SUPPORTING INFORMATION

Wavelength Dependent Efficient Photoreduction of Redox Mediators Using Type II ZnSe/CdS Nanorod Heterostructures

Haiming Zhu, Zheyuan Chen, Kaifeng Wu and Tianquan Lian*

Department of Chemistry, Emory University, Atlanta, Georgia 30322, United States

Supporting Information List:

S1. Materials and methods

S2. Fitting model and parameters for early time TA kinetics for ZnSe/CdS nanorod

S3. TA spectra and kinetics (0.1 ns – 1 μs) of ZnSe/CdS nanorod under 400 nm excitation

S4. UV−vis difference spectra of MV radical generation under 550 nm illmunation

S5. ns TA spectra and kinetics of ZnSe/CdS-MV^{2+} complex

S6. Comparison of early time TA spectra and kinetics of ZnSe/CdS nanorod in toluene and water.

S7. Fitting of MV$^{+\cdot}$ radical formation kinetics under 555 nm excitation

S1. Materials and methods

ZnSe/CdS dot-in-rod synthesis: ZnSe/CdS dot-in-rod (DIR) NRs were synthesized following a seeded growth method.[1] Briefly, ZnSe seeds were synthesized by injecting Se- Trioctylphosphine (TOP) solution and diethylzinc in hexane solution into octadecylamine at 280 °C and letting the reaction proceed for desired duration (to control particle size) before stopping the reaction by removing the heating source. In this study, we used ZnSe seeds showing first exciton peak at 370 nm for further DIR growth. To grow the CdS rod, 0.29 g ODPA, 0.08 g hexylphosphonic acid (HPA), 0.06 g CdO and 3 g TOPO were mixed in a 25mL flask and heated to 300°C under Argon flow. After CdO powder were fully dissolved and the solution became clear, 1.5 g Trioctylphosphine (TOP) was injected and the temperature was raised to 350 °C. ZnSe seeds (~0.8 μmol) and S precursor (0.12 g S in 1.5 g TOP) were swiftly injected. After 3 minutes, the heating mantle was removed and ZnSe/CdS DIR were precipitated with ethanol and redispersed in toluene for future use. The TEM images (Fig. 1a) indicate that these NRs are 20.3 ± 2.5 nm in length and have a bulb near one end.

Ligand exchange to make water soluble NCs: The ZnSe/CdS DIRs prepared above were transformed into water by ligand exchange with 3-mercaptopropionic acid (MPA).[2] Excess amount of MPA (20μL) was dissolved in 10 mL methanol and the pH of the solution was adjusted to above 10 with tetramethylammonium hydroxide. A few mg NCs were added and the solution was refluxed at 70°C overnight with N_2 in dark. The MPA capped NCs were precipitated with ethyl acetate and isolated by centrifugation and decantation. After drying, the precipitate was redissolved in water for further use.

Sample preparation: The aqueous sample of MPA-NC-MV^{2+} for transient absorption measurement were prepared in the same way as those for steady state MV^{2+} photoreduction experiment except for the ~five times higher NR concentrations in the TA sample.

Instruments for characterization: UV-Vis spectra were acquired using Agilent 8453 spectrometer equipped with a diode-array detector. The emission spectrum was recorded using FluoroMax 3 spectrofluorimeter. The transmission electron microscopy (TEM) images were acquired with JEOL JEM-1400 (60 kV). The femtosecond and nanosecond transient absorption (TA) and time-resolved fluorescence spectrometers used for these studies have been described elsewhere.[3,4] To correct for slight difference of excitation intensity of the data acquired by fs and ns instruments under the single exciton conditions, the signal size of the ns kinetics was slightly scaled such that these transient kinetics overlap at ~1ns. For all TA measurements, the samples were kept in a 1 mm cuvette and constantly stirred by a magnetic stirrer to avoid photodegradation. The polarizations of pump and probe pulses are in magic angle condition. Time-resolved fluorescence decay was measured by time-correlated-single photon counting under 400 nm excitation. The number of photons per NC in both TA and fluorescence measurement was much less than 1 so that the multiexciton contribution was negligible.

