Supporting information

Controlling charge separation and recombination rates in CdSe/ZnS type I core-shell quantum dots by shell thicknesses

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S1. size distribution histogram

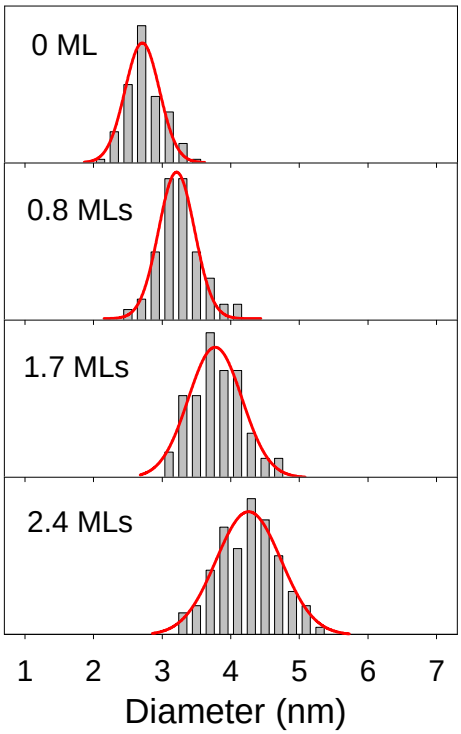

Figure S1. Size histograms (grey bars) for CdSe with 0, 0.8, 1.7 and 2.4 MLs of ZnS shells determined from TEM images. Each sample contains over 100 particles. These distributions are fit by Gaussian functions (red lines) with center and full-width-at-half-maximum of 2.71 (0.59), 3.21 (0.60), 3.77 (0.91), and 4.26 (1.10) nm for QDs with 0, 0.8, 1.7 and 2.4 MLs of ZnS shells, respectively.

S2. Femtosecond TA spectra of free QDs

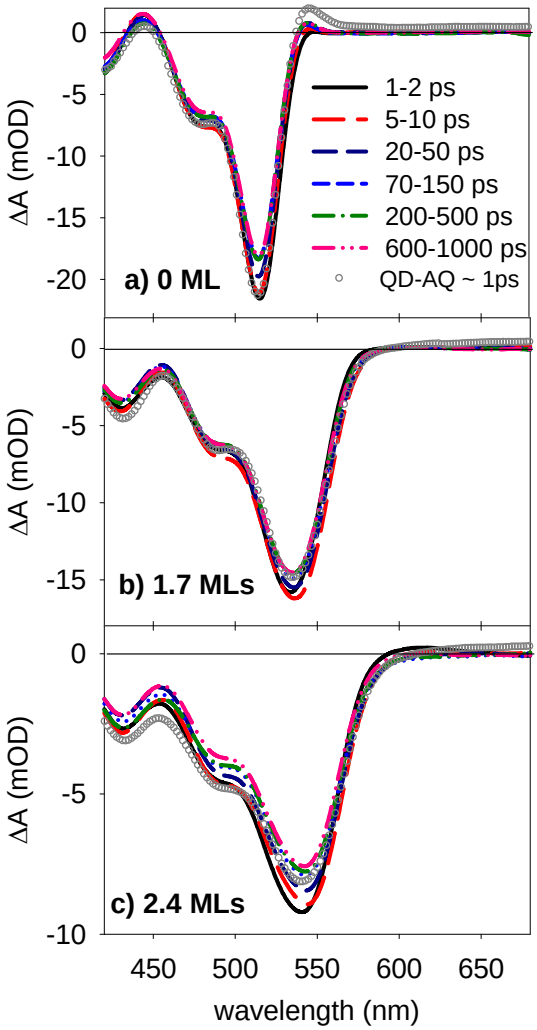

Figure S2. Average visible TA spectra of free CdSe/ZnS QDs (lines) with (a) 0, (b) 1.7, and (c) 2.4 MLs of ZnS shells at indicated delay time windows after 400 nm excitation. Also shown are TA spectra of correspond QD-AQ complexes at ~ 1ps (open circles).

