

Supporting Information

Exciton Dynamics in CdS-Ag₂S Nanorods with Tunable Composition Probed by Ultrafast Transient Absorption Spectroscopy

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I. Materials. All chemicals were used as received without further purification. Cadmium oxide (CdO, 99.99%), silver nitrate (AgNO₃, 99+%), cadmium nitrate tetrahydrate (Cd(NO₃)₂•4H₂O, 99+%), propylphosphonic acid (PPA, 95 %), sulfur (99+ %), p-benzoquinone (BQ, 98%), 4-aminothiophenol (AT, 97%), acetone (HPLC grade, 99+%), and the following anhydrous solvents: toluene (99+%), methanol (MeOH, 99+%), isopropanol (IPA, 99+%), acetonitrile (MeCN, 99+%) and tetrahydrofuran (THF, 99+%) were purchased from Aldrich. Octylamine (OA, 99%) and nonanoic acid (NA, 96%) were purchased from Fluka and Aldrich. Octadecylphosphonic acid (ODPA) was purchased from Polycarbon Industries (PCI Synthesis, 9 Opportunity Way, Newburyport, MA 01950, 978-463-4853). Trioctylphosphine oxide (TOPO, 99%) was purchased from Acros Organics and Aldrich. Trioctylphosphine (TOP, 97%) was purchased from Strem Chemicals. Trioctylphosphine sulfide (TOPS) was prepared by mixing TOP and sulfur together in a 1:1 molar ratio inside an argon-filled glove box followed by stirring the mixture at room temperature until the sulfur was fully dissolved (typically ~ 24 hours).

II. CdS nanorod synthesis. Colloidal CdS nanorods were synthesized under air-free conditions using standard Schlenk line techniques. First, CdO (206 mg), ODPA (1.09 g), PPA (6 mg), and TOPO (2.88 g) were added to a 25 mL, 3-neck, round-bottom flask. The contents of the flask were put under vacuum at ~ 250 milliTorr and at 120°C for 45 minutes to remove water. The flask was then put under argon and heated to 320°C for ~ 30 minutes to enable the complexation of cadmium ions with the alkylphosphonic acid ligands. The flask was cooled back to 120°C under argon and again evacuated for ~ 1.5 hours to remove water produced by the cadmium complexation. After the second evacuation step, the flask was put under argon and again heated to 320°C . During this time, 2 g of TOP was injected into the flask at approximately 275°C . After the temperature stabilized at 320°C , TOPS (0.65 g, 1 eq S:Cd) was injected, and the nanorods were grown $\sim 320^{\circ}\text{C}$. After 20 minutes of growth, a secondary aliquot of TOPS (0.65 g) was mixed with TOP (2.5 g) and injected slowly into the reaction flask via a syringe pump at a rate of 0.1 mL/min; the total injection time was ~ 40 minutes. Following this secondary injection, the solution was kept at 320°C for an additional 10 minutes, making a total reaction time of ~ 70 minutes from the initial TOPS injection. The heating mantle was removed, and toluene was added to the flask once it had cooled to $\sim 100^{\circ}\text{C}$. The CdS solution was transferred to an argon-filled vial for subsequent cleaning steps. Centrifugation was used to separate the nanorods from the remaining cadmium-phosphonate complex and TOPO. The nanorods were washed two times with the combination of a nonpolar solvent (toluene), surfactants (OA and NA), and a polar solvent (isopropanol). The surfactants nonanoic acid (NA) and octylamine (OA) help to break up the excess cadmium-phosphonate complex, which can form a gel when the reaction is cooled to room temperature. After each centrifugation, the supernatant was removed, and the precipitated nanorods were redispersed in fresh solvent. The final washing step was done without the

surfactants NA or OA. The presence of excess octylamine was found to inhibit cation exchange of the CdS nanorods, as it binds to Ag^+ ions in solution. After the washing steps, the nanorods were dispersed in toluene and stored in an argon-filled glove box. This recipe produces some branched structures (i.e., bipods, tripods, and tetrapods) along with the nanorods. However, the majority of branched structures are removed during the washing steps as they do not flocculate as easily as the nanorods and thus tend to stay in the supernatant. Statistics of the length and diameter of the nanorods are shown in Supporting Information Figure S1 below. The average and standard deviation of the length and diameter are 66 ± 14 nm and 5.3 ± 0.4 nm.

