

Supporting Information

Enhancing the activity of photocatalytic hydrogen evolution from CdSe quantum dots with a polyoxovanadate cluster

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Experimental Methods

Chemicals: Chemicals were purchased and used without further purification except where noted. For photocatalytic H₂ evolution experiments, solutions were prepared using ascorbic acid (EMD Chemicals), ethanol (200 proof, Koptec), sodium hydroxide (Fisher Scientific) and ultrapure H₂O. [NBu₄][BH₄] and VO(OiPr)₃ were purchased from Sigma-Aldrich and used as received. [NBu₄][PF₆] was purchased from Sigma-Aldrich, recrystallized thrice using hot methanol, and stored under dynamic vacuum for a minimum of two days prior to use.

CdSe Quantum Dot (QD) Synthesis: Inside a nitrogen filled glovebox, 0.79 g of Selenium was dissolved in 10 mL of 97% trioctylphosphine in a scintillation vial and allowed to stir at 50 C until all solid had dissolved. In a separate vial, 0.747 g of anhydrous Cadmium Acetate was dissolved in 12 ml of 97% trioctylphosphine and stirred at 50 C until all solid had dissolved. Outside of the glovebox, to a 100 mL three neck flask was added 7.8 g of trioctylphosphine oxide, 2.3 g of 98% hexadecylamine, and 0.171 g of 97% tetradecylphosphonic acid. The flask was purged with N₂ three times and heated to 100 C below 0.1 Torr with stirring for 30 minutes. After returning to N₂, 2.5 mL of the TOP/Se solution was injected, and the reaction was heated to 310 C, where 2.5 mL of the TOP/Cd solution was injected very quickly with a syringe. The flask was transferred to a heating mantle set to 260 C, and the reaction was allowed to stir for 7 minutes. The solution was cooled using a heat gun (set to low) and placed into a water bath. 15 mL of hexanes was injected into the reaction to prevent solidification of TOPO. The mixture was separated into 2 50-mL centrifuge tubes, where 10 ml of methanol and 25 mL of acetone was added. The product was centrifuged for 15 minutes at 8000 RPM. The clear supernatant was discarded, and the solid pellet was allowed to air dry. The solid was dispersed in 10 mL hexanes and placed in the centrifuge again for 15 minutes at 8000 RPM (repeated as needed). The final product was dissolved in hexanes.

CdSe-GSH Ligand Exchange: GSH (0.5 g), NaOH (0.4 g), and methanol (20 mL) is stirred under ambient conditions for several hours until dissolved. Next, a solution of CdSe QDs (75 nmol) in hexanes was added to a 50 mL falcon tube with 20 mL methanol and centrifuged for 15 minutes. The clear, colorless supernatant was discarded, and the QDs were resuspended in 6-7 mL chloroform. The CdSe QDs in chloroform were mixed with 11 mL of the GSH solution prepared previously. This mixture was left under N₂ flow overnight, until all the solvent evaporated. The QDs were resuspended in 20 mL of nanopure water (18.2 MΩ) and heated to 60 °C for 10 minutes. The QDs were transferred to a 50 mL falcon tube with 25 mL acetone and centrifuged for 20 minutes until precipitated. The clear, colorless supernatant

was decanted, and the QD pellet was resuspended in 300-500 μL of nanopure water. This procedure was modified from Zheng, *et al.*¹

CdSe-MPA/Cys Ligand Exchange: 0.2533 g of tetramethylammonium hydroxide pentahydrate was dissolved in 13.3 mL of methanol along with 0.109 moles of the desired ligand (Cys or MPA). 8.7 mL of a 11.4 μM solution of TOPO-CdSe QDs in hexanes was added to 7.33 mL of the methanol solution in a 100 mL round bottom flask. The flask was put under argon gas and refluxed at 65 C for 45 minutes. The solution was then divided into 2 centrifuge tubes, where 35 mL of ethyl ether and 10 mL of ethyl acetate were added. The tubes were placed into a centrifuge and spun at 8000 RPM for 15 minutes. The supernatant was disposed of, and the pellet was allowed to air dry. The resulting solid was dispersed in water.

Electrochemical experiments (CV): Concentrations of POV-alkoxide and $[\text{NBu}_4][\text{PF}_6]$ used were 1 mL and 100 mM respectively. Stock solution of 40 mM pH 6 phosphate buffer was prepared by dissolving 0.147 g disodium phosphate heptahydrate and 0.476 g of monosodium phosphate hydrate in 100 mL of deionized water. CV measurements were carried out using a Bio-Logic SP 200 potentiostat/galvanostat and the EC-Lab software suite. Cyclic voltammograms were recorded using a 3 mm diameter glassy carbon working electrode (CH Instruments, USA), a Pt wire auxiliary electrode (CH Instruments, USA), and a bare silver wire reference electrode (BASi, USA). All measurements were referenced against the Fc/Fc^+ couple. Cyclic voltammograms were iR compensated at 85% with impedance taken at 100 kHz using the ZIR tool included within the EC-Lab software.