S3. TA spectra of QD-AQ complexes

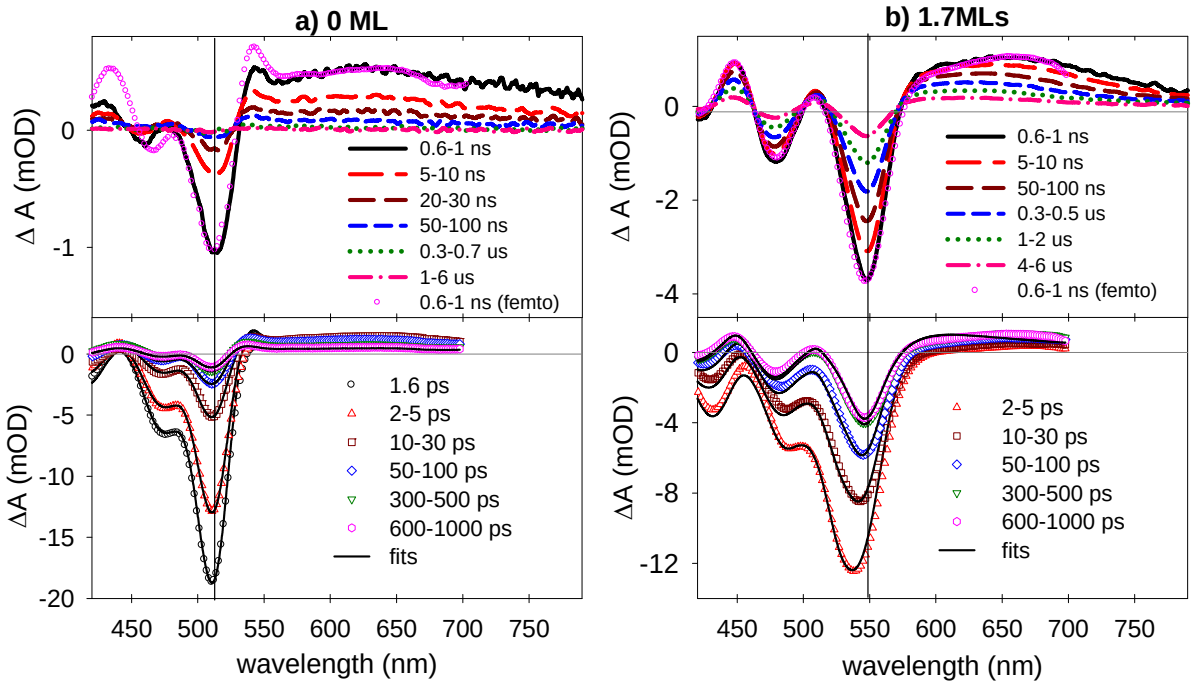

Figure S3. Averaged visible TA spectra of QD-AQ complexes with (a) 0 ML and (b) 1.7 MLs of ZnS shells at indicated delay time windows (0 - 1 ns: lower panels, 0.5 ns -6 μs: upper panels) after 400 nm excitation. The vertical scale in upper panels has been expanded to more clearly show the anion features. Solid lines in the lower panel are fits to the data (symbols) according to equation (3) in the text. The TA spectrum at 600-1000 ps (pink circles) from the lower panel has been reproduced in the upper panel to show the agreement between the TA spectra recorded using femtosecond and nanosecond spectrometers.

