SUPPORTING INFORMATION

Understanding the Role of the Sulfide Redox Couple (S^{2-}/S_n^{2-}) in Quantum Dot Sensitized Solar Cells

Vidhya Chakrapani,[1,§] *David Baker,*[1,2] *and Prashant V. Kamat*[1,2,3]*

University of Notre Dame,

Notre Dame, Indiana 46556

[1] Notre Dame Radiation Laboratory
[2] Department of Chemical and Biomolecular Engineering
[3] Department of Chemistry and Biochemistry
* Corresponding author: pkamat@nd.edu

§ Present address: School of Chemical & Biomolecular Engineering, Georgia Institute of Technology, Atlanta, GA 30332

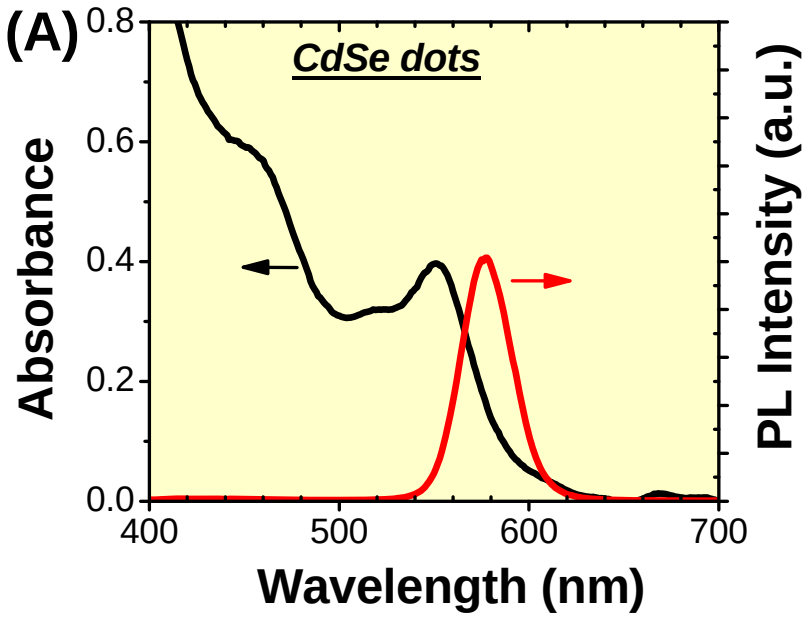

Figure S1. Absorption and emission spectra of TOPO-capped CdSe quantum dot in toluene.

Emission measurements:

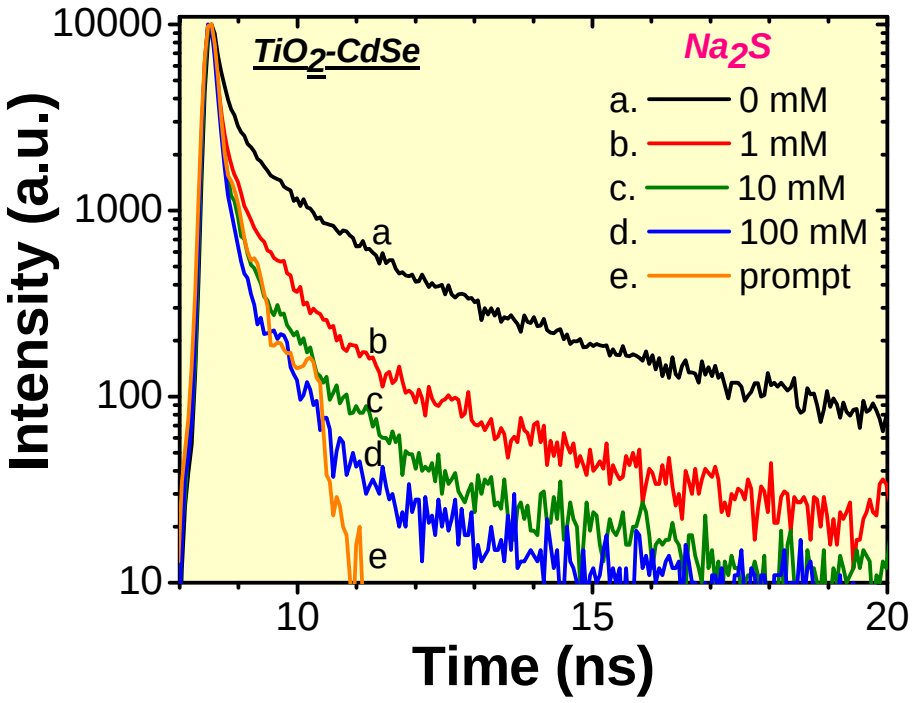

Figure S2: Emission decay monitored at 580 nm of CdSe quantum dots anchored on TiO_2 film in contact with varying concentration of Na_2S. The excitation wavelength was 373 nm. Also shown is the "prompt" instrument response measured against a blank SiO_2 nanoparticulate film.

