Electronic Supplementary Information

Photoinduced Electron Transfer from Quantum Dots to TiO_2: Elucidating the Involvement of Excitonic and Surface States

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Appendix S1. Preparation of Samples

The concentration of core-only CdSe QDs was equal in all mixed dispersions. The absorbance of the stock dispersion of CdSe QDs in 1:1 toluene/ethanol (by volume) at the first excitonic absorption maximum (500 nm) was approximately 0.15. Concentrations of the stock solution of MPA and the stock dispersions of metal oxides (in formula units) in 1:1 toluene/ethanol (by volume) were 1.5 mM and 33 mM, respectively. The mixed dispersions were prepared as follows:

Table S1. Compositions of mixed dispersions containing core-only CdSe QDs for spectroscopic analysis.

Sample (core-only CdSe QDs)	Volume of stock QD dispersion (mL)	Volume of stock MPA solution (mL)	Volume of stock MO_2 dispersion (mL)	Volume of solvent (1:1 toluene/EtOH) (mL)	Total volume (mL)
QD alone	10	0	0	5	15
QD/ZrO_2	10	0	3	2	15
QD/TiO_2	10	0	3	2	15
QD/MPA	10	1	0	4	15
QD-MPA-ZrO_2	10	1	3	1	15
QD-MPA-TiO_2	10	1	3	1	15

For mixed dispersions containing core/shell CdSe/ZnS QDs, the absorbance of the stock dispersion of QDs at the first excitonic maximum (500 nm) was approximately 0.05. Concentrations of the stock solution of MPA and the stock dispersions of metal oxides (in formula units) in 1:1 toluene/ethanol (by volume) were 1.5 mM and 33 mM, respectively. The mixed dispersions were prepared as follows:

Table S2. Compositions of mixed dispersions containing core/shell CdSe/ZnS QDs for spectroscopic analysis.

Sample (core/shell CdSe/ZnS QDs)	Volume of stock QD dispersion (mL)	Volume of stock MPA solution (mL)	Volume of stock MO_2 dispersion (mL)	Volume of solvent (1:1 toluene/EtOH) (mL)	Total volume (mL)
QD alone	20	0	0	10	30
QD/ZrO_2	20	0	6	4	30
QD/TiO_2	20	0	6	4	30
QD/MPA	20	4	0	6	30
QD-MPA-ZrO_2	20	4	6	0	30
QD-MPA-TiO_2	20	4	6	0	30

Appendix S2. Derivation of Equations 3 and 4 for Calculating Rate Constants of ET (k_{ET}) and Efficiencies of ET (η_{et})

Excited states of core-only CdSe QDs or core/shell CdSe/ZnS QDs within QD-MPA-ZrO_2 assemblies can decay radiatively or non-radiatively, as ET is not feasible. If the decay is mono-exponential then

$$< \tau >_{QD-MPA-ZrO2} = \frac{1}{k_r + k_{nr}} \quad \text{(S1)}$$

where k_r and k_{nr} are rate constants of radiative and non-radiative relaxation, respectively. For QD-MPA-TiO_2 assemblies, in addition to the radiative and non-radiative deactivation pathways, ET is also feasible due to favorable interfacial band energetics. Therefore,

$$< \tau >_{QD-MPA-TiO2} = \frac{1}{k_r + k_{nr} + k_{et}} \quad \text{(S2)}$$

An expression for k_{et} is derived by inverting equations 1 and 2 and taking the difference:

$$k_{et} = \left(\frac{1}{<\tau>_{QD-MPA-TiO2}} - \frac{1}{<\tau>_{QD-MPA-ZrO2}}\right) \quad \text{(3)}$$

The efficiency of electron transfer equals number of electrons transferred to TiO_2 (N_{et}) divided by the total number of initial photoexcited QDs (N_{total}):

$$\eta_{et} = \frac{N_{et}}{N_{total}} \times 100 \quad \text{(S4)}$$

The ratio of N_{et} to N_{total} equals the ratio of k_{et} to the sum of all rate constants of excited-state deactivation (k_{total}):

$$\frac{N_{et}}{N_{total}} = \frac{k_{et}}{k_{total}} = \frac{k_{et}}{k_r + k_{nr} + k_{et}} \quad \text{(S5)}$$

Using equations S2, 3, and S5, equation S4 can be rewritten as

$$\eta_{et} = \left(\frac{1}{<\tau>_{QD-MPA-TiO2}} - \frac{1}{<\tau>_{QD-MPA-ZrO2}}\right) \times < \tau >_{QD-MPA-TiO2} \times 100 \quad \text{(S6)}$$

Rearranging equation S6 yields

$$\eta_{inj} = \left(1 - \frac{<\tau>_{QD-MPA-TiO2}}{<\tau>_{QD-MPA-ZrO2}}\right) \times 100 \quad \text{(4)}$$