Photocatalytic H_2 Production: H_2 evolution experiments were performed as described previously.²⁻⁴ Stock solutions of CdSe QDs were prepared in H_2O (see preparation experimental details), stock solutions of $[\text{V}_6\text{O}_7(\text{OC}_2\text{H}_5)_{12}]^{-1}$ (2 mM) (see preparation experimental details) were prepared in ethanol, and stock solutions of ascorbic acid (1.5 M) were prepared in water. The pH of the aqueous solution of ascorbic acid was adjusted to pH 4.5 using NaOH (5 M). These stock solutions were diluted to desired concentrations - 1 μM CdSe, 100 μM $[\text{V}_6\text{O}_7(\text{OC}_2\text{H}_5)_{12}]^{-1}$, 0.5M ascorbic acid - to reach a total volume of 5 mL in a 40-mL scintillation vial. First, aqueous solutions were combined in each vial to a total volume of 2.5 mL (adjusting volume if necessary with ultrapure H_2O). The aqueous component in each vial was adjusted to pH 4.5 using NaOH if it deviated. Then, pure ethanol and ethanol stock solutions were added to reach a total volume of 5 mL. Vials were fitted with gas-tight septum screw caps. Each cap is equipped with a pressure transducer to monitor pressure changes in real time (MPX4259A series). After purging vials with a gas mixture of N_2/CH_4 (79:21), each vial was illuminated from below by a light-emitting diode

(Philips LumiLED Luxeon Star Hex green 700 mA LEDs) at 530 nm (± 10 nm). The LED power was set to 45 ± 5 mW and was measured with a Newport power meter (Model 1918-C). For the duration of the experiment, samples were mixed with an orbital shaker at 100 RPM in a cooling block set to 15°C.

After 48 hours of illumination, the amount of H₂ produced was determined by sampling the headspace via gas chromatography (GC) using a Shimadzu GC-2014 with a 5 Å molecular sieve column (30 m, 0.53 mm) and a thermal conductivity detector. The amount of H₂ evolved was quantified with a calibration curve, using CH₄ as an internal standard. Pressure curves were calibrated if necessary to correlate with the final amount of hydrogen produced as measured by GC. Uncertainty reported in the manuscript for H₂ generation, turnover numbers, and rates were determined by the standard deviation of three trials of each condition shown for CdSe-GSH and CdSe-MPA, and CdSe-Cys. The trends reported here from these trials were observed over multiple experiments and batches of quantum dots.

Photoluminescence Quenching: QD samples were placed in a quartz cuvette with a 1 cm path length for all absorption and emission characterization. A PerkinElmer Lambda 950 UV/Vis/NIR spectrophotometer was used to record all absorbance spectra. Following all syntheses and ligand exchanges, the CdSe QD concentration was calculated using the first excitonic absorbance transition as described by Yu, et. al.⁵ Photoluminescence (PL) spectra were measured with a modular fluorometer system (Acton Research) with a photomultiplier tube detector.

[V₆O₇(OC₂H₅)₁₂]⁻¹ Preparation: V₆O₇(OC₂H₅)₁₂⁻ was prepared according to previous literature.⁶

Supplementary Figures

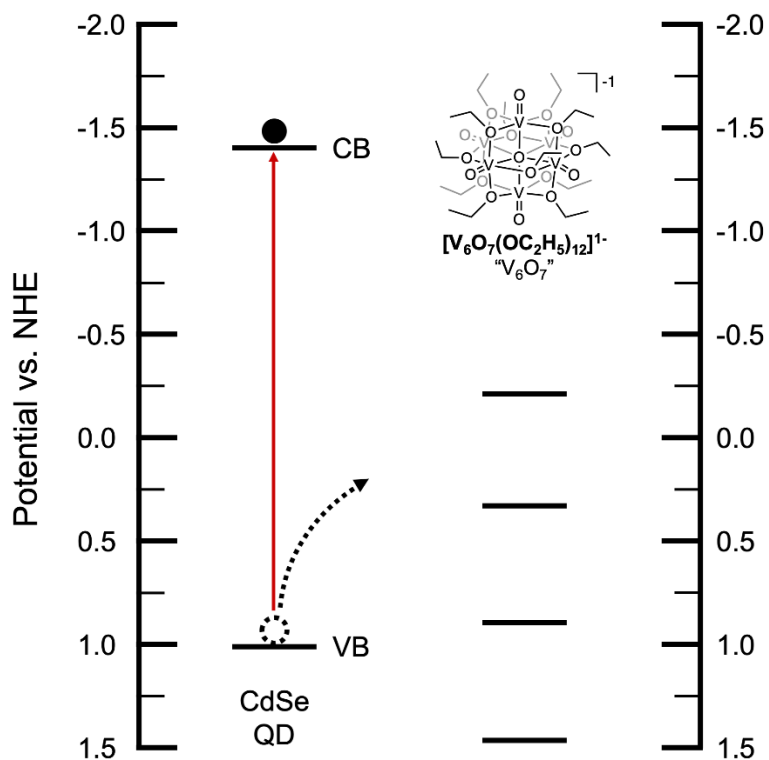


Figure S1. Relative energy levels of CdSe quantum dots⁷ and $[V_6O_7(C_2H_5)_{12}]^{1-}$ vs. NHE. Potentials of the polyoxovanadate-alkoxide clusters were originally recorded with respect to ferrocene/ferrocenium redox couple in acetonitrile and subsequently converted potentials referenced to the NHE electrode following previously reported procedures.^{6,8}