MV^{2+} photoreduction measurement: Light-driven MV^{2+} reduction was performed in a standard threaded-top fluorescence cuvette (Spectrocell, RF-3010-T) with a total volume

of ~3 ml and a path-length of 1 cm. The cuvette was filled with 2.0 ml reaction solutions of NRs (concentration to be specified below), MV^{2+} (2.0 mM), MPA as sacrificial electron donor (50 mM) (neutralized to 7 by NaOH before mixing) and buffer (50 mM phosphate, pH 7.5). The concentration of MPA-capped ZnSe/CdSe DIR for 415 nm illumination was adjusted to have absorbance of 1.46 (OD) at 415 nm. The concentration for 550 nm illumination was three times of that for 415 nm illumination with an absorbance at 550 nm of 0.32 OD. The narrow band (~20 nm) illuminations centered at 415 nm and 550 nm, respectively, were generated with a xenon lamp and different filter sets. The light beam was down-collimated to a beam diameter ~0.6 cm to ensure full passage through the sample cell. The light power was measured at the front of the reaction cell using a digital laser power meter (OPHIR, model NOVA II) to be 5.09 mW at 415 nm and 5.15 mW at 550 nm, respectively. The reaction cells were sealed with a rubber septum, degassed and filled with Argon. All procedures were performed with a minimum exposure to ambient light. Before illumination, the UV-Vis absorption spectrum of the solution was taken as zero time. The reaction was initiated by unblocking the stabilized illumination light source with constant stirring of the solution (by a magnetic stirrer). The UV-vis absorption spectra of the solution were taken after desired duration of illumination (seconds), interrupting the illumination by less than 5 s for each spectrum recording. Error bars on $MV^{+\cdot}$ concentrations were calculated from at least two independent experiments.

The $MV^{+\cdot}$ generation quantum yield is defined as $\Phi_{MV} = \Delta(MV^{+\cdot})/ \Delta(\hbar v)$ where $\Delta(MV^{+\cdot})$ is the $MV^{+\cdot}$ generation rates and $\Delta(\hbar v)$ is the photon absorption rates by the reaction solution, respectively. $MV^{+\cdot}$ generation rates, $\Delta(MV^{+\cdot})$, were obtained from the slope of the initial three points in Figure 3b. The photon absorption rate $\Delta(\hbar v)$ was calculated from the illumination power and the absorbance of the reaction solution. The amount of absorbed light were determined from sample absorbance, the measured power and the estimated reflection/scattering loss of the cuvette front window.

S2. Fitting model and parameters for early time TA kinetics for ZnSe/CdS nanorod

The B2 and B3 kinetics under 555 nm excitation (Figure 2b) were fitted by a single exponential rise with instantaneous formation (< 20 fs) and instrument-response time (~150 fs) and a much slower decay.

Under 400 nm excitation conditions (Figure 2d), the 550 nm and 480 nm kinetics were fit by a two exponential rise and a much slower decay process, using following equations:

$$\Delta A(550nm,t) = A_{B3}(550nm)[\alpha\exp(-t/\tau_{r1})+(1-\alpha)\exp(-t/\tau_{r2})-1] \qquad (S1)$$

$$\Delta A(480nm,t) = A_{B2}(480nm)[\alpha\exp(-t/\tau_{r1})+(1-\alpha)\exp(-t/\tau_{r2})-1] \qquad (S2)$$

The number 1 here accounts for the much slower decay component (>>20 ps).

The 455nm kinetics can be fit using the following equation:

$$\Delta A(455nm,t) = A_{B1}(455nm)[\exp(-t/\tau_{r0}) - \beta[\alpha\exp(-t/\tau_{d1})$$
$$+(1-\alpha)\exp(-t/\tau_{d2})] - (1-\beta)] + \Delta A_{B2}(455nm,t) \qquad (S3)$$

The second term $\Delta A_{B2}(455nm,t)$ accounts the contribution of B2 bleach at 455nm. It is given by equation S2 with the B2 amplitude at 455 nm determined from the TA spectra measured at 555 nm excitation (Figure 2a) according to the following equation:

$$\Delta A_{B2}(455nm,t) = 0.15\Delta A_{B2}(480nm,t) \qquad (S4)$$

β represents the portion that localize in early time while $(1-\beta)$ represents the portion that is trapped and decays much slower. The fitted results are shown in Figure 2d black line and the fitting parameters are listed below in Table S1.

Table S1. Fitting parameters for TA kinetic in Figure 2d.