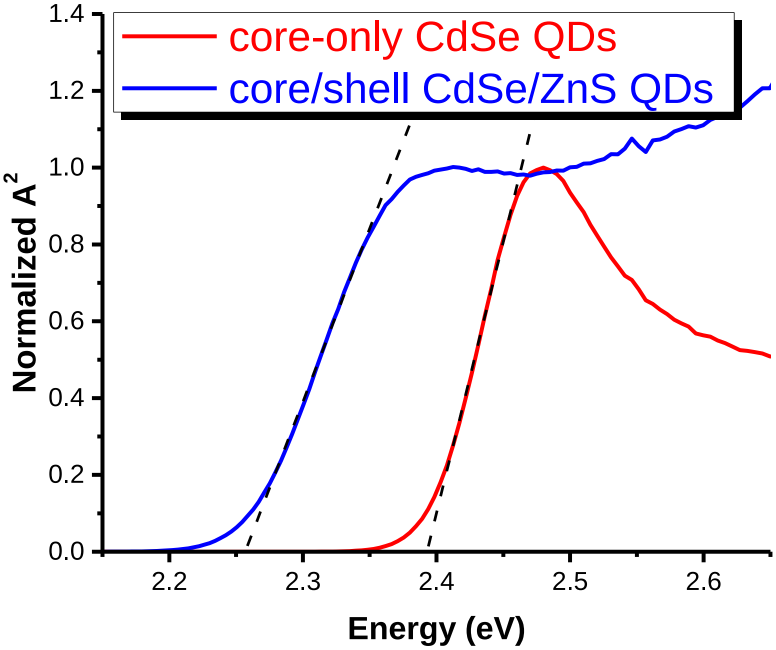
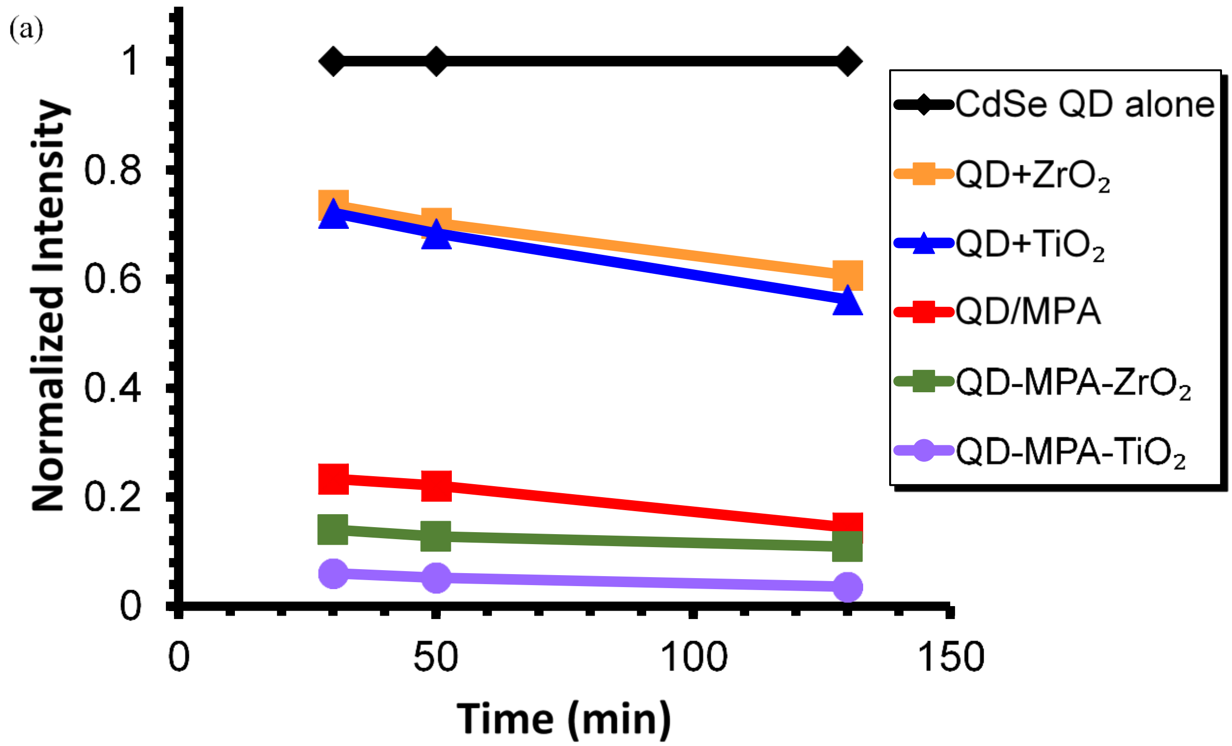
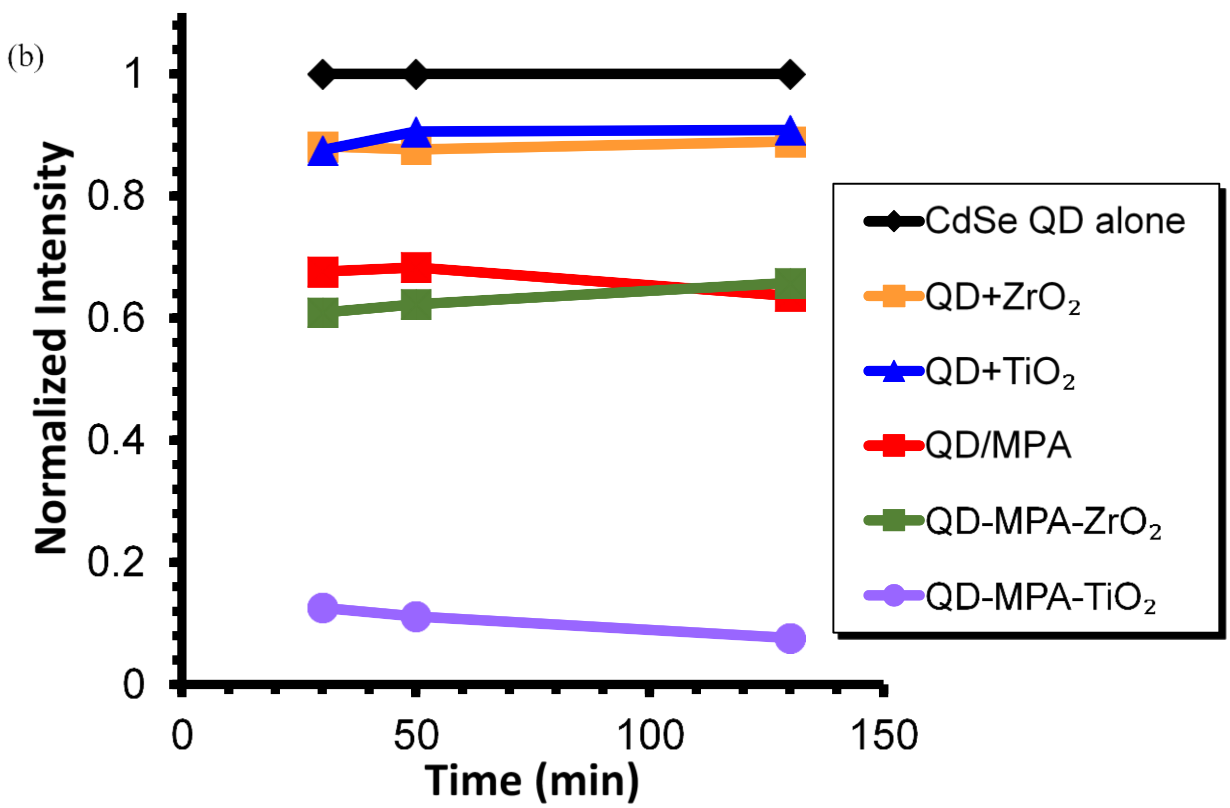


Fig. S1. Square of absorbance (normalized) as a function of energy for core-only CdSe QDs and core/shell CdSe/ZnS QDs. Superimposed on the data (dashed black lines) are linear fits to low-energy tails of first excitonic bands.