Emission Lifetime Analysis

$$y = y_0 + B_1 e^{-\frac{t}{\tau_1}} + B_2 e^{-\frac{t}{\tau_2}} + B_3 e^{-\frac{t}{\tau_3}} \qquad \text{Equation 1}$$

Equation 1 is the equation used to fit emission lifetime data. The average lifetime <τ> was determined using the equation:

$$<\tau>=\frac{\sum_{i=1}^{3} B_i \tau_i^2}{\sum_{i=1}^{3} B_i \tau_i} \qquad \text{Equation 2}$$

$$A_i = \frac{B_i \tau_i}{\sum_{j=1}^{3} B_j \tau_j} \qquad \text{Equation 3}$$

Equation 3 was used to calculate the relative amplitude (A) of each deconvoluted emission lifetime. The term relative amplitude refers to the fraction of emission contributed from one specific deconvoluted lifetime (emission from one deconvoluted lifetime divided by the total sum of all emission from all deconvoluted lifetimes).

SiO_2-CdSe	**A_1**	**τ_1 (ns)**	**A_2**	**τ_2 (ns)**	**A_3**	**τ_3 (ns)**	**<τ> (ns)**	**χ^2**
NaOH	0.30	0.48	0.41	2.57	0.29	11.70	4.58	1.5
1 mM Na_2S	0.19	0.14	0.30	1.34	0.51	6.70	3.84	1.9
10 mM Na_2S	0.18	0.13	0.30	1.32	0.52	6.62	3.85	1.8
100 mM Na_2S	0.24	0.11	0.29	1.12	0.47	6.22	3.30	1.4

Table S1. Summary of triexpotential fit parameters for SiO_2-CdSe exposed to Na_2S solution of different concentration.

Femto second absorption kinetic analysis

The bleaching kinetics was fitted with a stretched exponential according to the equation:

$$\Delta OD = y_0 + A\exp\left[-\left(\frac{t}{\tau_{avg}}\right)^{\beta}\right] \qquad \text{Equation 4}$$

where τ_{avg} is the average time constant. The results are summarized below.

	y_0	A	β	τ *(ps)*
NaOH	0.3	0.695	0.594	1313 ± 96
Na_2S	0.25	0.727	0.698	645 ± 15

Table S2. Summary of stretched exponential fitting analysis of femto-second transient decay kinetics of CdSe-SiO_2 film in various electrolytes.

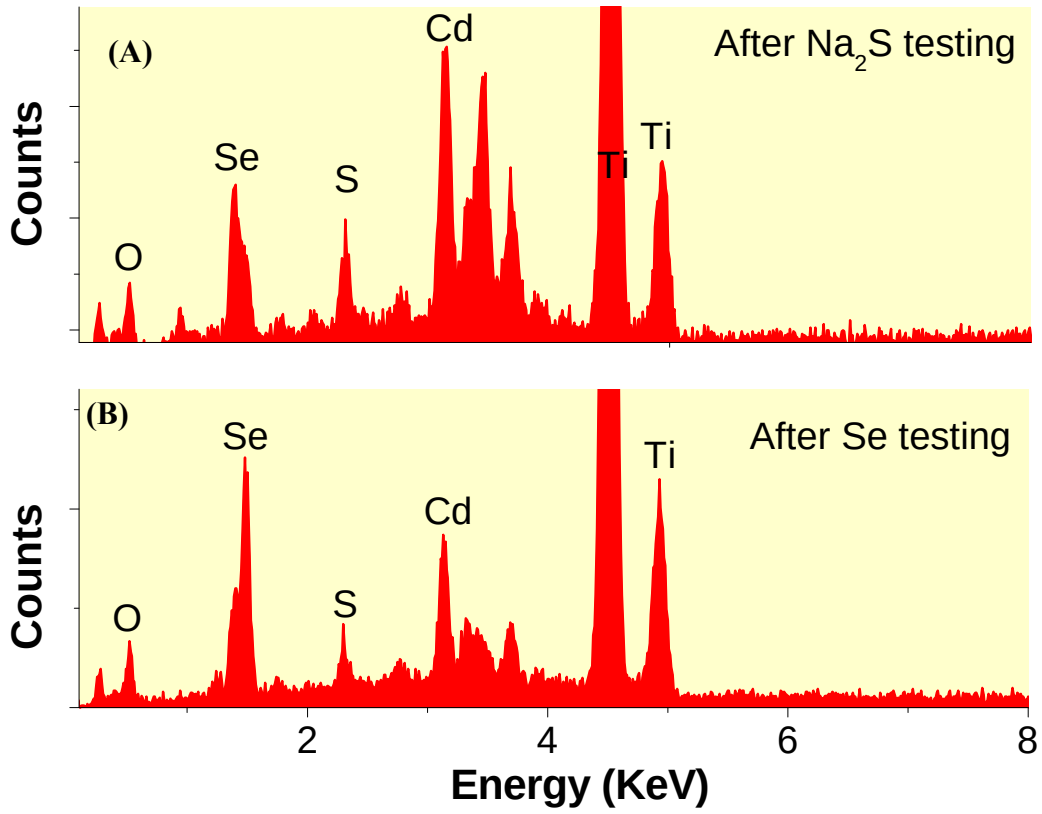

Figure S3. EDS spectrum of CdSe-TiO2 electrode after photoelectrochemical testing in (A). Pure Na_2S electrolyte, showing intense S peak. (B) After testing in Na_2S electrolyte containing Se.