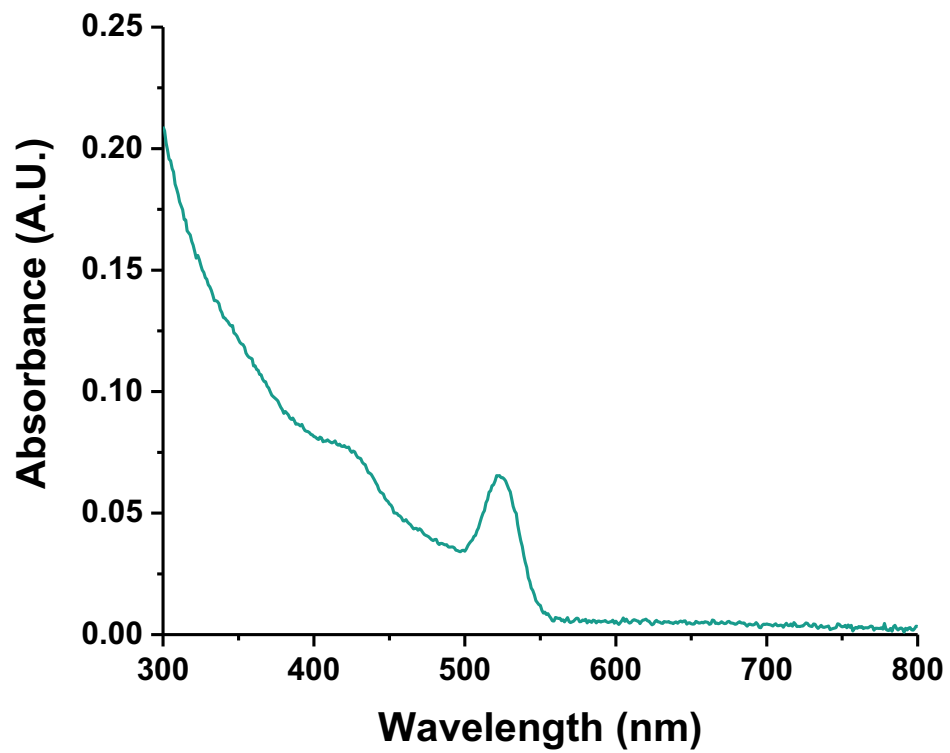


Figure S2. Representative electronic absorption spectrum of CdSe synthesized to have a first excitonic absorption of 525 nm (\pm 5 nm) coated with TOP.

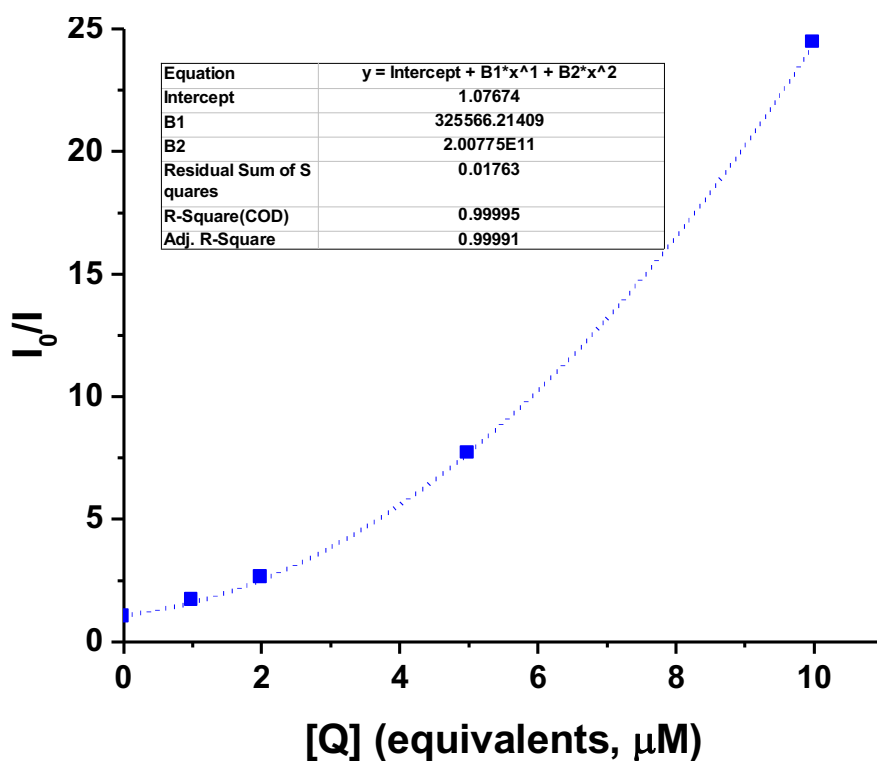


Figure S3. Stern-Volmer plot of luminescence intensity with increasing concentration of $[\text{V}_6\text{O}_7(\text{OC}_2\text{H}_5)_{12}]^{-1}$. All samples contained 1 μM CdSe-TOP QDs with 0-10 equivalents of $[\text{V}_6\text{O}_7(\text{OC}_2\text{H}_5)_{12}]^{-1}$ in dichloromethane. The blue dashed line represents a fit using a second-order polynomial with constants and R^2 -value as reported in the table above.