III. Inductively coupled plasma atomic emission spectroscopy. ICP-AES was used to determine the Cd^{2+} concentration for the CdS nanorod solution to be used in the subsequent cation exchange reactions. A Cd ICP/DCP standard solution (10,000 $\mu\text{g/mL}$ Cd^{+2} in 2% HNO_3 , Aldrich) was diluted into a series of Cd^{2+} concentrations spanning several orders of magnitude (50 ppb – 100 ppm). The acid concentrations were the same (1.2% nitric acid) in all of the standards. The area-integrated atomic emission lines (Cd: 228.8, 226.5, and 214.4 nm) were free from inter-element interferences and displayed a linear response over the entire concentration range measured. The Cd concentration of the sample fell well within the linear dynamic range for these atomic lines. The organic solvent was removed from the CdS nanorod solution by passing filtered (0.25 μm pore-size) air over the solution. The remaining solid was then digested by adding a solution of concentrated nitric acid (69%, Ultra High Purity Trace Select by Fluka, Cd assay $\leq 0.00000005\%$). Three aliquots were measured for the sample, and the emission intensities were averaged over the three aliquots and the three emission lines. The molar

extinction coefficient in terms of Cd^{2+} concentration for the CdS nanorod solution was $\sim 3000 \text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$ at 300 nm as measured by visible absorption spectroscopy.

IV. Cation exchange of CdS nanorods.

Supporting Information Table 1. Reaction conditions used to synthesize CdS-Ag₂S binary nanorods and Ag₂S nanorods by Ag⁺ cation exchange of CdS nanorods

Sample #	Ag ⁺ /Cd ²⁺	[AgNO ₃] (moles) in methanol (mL) and toluene (mL)	[CdS] (moles) in toluene (mL)	Ag ₂ S/CdS (by TEM)	Sample shown in Figure X
1	4.0	1.2×10^{-5} mol Ag ⁺ in 0.8mL MeOH + 1.6 mL toluene	3.0×10^{-6} mol CdS in 0.585 mL toluene		Figs. 3,4
2	0.5	1.5×10^{-6} mol Ag ⁺ in 0.8mL MeOH + 1.6 mL toluene	3.0×10^{-6} mol CdS in 0.585 mL toluene	0.12	Figs. 6,7,9
3	1.0	3.0×10^{-6} mol Ag ⁺ in 0.8mL MeOH + 1.6 mL toluene	3.0×10^{-6} mol CdS in 0.585 mL toluene	0.19	Figs. 6,7,9
4	1.5	4.5×10^{-6} mol Ag ⁺ in 0.8mL MeOH + 1.6 mL toluene	3.0×10^{-6} mol CdS in 0.585 mL toluene	0.30	Figs. 6,7,9
5	1.05	2.0×10^{-6} mol Ag ⁺ in 0.645mL MeOH + 2 mL toluene	1.9×10^{-6} mol CdS in 0.170 mL toluene		Fig. 8, S3
6	2.2	6.5×10^{-6} mol Ag ⁺ in 0.8mL MeOH + 1.6 mL toluene	3.0×10^{-6} mol CdS in 0.585 mL toluene		Used for back exchange below
	Cd ²⁺ /Ag ⁺	[Cd(NO ₃) ₂]	[Ag ₂ S]		
7	~ 100	5.8×10^{-4} mol Cd ²⁺ in 0.8 mL MeCN	$\sim 3.0 \times 10^{-6}$ mol Ag ₂ S in 1.6 mL THF + $\sim 250 \mu\text{L}$ TBP		Figs. 3,4,5