(a)
1
0.8
0.6
0.4
0.2
0
Normalized Intensity
0
50
100
150
Time (min)
CdSe QD alone
QD+ZrO2
QD+TiO2
QD/MPA
QD-MPA-ZrO2
QD-MPA-TiO2


(b)
1
0.8
0.6
0.4
0.2
0
Normalized Intensity
0
50
100
150
Time (min)
CdSe QD alone
QD+ZrO2
QD+TiO2
QD/MPA
QD-MPA-ZrO2
QD-MPA-TiO2

(c)

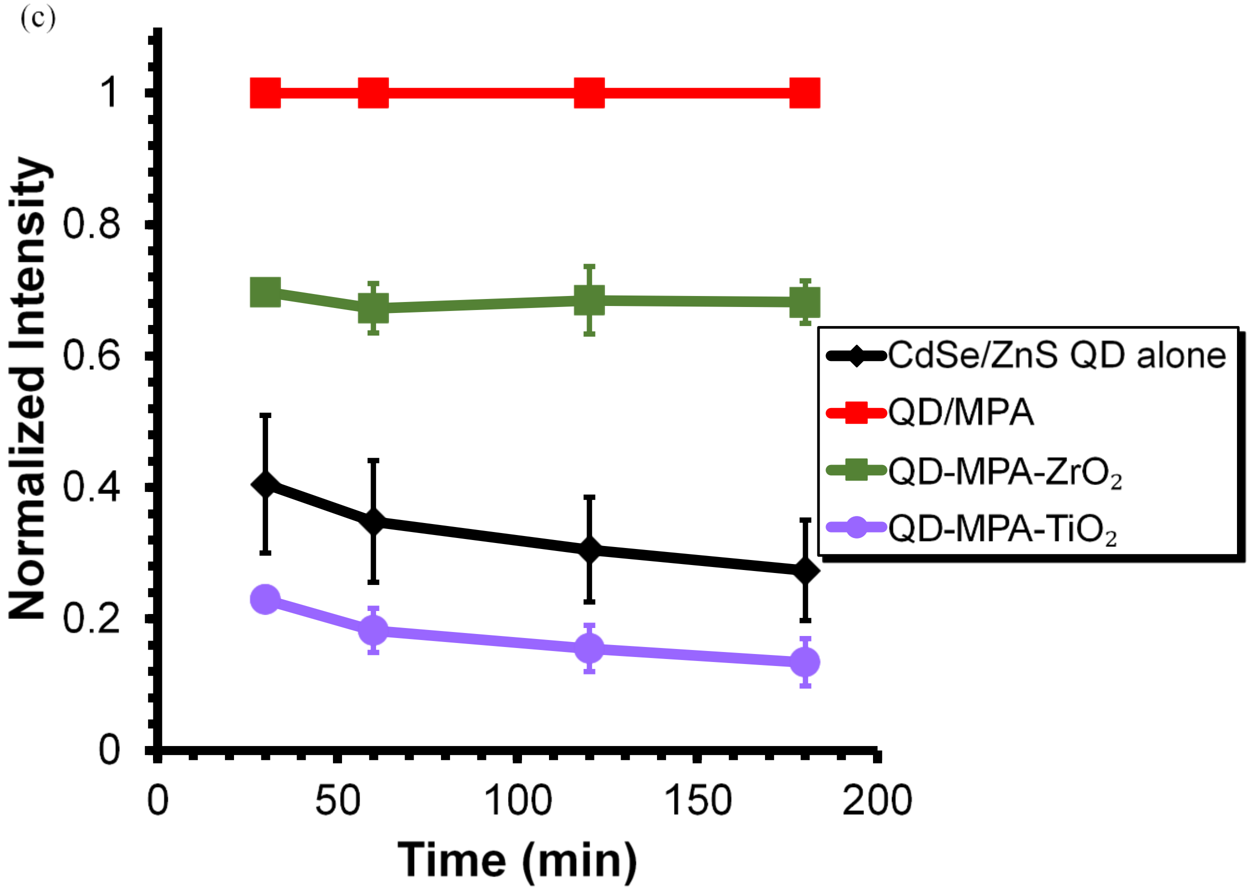
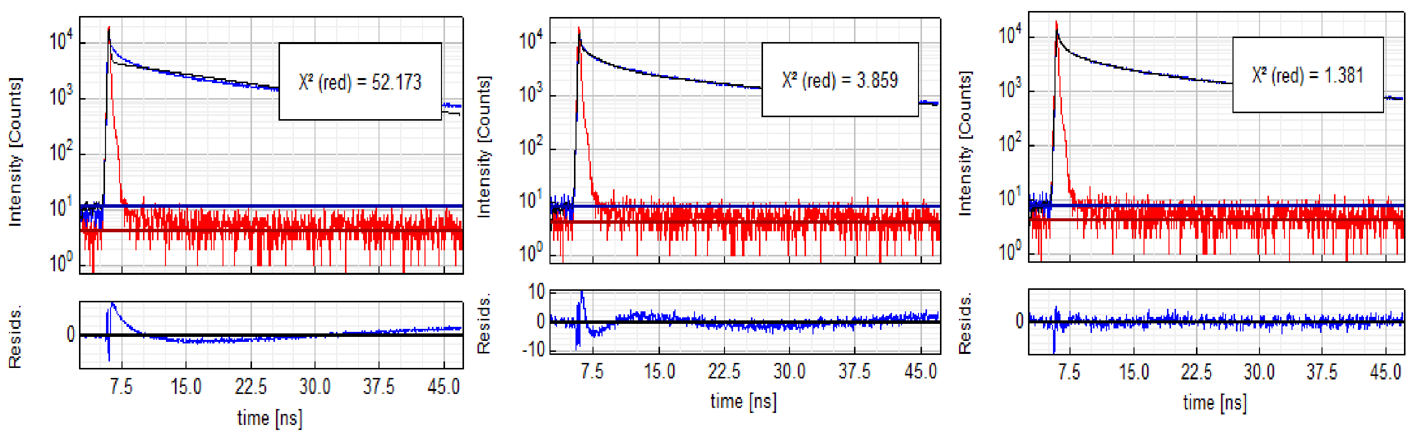