As illustrated in Fig. 2, the addition of 10-15 equivalents of clusters resulted in almost a complete loss of luminescence. Stern-Volmer analysis was performed in order to better understand the QD-cluster interaction. As outlined in equations S1 and S2, static and dynamic quenching, respectively, can be modeled as:

$$\frac{I_0}{I} = 1 + k_s[\text{Q}] \quad (\text{S1})$$

$$\frac{I_0}{I} = 1 + k_q\tau_0[\text{Q}] \quad (\text{S2})$$

where I and I_0 are the fluorescence intensities with and without quencher, respectively, $[\text{Q}]$ is the concentration of quencher added, k_s and k_q are the static and bimolecular quenching rates, respectively, and τ_0 is the excited state lifetime in the absence of quencher.⁹ As equations S1 and S2 demonstrate, either static *or* dynamic quenching is expected to follow a linear dependence with increasing concentration of quencher. However, if both static *and* dynamic quenching occurs in the sample, the following relation holds:

$$\frac{I_0}{I} = (1 + k_q\tau_0[\text{Q}])(1 + k_s[\text{Q}]) \quad (\text{S3})$$

In such a case, the Stern-Volmer plot is expected to be non-linear due to the second-order dependence on quencher concentration. Fig. S3 shows that the quenching data fits well to a second-order polynomial and thus supports that both static and dynamic mechanisms are present in this system.

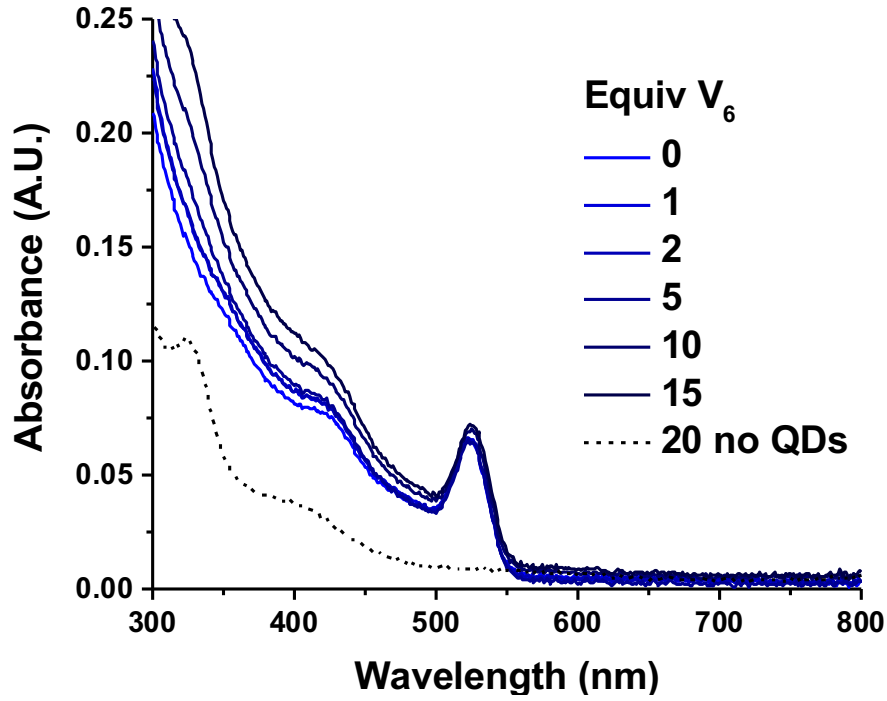


Figure S4. The absorbance spectra of CdSe-TOP with increasing concentration of $[\text{V}_6\text{O}_7(\text{OC}_2\text{H}_5)_{12}]^{-1}$ (solid blue to black) as well as $20 \mu\text{M} [\text{V}_6\text{O}_7(\text{OC}_2\text{H}_5)_{12}]^{-1}$ without QDs (dashed). All QD samples contained $1 \mu\text{M}$ CdSe-TOP QDs with 0-15 equivalents of $[\text{V}_6\text{O}_7(\text{OC}_2\text{H}_5)_{12}]^{-1}$ in dichloromethane.

As mentioned in the main text, in addition to charge transfer, energy transfer is expected to contribute to the fluorescence quenching of the QDs as there is some overlap between the emission of the QDs and absorption of $[\text{V}_6\text{O}_7(\text{OC}_2\text{H}_5)_{12}]^{-1}$ (**Figure S4**). The expected yield of energy transfer, E , can be determined as:

$$E = \frac{1}{1 + \left(\frac{r}{R_0}\right)^6} \quad (\text{S4})$$

where r is the center-to-center distance of the QDs and clusters and R_0 is the Förster distance, the distance at which energy transfer efficiency is 50% which can be estimated by:

$$R_0^6 = \frac{2.07 \cdot \kappa^2 \cdot \phi_{\text{QD}} \cdot J}{128 \pi^5 \cdot N_A \cdot n^4} \quad (\text{S5})$$

where κ^2 is the dipole orientation factor (assumed to be $2/3$ for these quasi-spherical structures), ϕ_{QD} is the fluorescence QY for the QD without cluster present (measured previously)¹⁰, N_A is Avagadro's number, n is the refractive index of DCM, and J is the spectral overlap integral in units of $\text{M}^{-1} \text{cm}^{-1} \text{nm}^4$, calculated as:

$$J = \int \overline{F_D}(\lambda) \epsilon_A(\lambda) \lambda^4 d\lambda \quad (\text{S6})$$

where $\overline{F_D}(\lambda)$ is the fluorescence of the donor with area normalized to 1, $\epsilon_A(\lambda)$ is the extinction coefficient¹¹ of $[\text{V}_6\text{O}_7(\text{OC}_2\text{H}_5)_{12}]^{-1}$ at wavelength λ . From this, we obtain an overlap of $3.97 \cdot 10^{13} \text{M}^{-1} \text{cm}^{-1} \text{nm}^4$ and a resulting R_0 of 1.96 nm. This value is quite small given the minimal cluster absorbance (**Figure 2**). Assuming the smallest center-to-center distance possible of 2.5 nm,^{5, 12} we achieve a maximum potential E of 19% which, when compared to the 40% quenching observed with 1 equivalent of cluster added (**Figure 2, inset**), reveals that the majority of quenching is due to charge transfer.

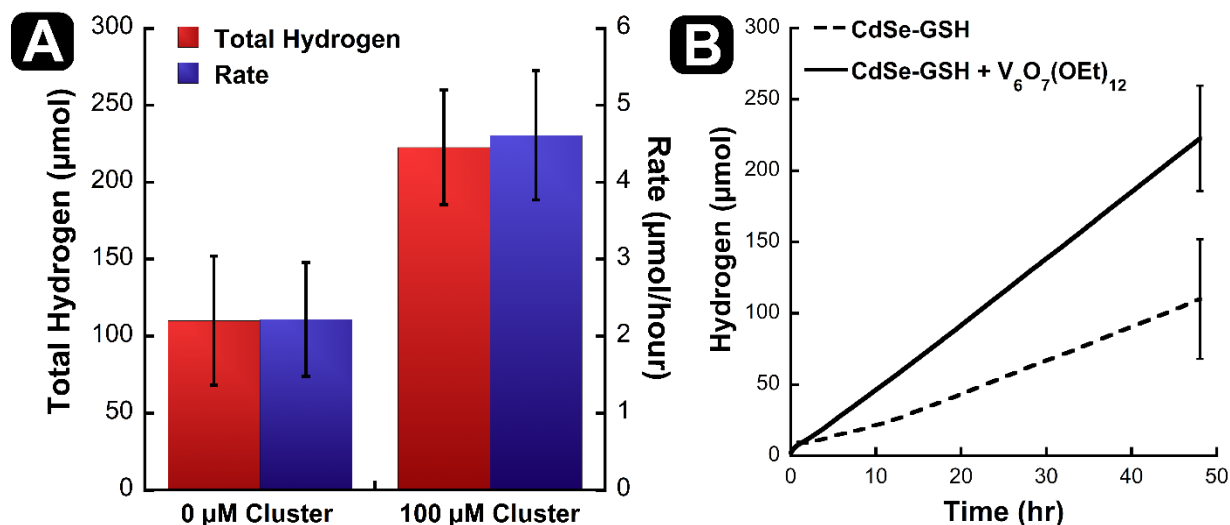


Figure S5. A) Total hydrogen production and rate assessed over 48 hours in the absence (0.5 M ascorbate, 1 μM CdSe-GSH, 1:1 EtOH:H₂O) and presence (0.5 M ascorbate, 1 μM CdSe-GSH, 1:1 EtOH:H₂O, 100 μM [V₆O₇(OEt)₁₂]⁻¹) of POV cluster (n = 3). Samples are irradiated with 530 nm light and temperature is held at 15°C over the course of the experiment. B) Hydrogen evolution over time with conditions described in (A) and total hydrogen averaged at each time point in the curve. Standard deviations at the final time point reflect the standard deviation in total hydrogen evolved at the final time point as shown in (A).

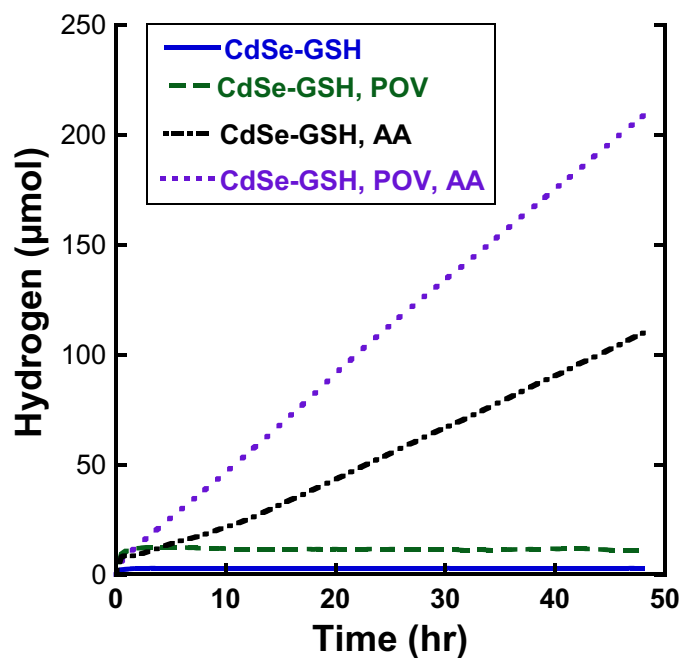


Figure S6. Control experiments in the absence of ascorbic acid are shown. Trials containing CdSe-GSH (1 μM) in the absence (blue solid line) and presence (green dashed line) of POV cluster (100 μM) in a 1:1 mixture of MeCN:H₂O, produce 3 μmol and 11 μmol of H₂, respectively. Shown for reference are representative trials of CdSe-GSH (1 μM) paired with ascorbic acid (0.5 M) and POV cluster (100 μM) in a 1:1 mixture of EtOH:H₂O as discussed in the main text and Figure S5.