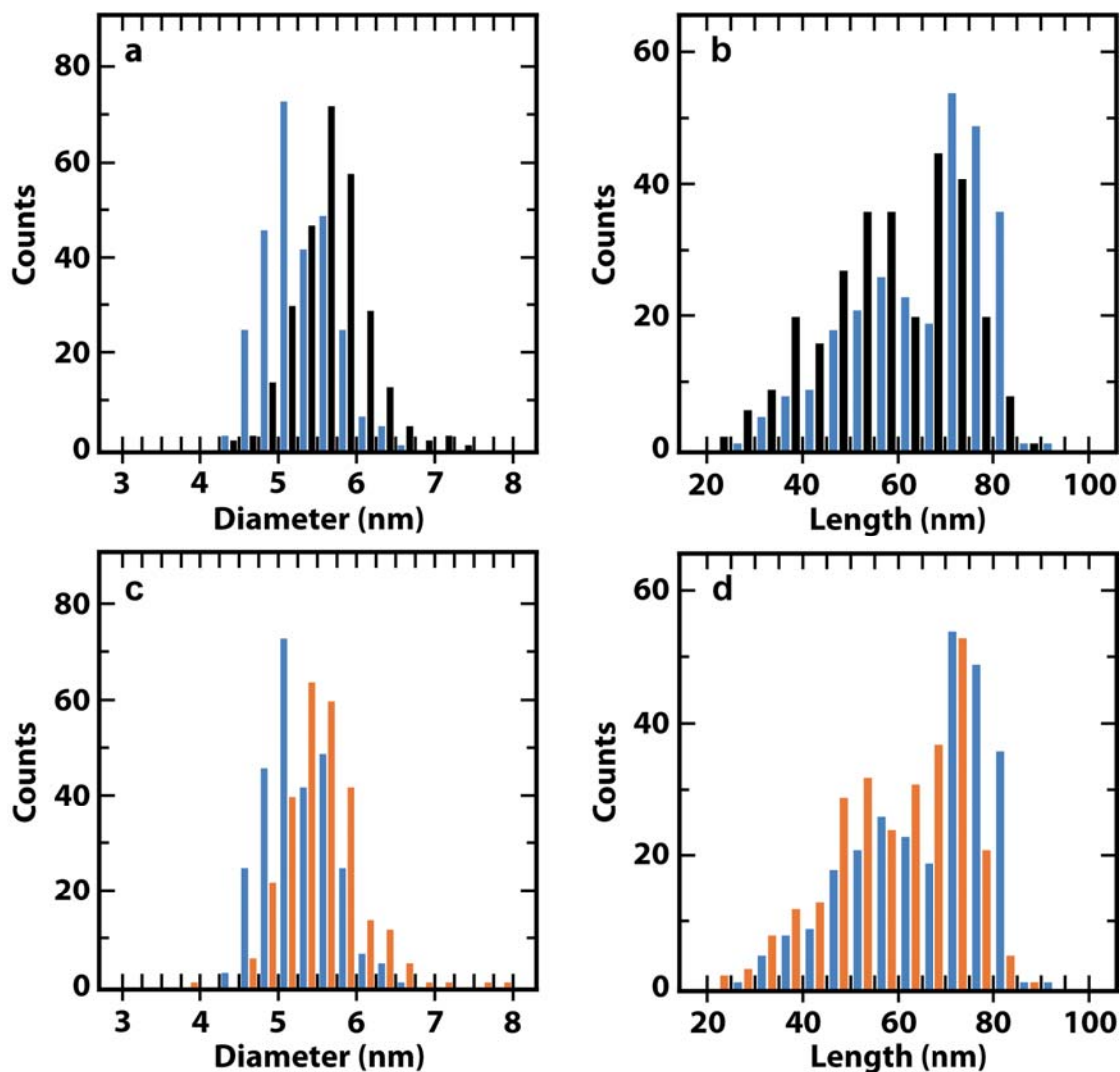


Figure S1: Size distributions of the initial CdS nanorods, converted Ag_2S nanorods, and back-converted CdS nanorods. a) Diameter distributions of the initial CdS nanorods (blue) and converted Ag_2S nanorods (black). b) Length distributions of the same samples. c) Diameter distributions of the initial CdS nanorods (blue) and back-converted CdS nanorods (orange). d) Length distributions of the same samples. The colors of the histograms in this figure match the borders of the TEM images in Figure 3 and the optical spectra plotted in Figure 4 for the same samples.

V. Chemical quenching experiments

Supporting Figure 2 compares the transient absorption dynamics of CdS nanorods with the addition of *p*-benzoquinone (BQ), an electron acceptor, and 4-aminothiophenol (AT), an electron donor; or, hole trap. The molar concentration of either BQ or AT was made approximately equal to that of Cd^{2+} within the CdS nanorods in solution ($\sim 1 \times 10^{-6}$ moles). An equimolar solution of benzoquinone molecules adsorbed to the nanocrystal surface has been shown to accept electrons in < 200 -fs, forming a charge-transfer complex that decays with a lifetime of 2.7-ps, effectively shortening the recovery of the dynamics.[1] The intraband signal in this case is quenched with a time constant of $\tau_{\text{decay}}^{(\text{BQ})} = 113 \pm 25$ -ps. On the other hand, the thiol group of the 4-aminothiophenol (AT) molecules readily passivates dangling bonds that would normally trap electrons on the nanocrystal surface and thereby lengthens the intraband signal. The decay is found to be $\tau_{\text{decay}}^{(\text{AT})} = 464 \pm 107$ -ps for samples with AT, as shown in Supporting Figure 2. Therefore, the transient absorption signals are determined to arise from excited state electrons.