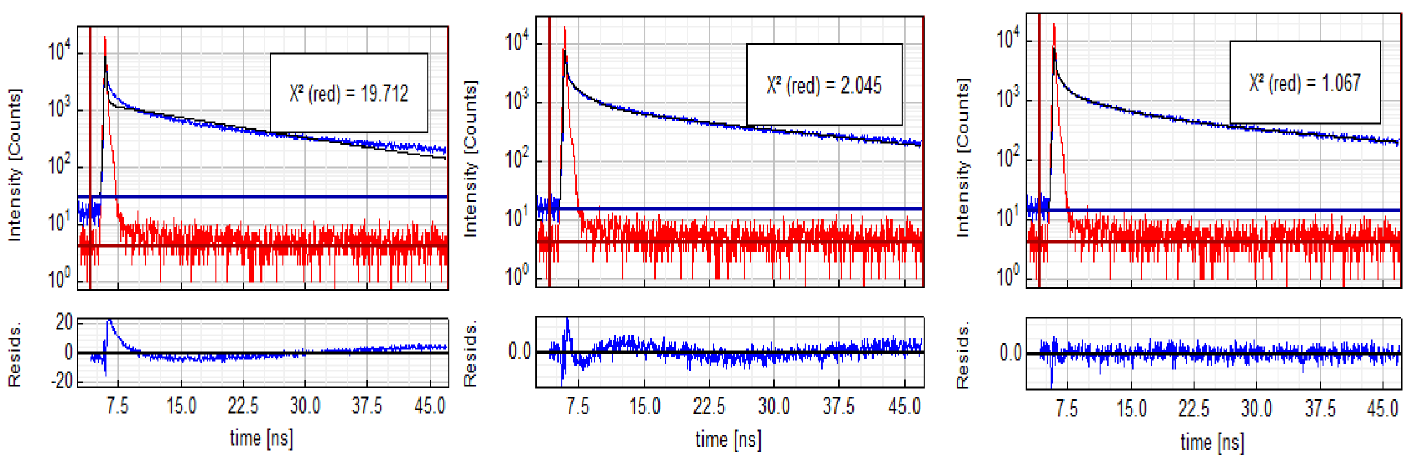
Fig. S2. Normalized emission intensity as a function of equilibration time for dispersions containing core-only CdSe QDs measured at the band-edge maximum of 515 nm (a) and the surface maximum of 750 nm (b) and for dispersions containing core/shell CdSe/ZnS QDs measured at the band-edge maximum of 540 nm (c). Graphs *a* and *b* contain representative data from one of three replicate measurements on such samples. Graph *c* contains averaged values from three measurements; error bars correspond to plus-or-minus one standard deviation relative to the average.

Fig. S3. Top graphs: TRPL decay traces (blue), IRF (red), and multiexponential reconvolution fits from eq. 1 (black) from representative measurements for each type of QD-containing dispersion at various wavelengths. Bottom graphs: corresponding residuals (data minus fit). Each set of graphs shows fits to monoexponential (left), biexponential (middle), and triexponential (right) functions. Corresponding chi-square values are in the insets.

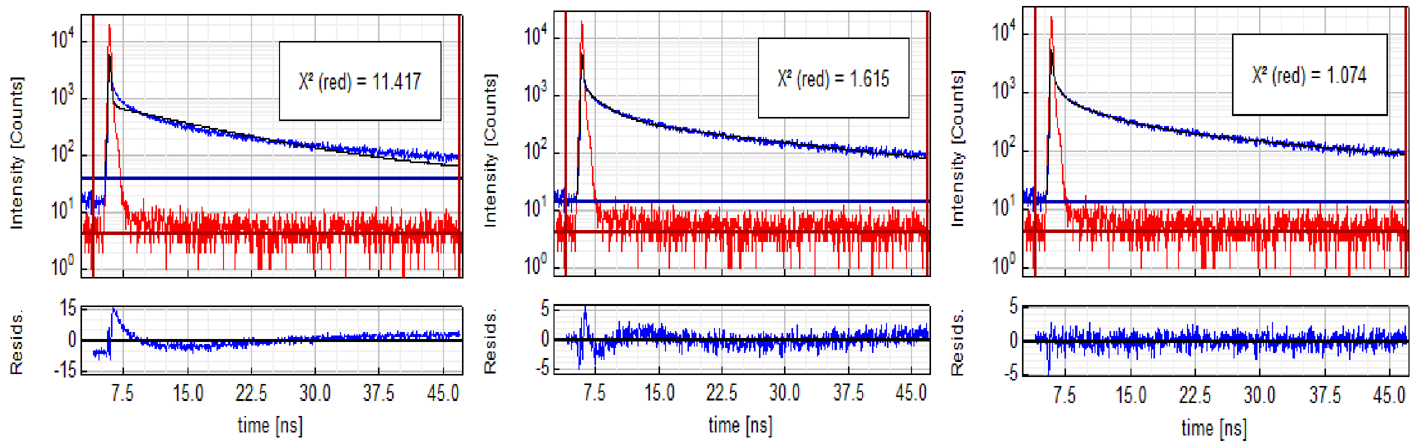
Core-only CdSe QDs alone (λ_{em} = 515 nm):



