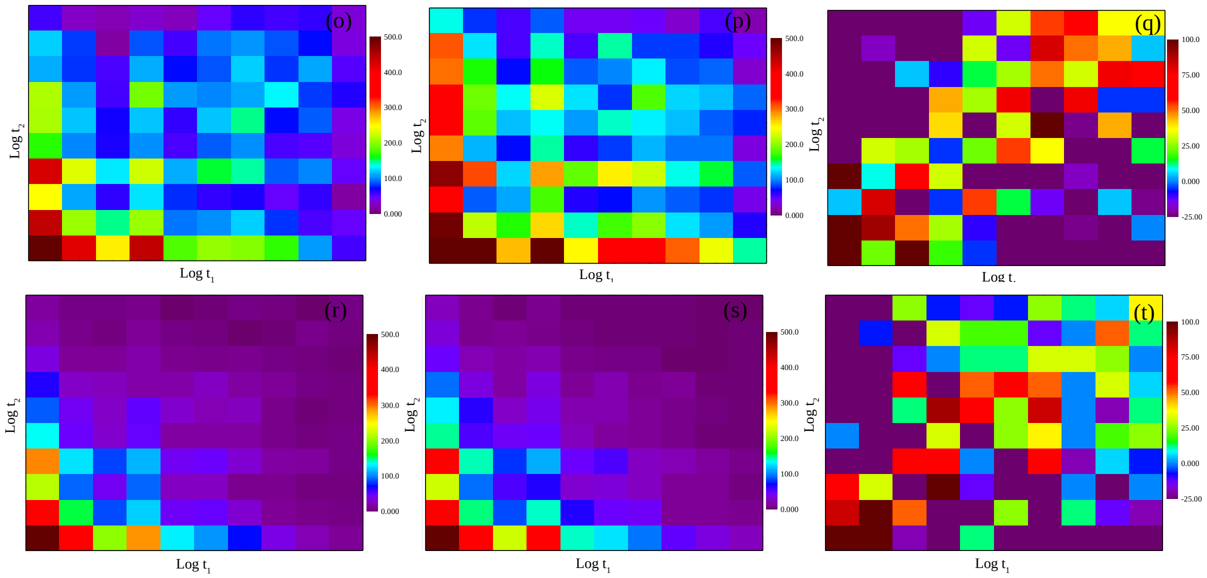
ON-event durations

OFF-event durations

Sample	A_{rel}	m	k [sec^{-1}]	t_c (k^{-1}) [sec]	B_{rel}	j [sec^{-1}]	t_D (j^{-1}) [sec]
Blue	85.32	1.38 ± 0.01	0.0828	12.08 ± 0.71	14.68	5.4362	0.1840 ± 0.005
Green	87.86	1.38 ± 0.01	0.0935	10.70 ± 0.65	12.14	5.3255	0.1878 ± 0.011
Red	89.05	1.38 ± 0.01	0.1297	7.71 ± 0.44	10.95	4.6713	0.2141 ± 0.006
Orange	88.75	1.31 ± 0.03	0.1408	7.10 ± 0.43	11.25	3.5971	0.2780 ± 0.008

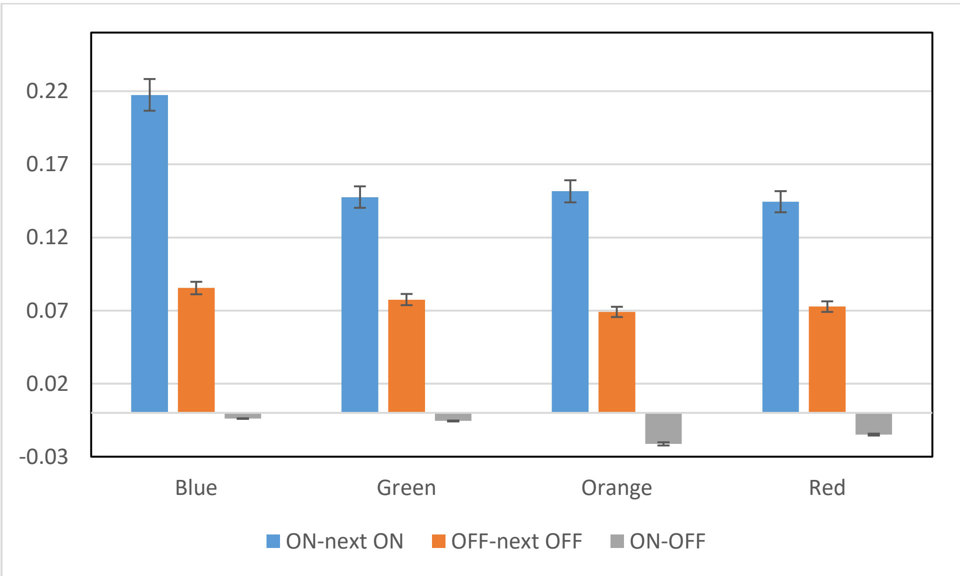
S8: 2D joint probability distribution analysis for blue, green and red emitting CGASS QDs respectively.