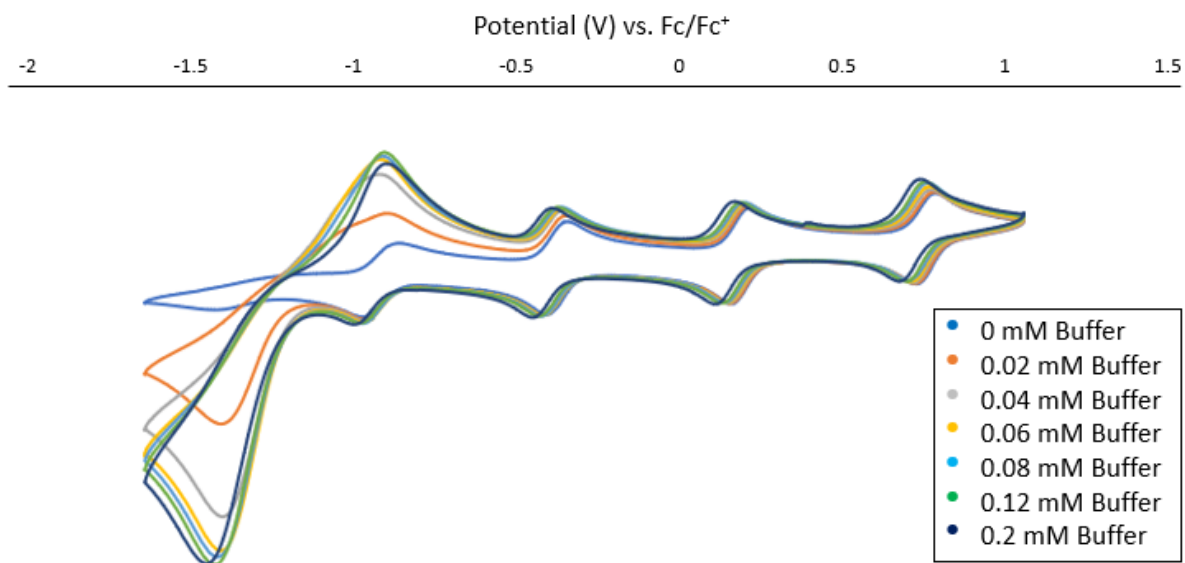


Figure S7. Comparison of CV of $V_6O_7(OEt)_{12}$ as pH 6 phosphate buffer (40 mM) is titrated into solution. 1 mM cluster with: 0 mM buffer (blue), 0.02 mM buffer (orange), 0.04 mM buffer (gray), 0.06 mM buffer (yellow), 0.08 mM buffer (teal), 0.12 mM buffer (green), 0.2 mM buffer (navy). All samples are run with 0.1 M $TBAPF_6$ as supporting electrolyte, potential is corrected against the Fc/Fc^+ couple.