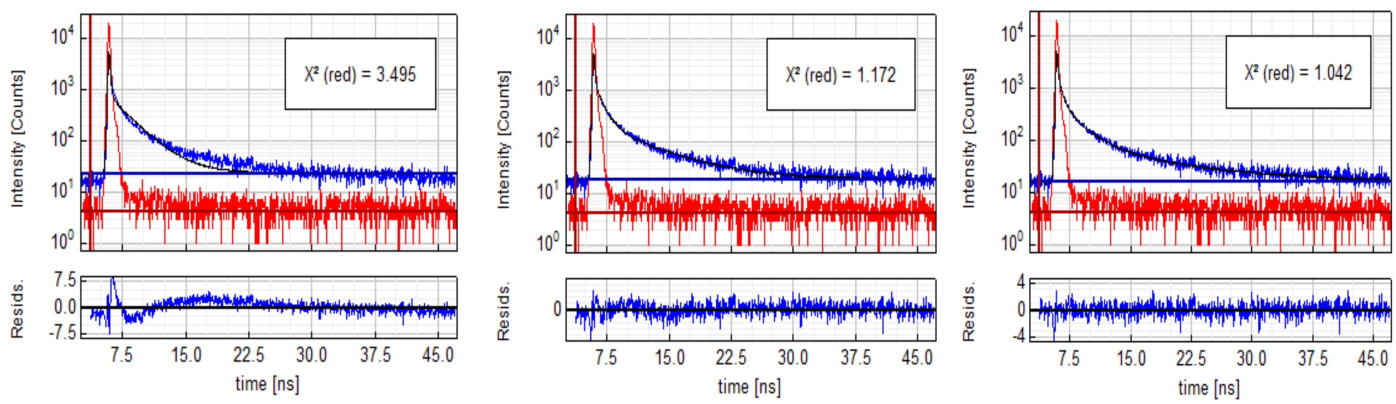
Core-only CdSe QD/MPA (λ_{em} = 515 nm):



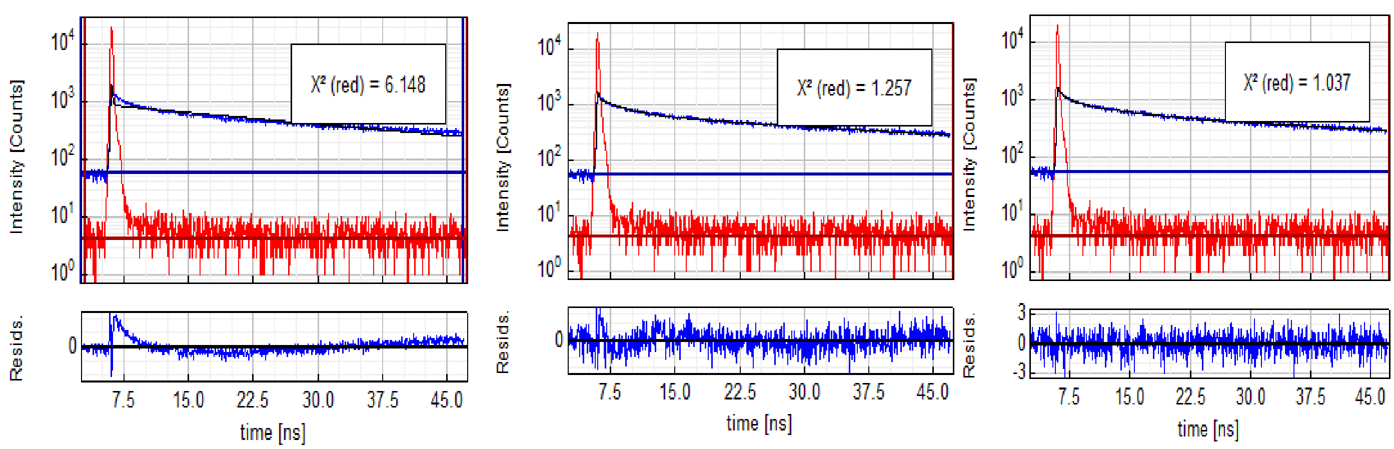
Core-only CdSe QD-MPA-ZrO_2 (λ_{em} = 515 nm):



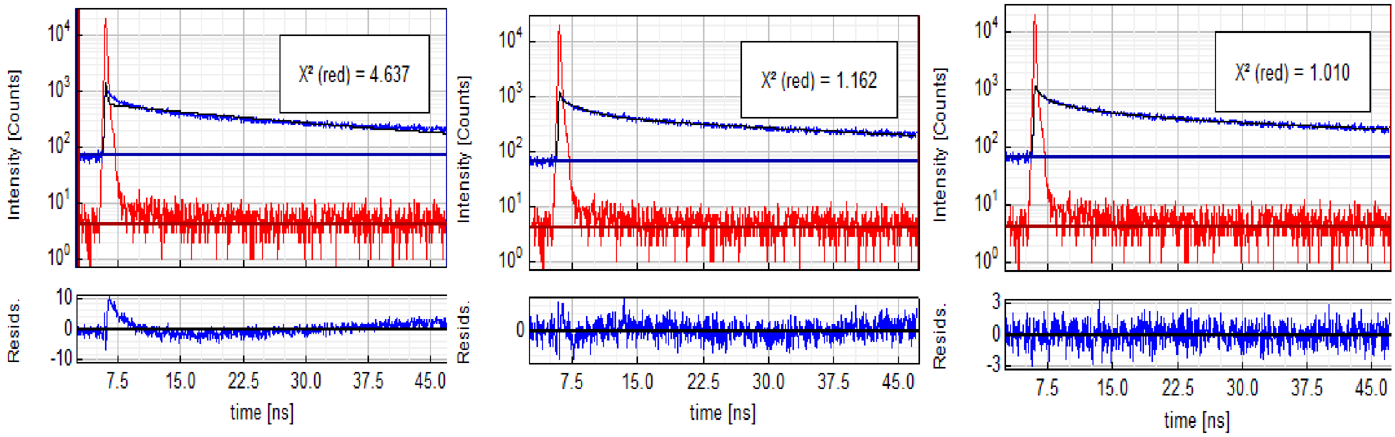
Core-only CdSe QD-MPA-TiO_2 (λ_{em} = 515 nm):