Visualization of the correlations between two successive ON- and OFF-event durations. Two-dimensional joint probability distributions for two adjacent ON-event durations (a) blue, (i) green, (o) red. [for two adjacent OFF-event durations (d) blue, (l) green, (r) red.]. Two-dimensional joint probability distributions for two ON-event at a larger separation (fifty intervals) (b) blue, (j) green, (p) red. [for two OFF-event at a larger separation (fifty intervals) (e) blue, (m) green, (s) red.]. Two-dimensional difference histogram for ON-event durations (c) blue, (k) green, (q) red. [for OFF-event durations (f) blue, (n) green, (t) red.].

S9: Pearson's linear correlation coefficient for subsequent event durations (ON-ON, OFF-OFF, ON-OFF).



For all four differently emitting CGASS QDs Pearson's linear correlation coefficient has been calculated for adjacent event durations (R)

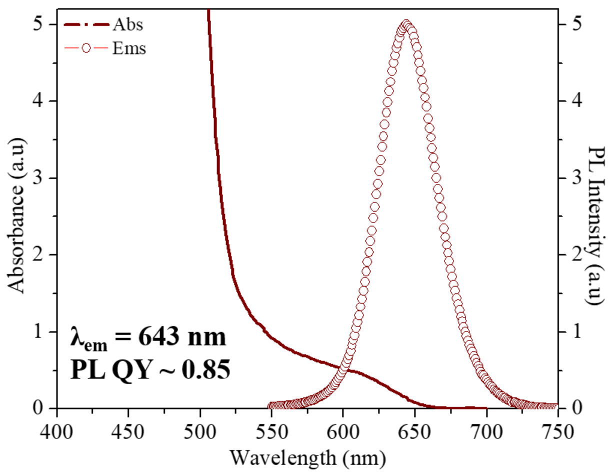
S10: Synthesis of CdSe/CdS CS QDs.

Synthesis of CdSe/CdS core/shell QDs

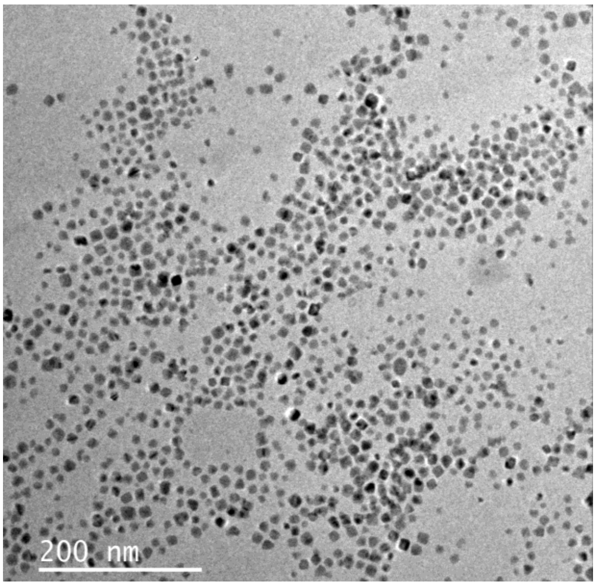
Synthesis of CdSe core- Standard hot-injection technique has been followed.[5] To synthesize CdSe we have taken Cd:Se = 1:2.5 precursor ratio. Cd precursor solution is prepared by mixing 0.1 mmol of CdO, 1 G TOPO and 0.2 mmol OA and heated to 320 ℃ under N2 flow to form an optically clear solution. This solution is then cooled down to 280 ℃ and Se precursor solution has been injected to this solution. Se precursor solution has been prepared by adding 0.25 mmol of Se in 1 mL TOP. After the injection, the nanocrystals are allowed to grow for 1 min and MeOH has been injected to stop the growth. The reaction mixture is then centrifuged and decanted to obtain the precipitate of QD. The QDs are dispersed in toluene for further processing. CdSe QDs with first absorption peak ~ 574 nm has been obtained.