S4. Comparison of kinetics of excited state decay and charge separated state formation

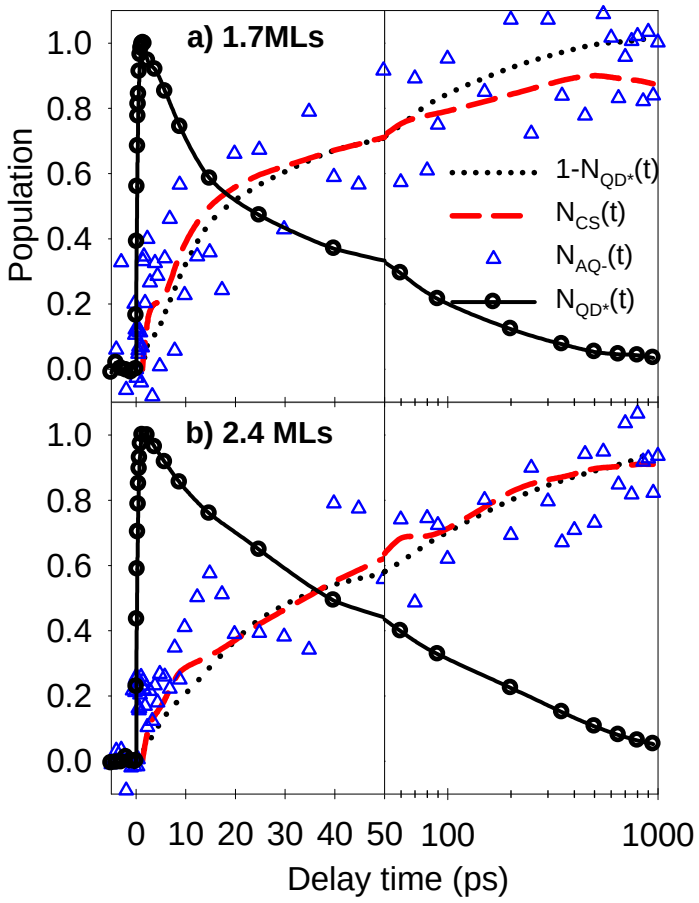

Figure S4. Comparison of kinetics of excited state decay ($N_{QD*}(t)$, open black circles) and charge separated state ($N_{CS}(t)$, red lines) and anion ($N_{AQ}-(t)$, open blue triangles) formation for QD-AQ complexes with a) 1.7 and (b) 2.4 MLs of ZnS shells. $N_{QD*}(t)$ and $N_{CS}(t)$ are obtained from fitting the transient data according equation (3). $N_{AQ}-(t)$ is the transient signal at 640-660 nm. Also shown as the dotted lines is (1- $N_{QD*}(t)$. Both $N_{CS}(t)$ and $N_{AQ}-(t)$ have been scaled such that their rises agree with (1- $N_{QD*}(t)$).

S5. Calculated and measured 1S exciton peak position

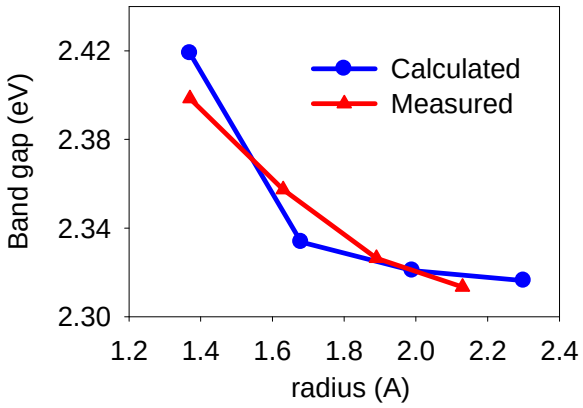

Figure S5. Calculated and measured 1S exciton peak position in CdSe/ZnS QDs as a function of the ZnS shell thickness. The measured absorption spectra are shown in Figure 2. The calculation is described in the main text.

S6. Average charge separation and recombination rates determined by different approaches.