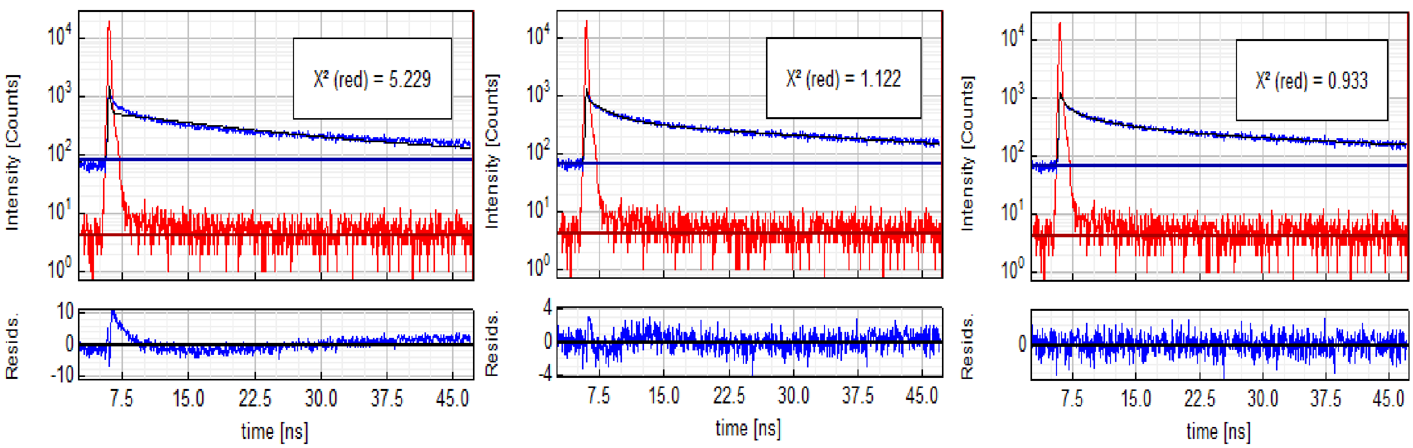
Core-only CdSe QDs alone (λ_{em} = 622 nm):



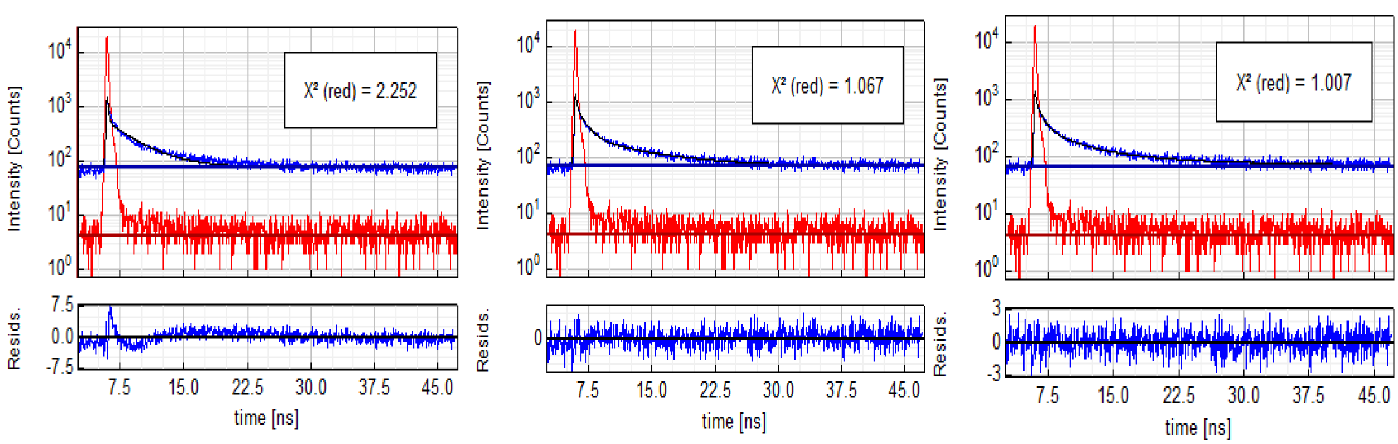
Core-only CdSe QD/MPA (λ_{em} = 622 nm):



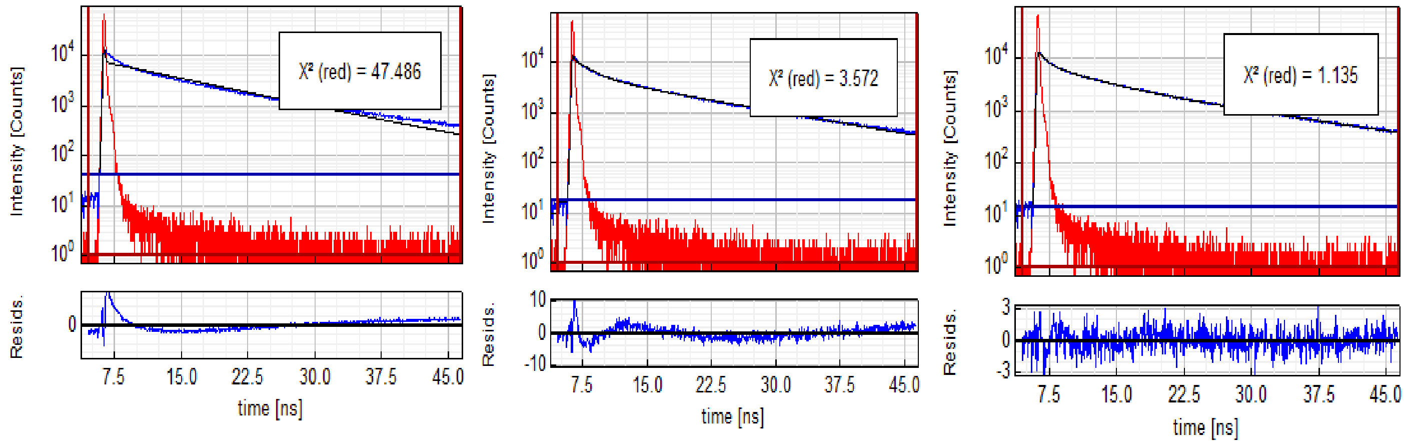
Core only CdSe QD-MPA-ZrO_2 (λ_{em} = 622 nm):