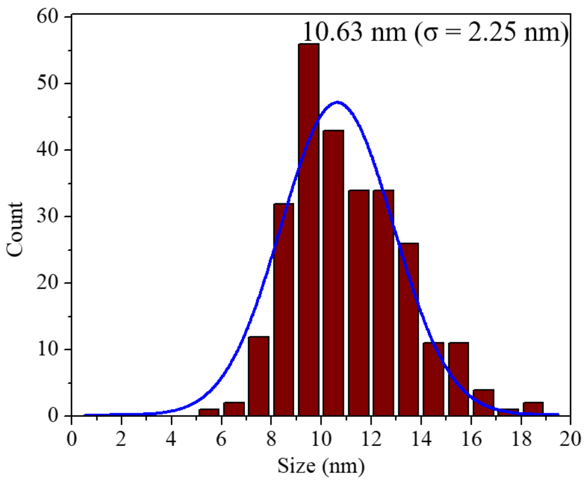
Shelling over the core - The growth of core/shell nanocrystals has been achieved using the SILAR technique[5], which is based on alternating injections of the Cd- and S-precursors into the solution containing the CdSe-core QDs. For shelling 0.1 M Cd- and S- precursor solutions are used. As synthesized CdSe core has been taken in 3mL ODE and heated up to 250 ℃. To this solution calculated amount of Cd- and S-precursors have been added alternatively. 10 min gap between each addition is maintained. The reaction is stopped after 3 hr by adding MeOH. QDs have been purified by solvent extraction technique. For CS QDs first absorption peak ~ 600 nm has been obtained.

S11: Absorption and emission spectrum for CS QD.

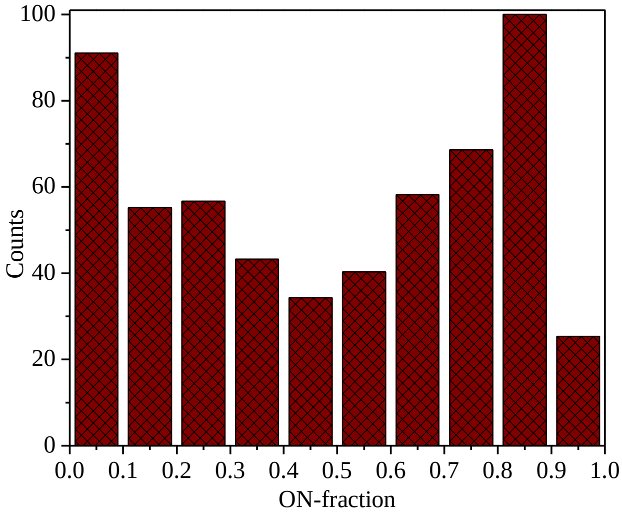


S12: TEM image and size distribution of CS QDs.