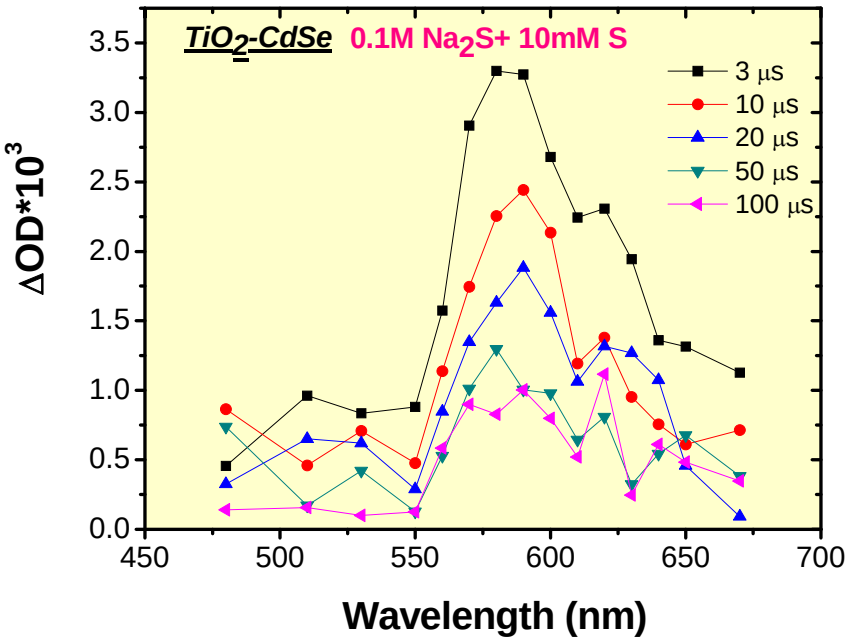

Figure S4. Nanosecond absorption spectra recorded at different time intervals after 532 nm laser pulse excitation (5 mJ/pulse, pulse width~10 ns) of CdSe-TiO_2 film in 0.1 M Na_2S solution containing 10 mM S.

	y0	A1	t1	A2	t2	<t>
Na2S	0	0.60686	2.00E-04	4.74E-01	9.37E-06	1.93E-04
Na2S+ 10mM S	0.00E+00	0.40707	2.68E-04	0.64075	1.15E-05	2.51E-04
Na2S+ 5mM Se	0	0.58453	4.43E-05	4.35E-01	4.80E-06	4.14E-05

Table S3. Summary of bi-exponential fitting parameters of CdSe-TiO_2 film in contact with different electrolytes monitored at 590 nm wavelength.

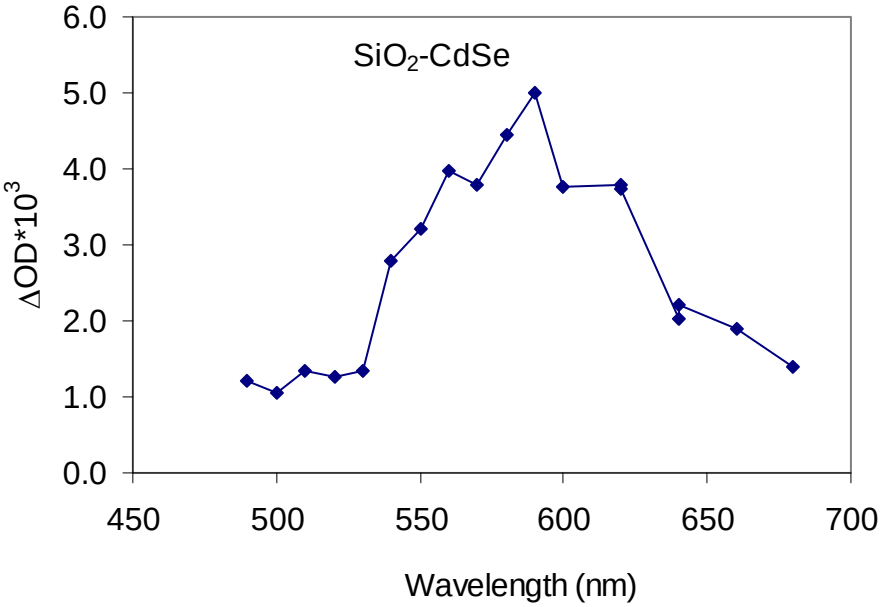

Figure S5. Nanosecond absorption spectra recorded at 20 μs after 532 nm laser pulse excitation (5 mJ/pulse, pulse width~10 ns) of SiO_2-CdSe film in 0.1 M Na_2S solution containing 10 mM S.