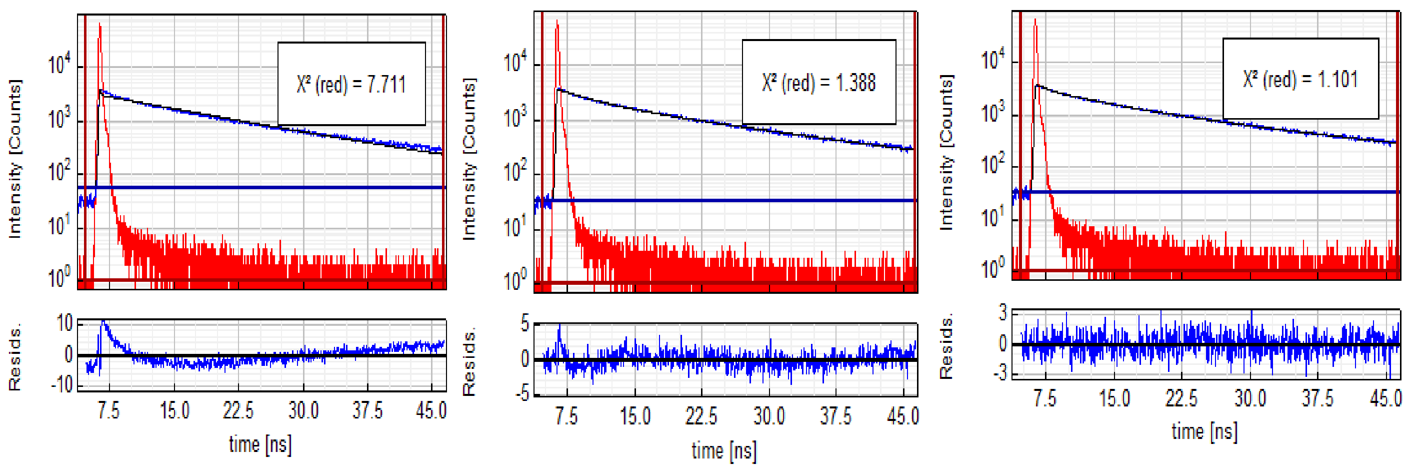
Core-only CdSe QD-MPA-TiO_2 (λ_{em} = 622 nm):



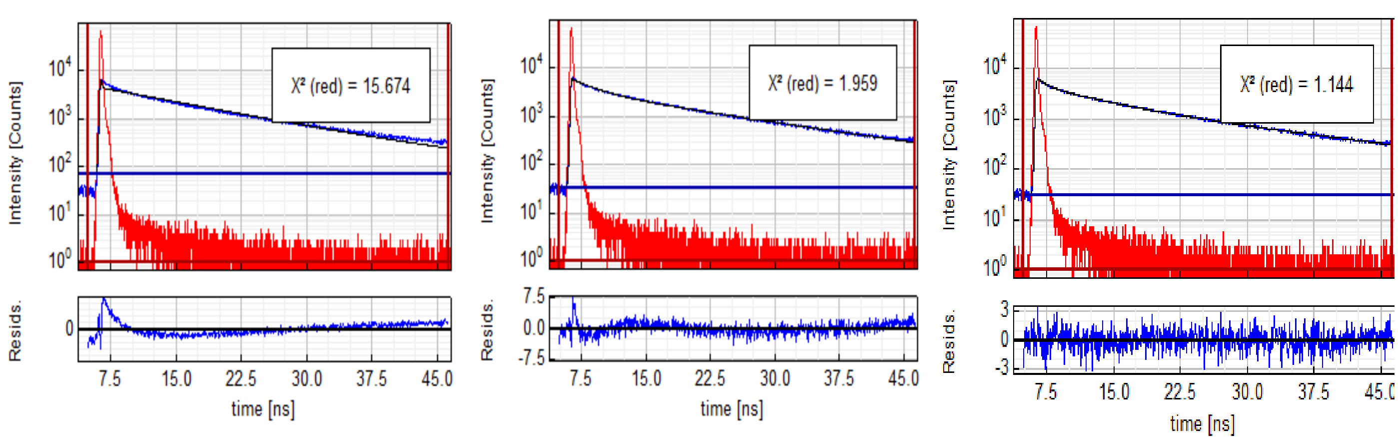
Core/shell CdSe/ZnS QDs alone (λ_{em} = 540 nm):



Core/shell CdSe/ZnS QD/MPA (λ_{em} = 540 nm):



Core/shell CdSe/ZnS QD-MPA-ZrO_2 (λ_{em} = 540 nm):



Core/shell CdSe/ZnS QD-MPA-TiO_2 (λ_{em} = 540 nm):

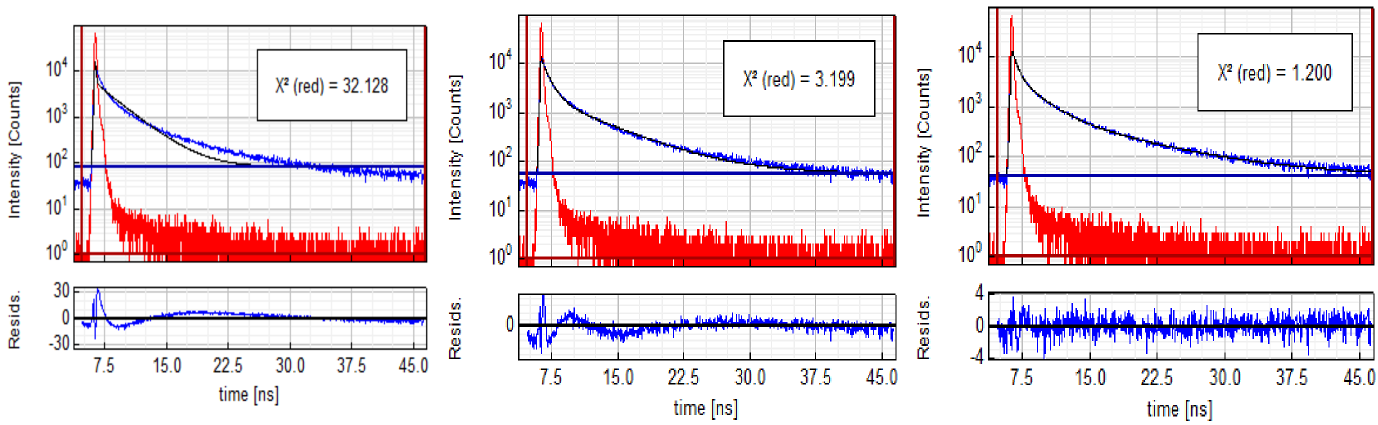


Table S3. Values of A_i and τ_i from fits to representative emission decay traces within the band-edge (BE) and surface (S) emission bands for dispersions containing core-only CdSe QDs.