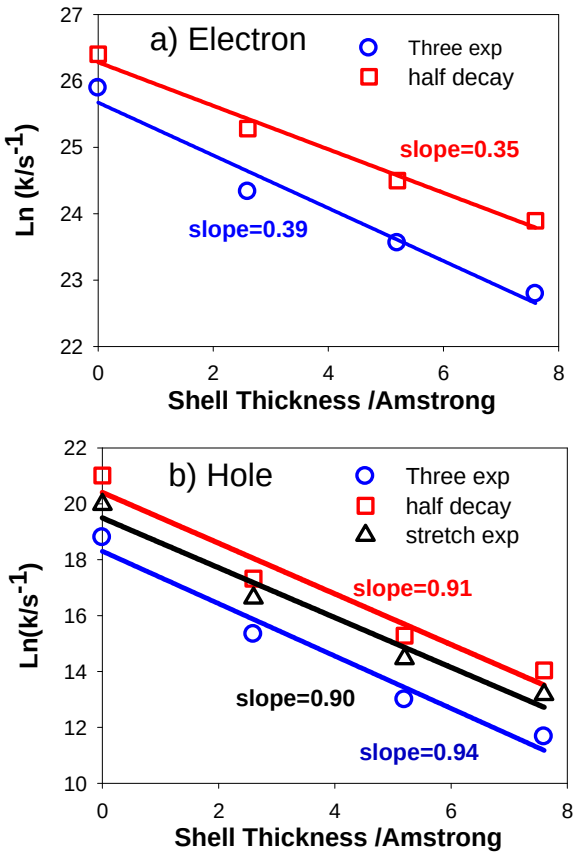

Figure S6. Comparison of the shell thickness dependences of a) charge separation and b) recombination rates calculated by different methods. The slopes for charge separation rates determined from amplitude weighted averaged time constant and half lifetime are β=0.39 and 0.35, respectively. The slopes for charge recombination rates determined from amplitude weighted averaged time constant, half lifetime, and stretched exponential time constants are β=0.94, 0.91 and 0.90, respectively.

S7. Fitting parameters for the 1S exciton bleach formation and recovery kinetics in free CdSe/ZnS QDs.

Table S1 Fitting parameters for the QD* decay kinetics in free QD samples

ZnS thickness	$k_{0,}$ ps^{-1}	$k_{1,}$ ns^{-1} (A1, %)	$k_{2,}$ ns^{-1} (A2, %)	$k_{3,}$ ns^{-1} (A3, %)	$K_{4,}$ ns^{-1} (A4, %)
0 ML	2.97	58.0 (13)	0.26 (19)	0.04 (47)	0.008 (21)
0.8 ML		38.8 (7)	0.25 (18)	0.04 (55)	0.008 (20)
1.7 MLs		50.7 (8)	0.20 (8)	0.06 (61)	0.015 (23)
2.4 MLs		40.6 (14)	0.27 (11)	0.06 (54)	0.018 (21)

S8. Fitting parameter for charge separation kinetics

Table S2: Fitting parameters for the QD* decay kinetics in QD-AQ complexes according to equation (4)

ZnS thickness	$k_{0,}$ ps^{-1}	$k_{cs,1,}$ ps^{-1} (A1, %)	$k_{cs,2,}$ ps^{-1} (A2, %)	$k_{cs,3,}$ ps^{-1} (A3, %)	Half life (ps)
0 ML	2.97	0.71 (67)	0.084 (32)	0.01 (1)	3.4
0.8 ML		0.15 (67)	0.018 (32)	0.002 (1)	10.5
1.7 MLs		0.069 (67)	0.0081 (32)	0.001 (1)	23.6
2.4 MLs		0.032 (67)	0.0038 (32)	$4.5*10^{-4}$ (1)	45

S9. Fitting parameter for charge recombination kinetics

Table S3: Fitting parameters for the anion decay kinetics of QD-AQ samples according to equation (5)*

ZnS thickness	τ_R*, ns^{-1}	α*	Half-life (ns)
0 ML	2.2	0.38	0.75
0.8 ML	63	0.35	30
1.7 MLs	523	0.30	230
2.4 MLs	1788	0.31	800

*τ_R and α are the characteristic times and exponents of stretched exponential fits.