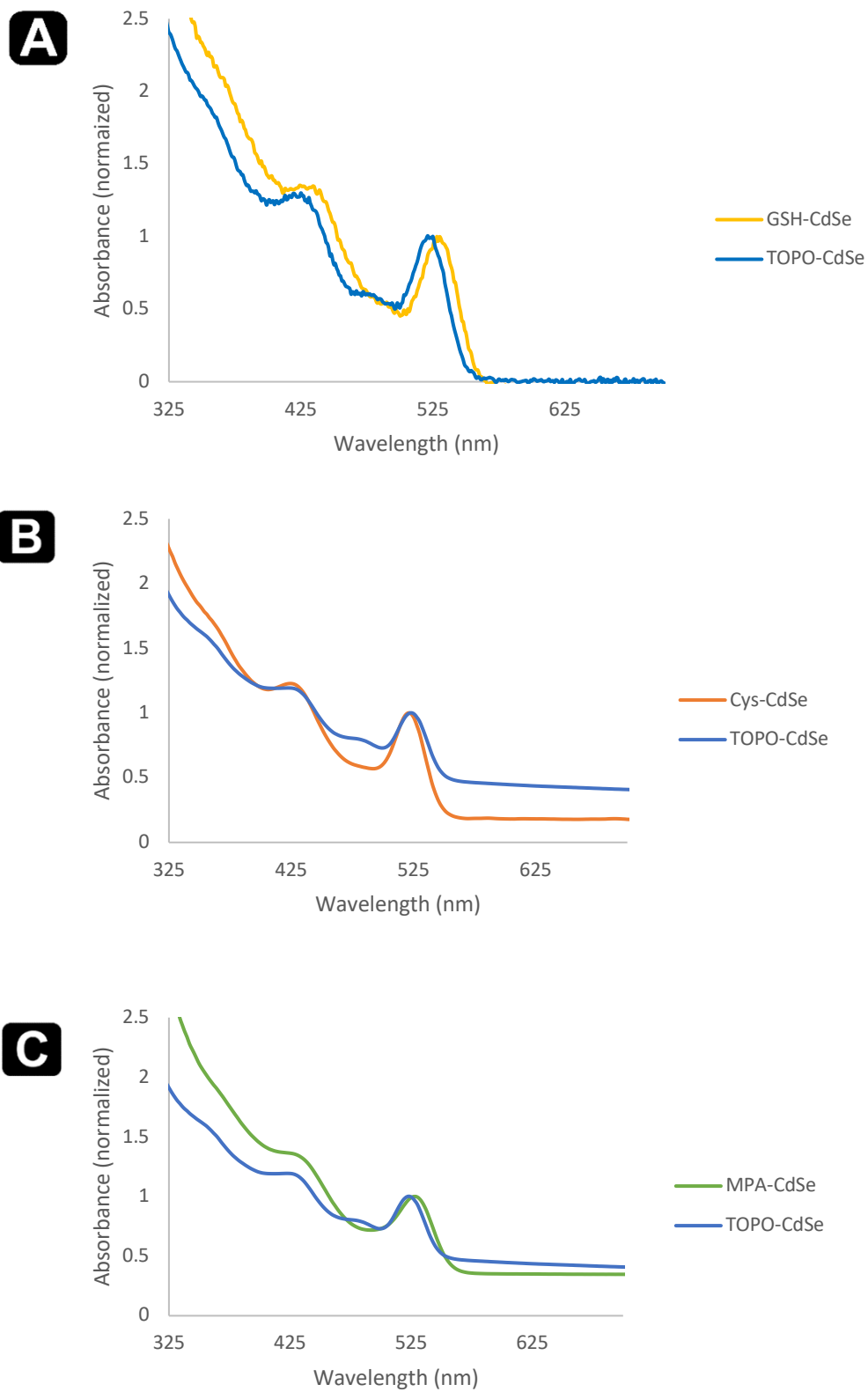


Figure S8. Electronic absorption spectra of CdSe after exchanging TOPO for A) GSH, B) Cys, and C) MPA

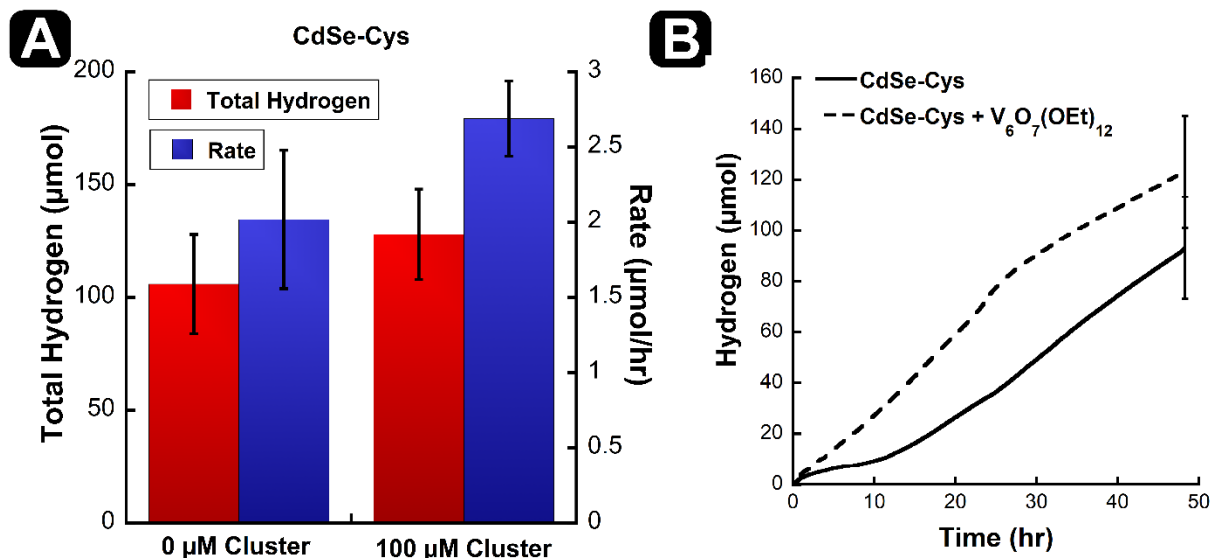


Figure S9. A) Total hydrogen production and rate assessed over 48 hours in the absence (0.5 M ascorbate, 1 μM CdSe-Cys, 1:1 EtOH:H₂O) and presence (0.5 M ascorbate, 1 μM CdSe-Cys, 1:1 EtOH:H₂O, 100 μM [V₆O₇(OEt)₁₂]⁻¹) of POV cluster (n = 3). Samples are irradiated with 530 nm light and temperature is held at 15°C over the course of the experiment. B) Hydrogen evolution over time with conditions described in (A) and total hydrogen averaged at each time point in the curve. Standard deviations at the final time point reflect the standard deviation in total hydrogen evolved at the final time point as shown in (A).