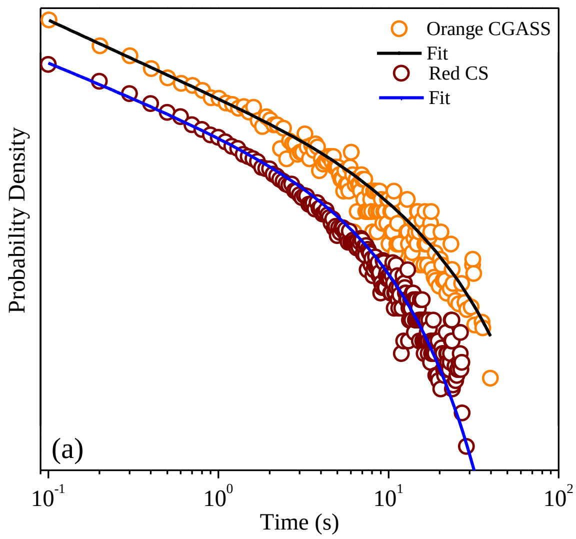


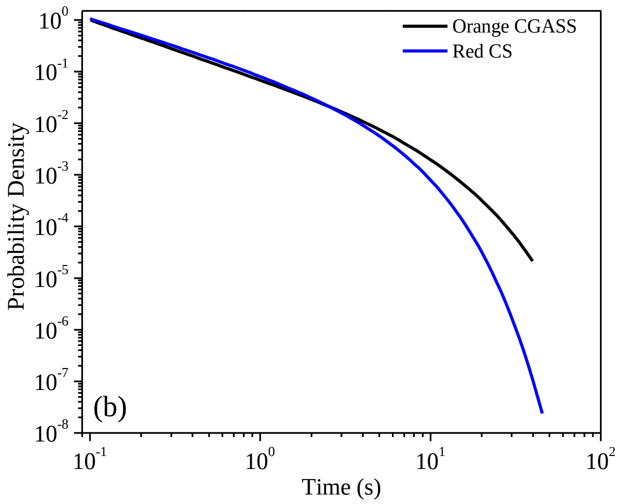


S13: ON-fraction of CS QDs.

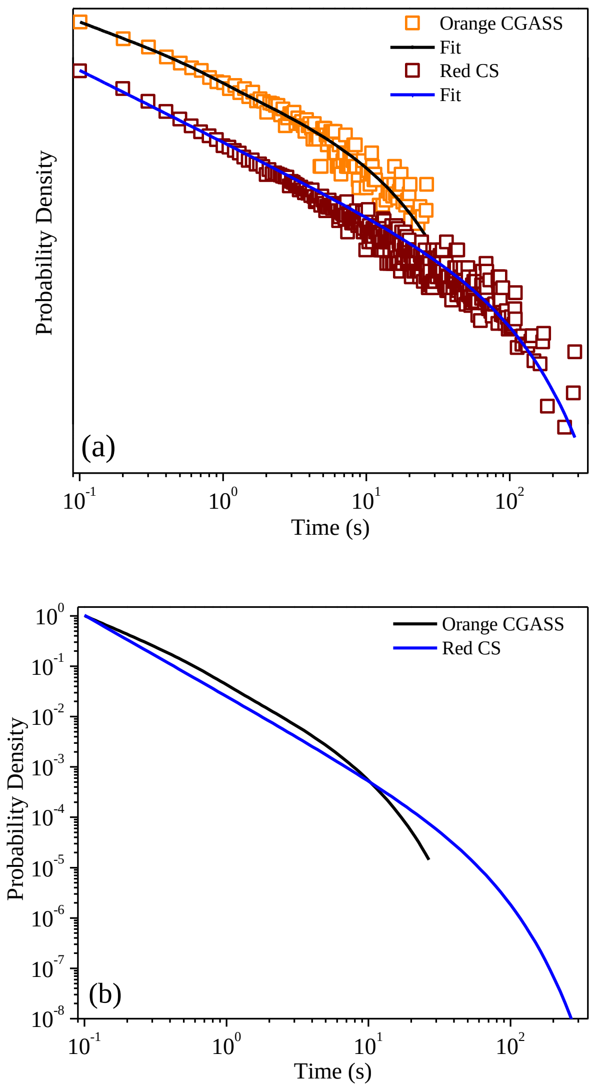


S14: Comparison of probability density distribution for ON-event durations for orange CGASS and CS QDs (a) decay traces (Plots have been shifted in Y-axis for better visual appearance), (b) fitted lines.





S15: Comparison of probability density distribution for OFF-event durations for orange CGASS and CS QDs (a) decay traces (Plots have been shifted in Y-axis for better visual appearance), (b) fitted lines.



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