Sample	Emission wavelength (λ_{em}) (nm)	A_1 (norm.)	τ_1 (ns)	A_2 (norm.)	τ_2 (ns)	A_3 (norm.)	τ_3 (ns)
QDs alone	513 (BE)	0.48±0.02	0.70±0.03	0.290±0.005	5.0±0.1	0.229±0.001	32.0±0.3
	672 (S)	0.30±0.05	0.9±0.2	0.30±0.01	7.0±0.4	0.398±0.004	58±2
QD/MPA	513 (BE)	0.57±0.03	0.82±0.04	0.251±0.007	5.5±0.2	0.177±0.002	33.8±0.5
	672 (S)	0.35±0.06	0.8±0.1	0.31±0.01	6.8±0.4	0.336±0.005	57±0.2
QD-MPA-ZrO_2	513 (BE)	0.55±0.04	0.80±0.06	0.31±0.01	4.7±0.2	0.147±0.002	30.1±0.7
	672 (S)	0.42±0.05	0.9±0.1	0.31±0.02	6.3±0.3	0.269±0.004	51±2
QD-MPA-TiO_2	513 (BE)	0.70±0.05	0.60±0.04	0.26±0.01	2.6±0.1	0.043±0.003	11.5±0.6
	672 (S)	0.59±0.06	0.60±0.07	0.33±0.02	3.3±0.2	0.082±0.005	19±2

Table S4. Values of $<\tau>$ within the band-edge emission band and corresponding values of k_{et} and η_{et} for dispersions containing core-only CdSe QDs.

Emission wavelength (λ_{em}) (nm)	$<\tau>_{QD\ alone}$ (ns)	$<\tau>_{QD/MPA}$ (ns)	$<\tau>_{QD-MPA-ZrO2}$ (ns)	$<\tau>_{QD-MPA-TiO2}$ (ns)	$k_{et}/10^8$ (s^{-1})	η_{et} (%)
487	27±1	25±2	18±3	3.2±0.9	2.5±0.8	82±6
500	27.1±0.6	26±1	21±1	4.0±0.6	2.0±0.4	81±3
513	26.5±0.4	26.8±0.8	22.2±0.9	4.7±0.4	1.7±0.2	79±2
525	28.4±0.6	26±1	22±1	6.0±0.9	1.2±0.3	73±4
538	29.5±0.9	31±2	24±2	7±1	1.1±0.3	71±5

Table S5. Values of $<\tau>$ within the surface emission band and corresponding values of k_{et} and η_{et} for dispersions containing core-only CdSe QDs.

Emission wavelength (λ_{em}) (nm)	$<\tau>_{QD\ alone}$ (ns)	$<\tau>_{QD+MPA}$ (ns)	$<\tau>_{QD-MPA-ZrO2}$ (ns)	$<\tau>_{QD-MPA-TiO2}$ (ns)	$k_{et}/10^7$ (s^{-1})	η_{et} (%)
610	43±1	39±2	42±3	15±3	4±2	64±8
622	48±2	45±3	34±2	10±2	7±2	71±6
635	45±2	44±2	37±2	13±3	5±2	65±8
647	45±2	42±2	41±2	14±2	5±1	66±5
660	48±2	47±2	45±3	11±2	7±1	76±5
672	53±2	52±3	46±3	11±1	7±1	76±3
685	57±2	47±3	45±3	11±1	7±1	76±3
697	61±4	56±4	41±3	11±1	7±1	73±3
710	56±3	55±4	49±4	13±2	6±1	74±5
722	50±3	44±3	46±4	12±2	6±2	74±5

Table S6. Values of $<\tau>$ within the band-edge emission band and corresponding values of k_{et} and η_{et} for dispersions containing core/shell CdSe/ZnS QDs.

Emission wavelength (λ_{em}) (nm)	$<\tau>_{QD\ alone}$ (ns)	$<\tau>_{QD+MPA}$ (ns)	$<\tau>_{QD-MPA-ZrO2}$ (ns)	$<\tau>_{QD-MPA-TiO2}$ (ns)	$k_{et}/10^8$ (s^{-1})	η_{et} (%)
500	13.7±0.4	22±1	16.8±0.8	2.5±0.2*	3.3±0.4	85±2
513	13.8±0.2	18.3±0.5	14.9±0.3	3.1±0.2	2.6±0.2	80±1
525	13.3±0.2	18.0±0.4	14.4±0.6	3.5±0.1	2.2±0.1	76±1
537	13.3±0.1	18.0±0.3	15.1±0.2	4.2±0.1	1.7±0.1	72±1
550	14.0±0.2	18.4±0.4	15.5±0.3	4.8±0.1	1.4±0.1	69±1
563	15.0±0.3	21.0±0.6	16.8±0.4	5.7±0.2	1.2±0.1	66±2
575	16.7±0.6	22±1*	18±0.7*	6.3±0.5	1.1±0.1	66±3

* biexponential fits.

Table S7. Values of A_i and τ_i from fits to representative emission decay traces within the band-edge (BE) emission band for dispersions containing core/shell CdSe/ZnS QDs.

Sample	Emission wavelength (λ_{em}) (nm)	A_1 (norm.)	τ_1 (ns)	A_2 (norm.)	τ_2 (ns)	A_3 (norm.)	τ_3 (ns)
QDs alone	513 (BE)	0.38±0.02	0.80±0.04	0.329±0.003	5.23±0.07	0.286±0.002	16.9±0.1
QD/MPA	513 (BE)	0.24±0.02	1.1±0.1	0.469±0.006	8.6±0.1	0.295±0.003	23.9±0.3
QD-MPA-ZrO_2	513 (BE)	0.27±0.02	0.80±0.08	0.350±0.006	5.6±0.1	0.381±0.002	17.4±0.1
QD-MPA-TiO_2	513 (BE)	0.71±0.02	0.40±0.01	0.237±0.005	2.0±0.1	0.051±0.001	7.7±0.1