		τ_{r1}	τ_{r2}	α	
550nm (B3)		0.487±0.061 ps	9.70±0.82 ps	0.91±0.02	
480nm (B2)		0.417±0.042 ps	9.02±1.25 ps	0.92±0.03	
	τ_{r0}	τ_{d1}	τ_{d2}	α	β
455nm (B1)	0.053±0.011 ps	0.498±0.057 ps	9.09±1.02 ps	0.89±0.03	0.81±0.04

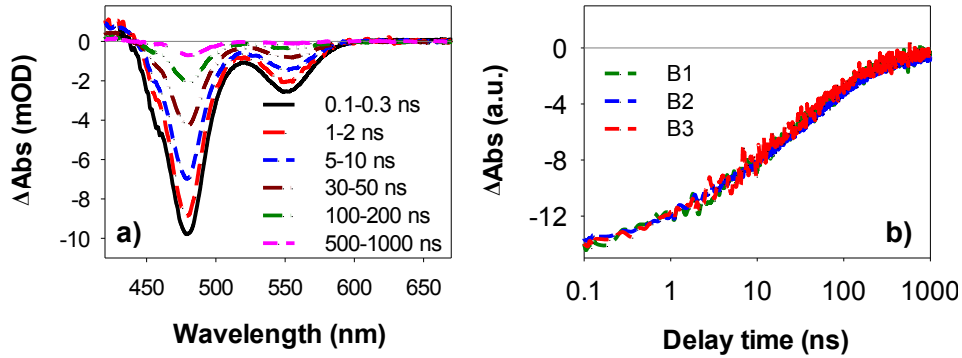**S3. TA spectra and kinetics (0.1 ns – 1 μs) of ZnSe/CdS nanorods under 400 nm excitation**

Figure S1. TA spectra (a) and kinetics (b) of ZnSe/CdS nanorods at 0.1 ns – 1 μs after 400 nm excitation. The kinetics at the peaks of B1, B2, and B3 bands have been normalized for better comparison.

S4. UV−vis difference spectra of MV$^{+\cdot}$ radical generation under 550 nm illumination
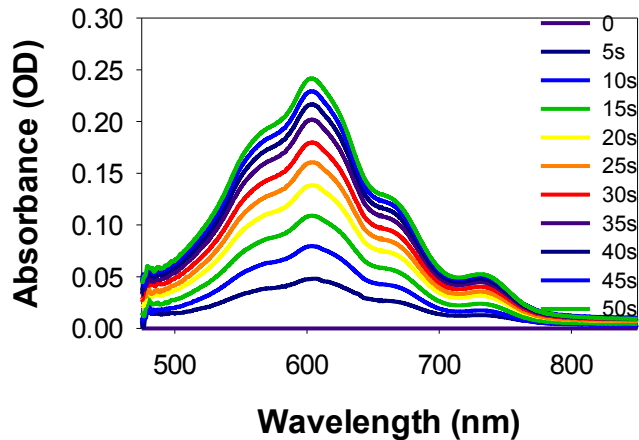
Figure S2. UV−vis difference spectra (after−before irradiation) of a solution containing ZnSe/CdS DIR, MV^{2+} and MPA after indicated time of 550 nm illumination.

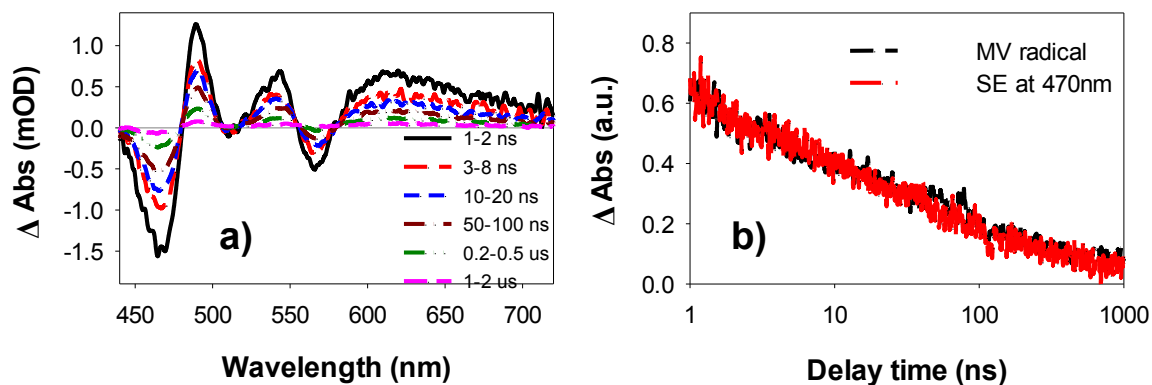## S5. Nanosecond TA spectra and kinetics of ZnSe/CdS-MV^{2+} complexes

Figure S3. ns TA spectra (a) and kinetics (b) of ZnSe/CdS-MV^{2+} complex dispersed in toluene solution under 555 nm excitation, showing identical decay kinetics between $MV^{+\cdot}$ radical and SE signal at 470 nm.