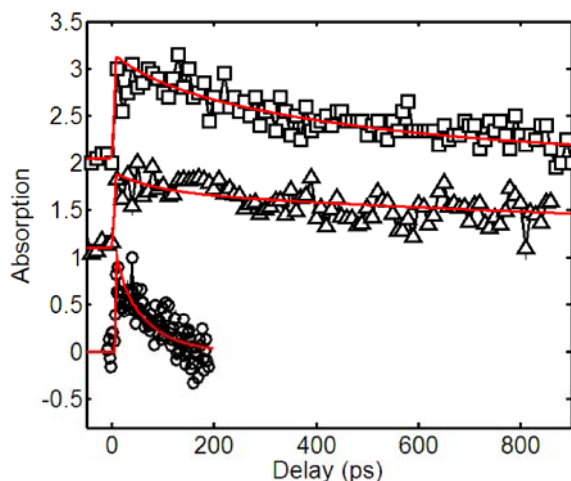


Figure S2. Transient absorption (\square) dynamics of 4.9-nm CdS nanorods is affected by the presence of BQ molecules adsorbed to the surface, which shuttles electrons out of the conduction

band, leading to disappearance of the intraband signal (\circ). AT, on the other hand, passivates surface states, elongating the dynamics (Δ).

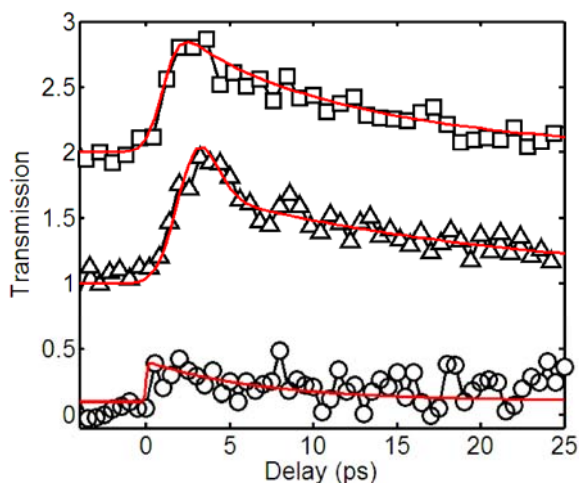


Figure S3. Optically exciting a CdS-Ag₂S nanorod ($\text{Ag}^+/\text{Cd}^{2+} = 1.05$) at 800-nm and probing in the mid-infrared yields transient absorption dynamics (\square) of electrons relaxing to states within the band gap of CdS. In the presence of equimolar amounts of AT, the dynamics (Δ) is largely unaffected, indicating the inability of AT to passivate the type of defect centers probed at 800-nm. The electron absorption signal is almost completely quenched (\circ) when BQ is added to the solution.

Supporting Figure 3 shows the dynamics of cation-exchanged nanorods ($\text{Ag}^+/\text{Cd}^{2+} = 1.05$) excited by a $\lambda_{\text{pump}} = 800$ nm pump and probed at $\lambda_{\text{probe}} = 4.0$ μm . A monoexponential fit to the decay yielded a time constant of $\tau_{\text{decay}} = 7.5 \pm 0.8$ ps. The addition of electron-donating AT molecules (Supporting Figure 3, middle) yielded dynamics best fit by a biexponential decay,

with $\tau_{\text{decay},1}^{(\text{AT})} = 1.8 \pm 1.0\text{-ps}$ and $\tau_{\text{decay},2}^{(\text{AT})} = 11.0 \pm 3.3\text{-ps}$. In contrast to the elongation of the dynamics observed in the parent nanorods (Supporting Figure 2), the AT molecules do not significantly affect the transient absorption signal from these states. For the purposes of experimental control, the electron-withdrawing BQ molecules effectively compete with the electron's defect absorption pathway, in fact quenching the signal (Supporting Figure 3, bottom).

1. C. Burda, S. Link, M. Mohamed and M. El-Sayed, Journal Physical Chemistry B, *The relaxation pathways of CdSe nanoparticles monitored with femtosecond time-resolution from the visible to the IR: Assignment of the transient features by carrier quenching* **105** (49), 12286-12292 (2001).