S6. Comparison of TA spectra and kinetics of ZnSe/CdS NRs in toluene and water measured at 400 nm excitation.
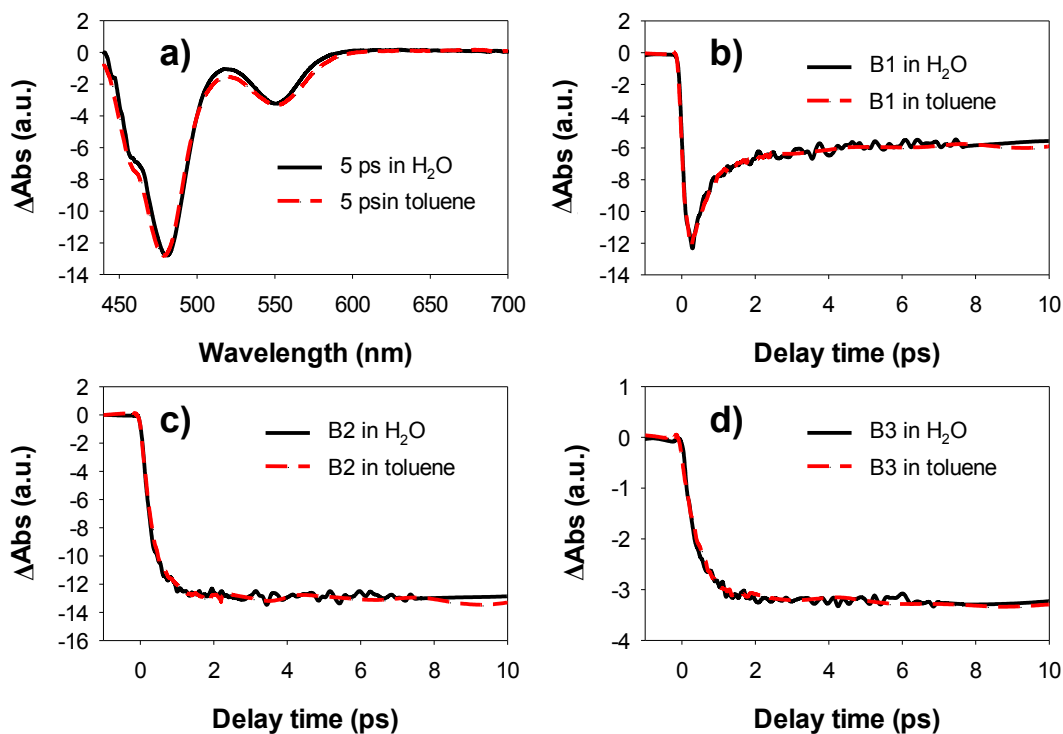
Figure S4. Comparison of TA spectra at 5 ps (a) and kinetics at B1 (b), B2 (c), B3 (d) transitions of ZnSe/CdS nanorods in toluene (red dashed lines) and water (black solid lines). Excitation wavelength: 400 nm.

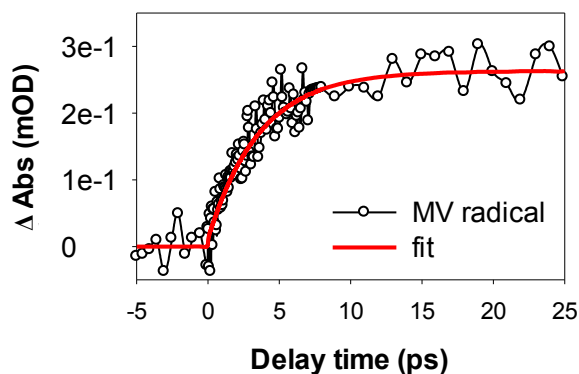## S7. Fitting of $MV^{+\cdot}$ radical formation kinetics under 555 nm excitation

Figure S5. Single exponential fitting of $MV^{+\cdot}$ radical formation kinetics under 555 nm excitation

References

(1)   Dorfs, D.; Salant, A.; Popov, I.; Banin, U. *Small* **2008**, *4*, 1319.
(2)   Aldana, J.; Wang, Y. A.; Peng, X. G. *J. Am. Chem. Soc.* **2001**, *123*, 8844.
(3)   Zhu, H.; Song, N.; Lian, T. *J. Am. Chem. Soc.* **2011**, *133*, 8762.
(4)   Song, N.; Zhu, H.; Jin, S.; Zhan, W.; Lian, T. *ACS Nano* **2011**, *5*, 613.