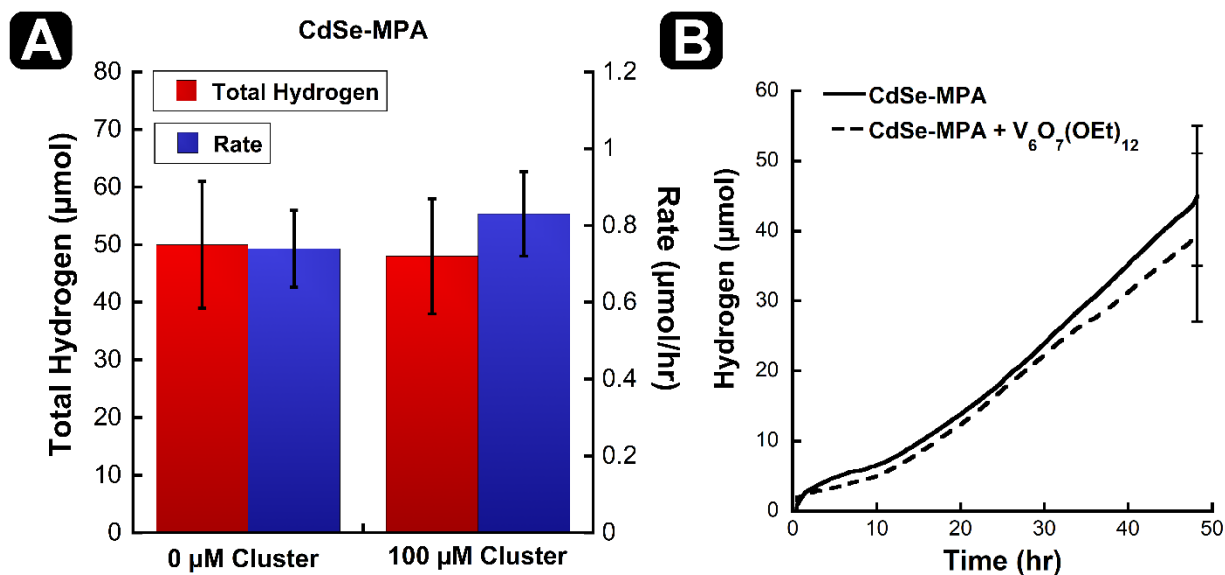


Figure S10. A) Total hydrogen production and rate assessed over 48 hours in the absence (0.5 M ascorbate, 1 μM CdSe-MPA, 1:1 EtOH:H₂O) and presence (0.5 M ascorbate, 1 μM CdSe-MPA, 1:1 EtOH:H₂O, 100 μM [V₆O₇(OEt)₁₂]⁻¹) of POV cluster (n = 3). Samples are irradiated with 530 nm light and temperature is held at 15°C over the course of the experiment. B) Hydrogen evolution over time with conditions described in (A) and total hydrogen averaged at each time point in the curve. Standard deviations at the final time point reflect the standard deviation in total hydrogen evolved at the final time point as shown in (A).

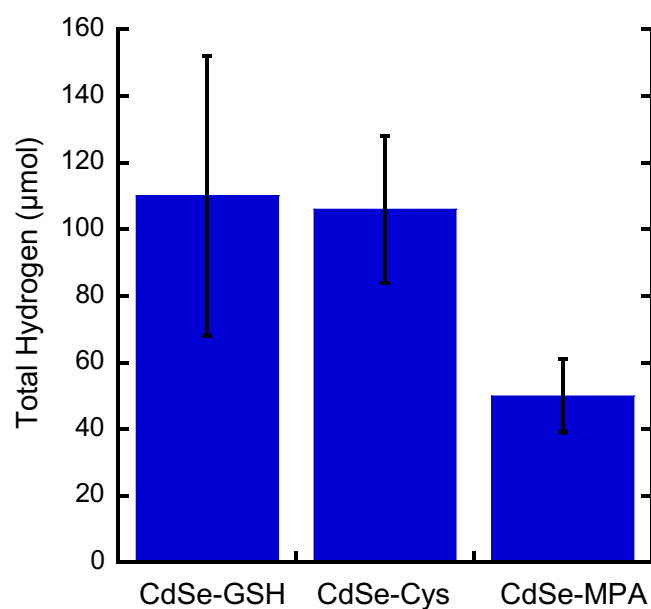


Figure S11. A comparison of the total of hydrogen evolved after 48 hours from CdSe QDs (1 μM) capped with different ligands, GSH, Cys, and MPA in the presence of 0.5 M ascorbate in a 1:1 EtOH:H₂O mixture irradiated with 530 nm light at 15°C (n = 3).

Quantum Yield Measurements

The quantum yield for hydrogen generation was calculated as previously reported.² Quantum yield (Φ_{H_2}) is equal to the amount of H_2 produced relative to the number of photons absorbed.

$$\Phi_{H_2} = 2 \frac{k}{q_p} \quad (S7)$$

This equation accounts for the two photons used to produce one mole of hydrogen. The rate of H_2 production is k , and q_p is the photon flux.

$$k = \frac{H_2(mol)}{t(s)} \quad (S8)$$

To calculate k , the moles of H_2 produced are divided by the time of the experiment.

$$q_p = \frac{n(mol)}{t(s)} = \frac{P_{abs} \times \lambda}{c \times h \times A} \quad (S9)$$

$$P_{abs} = P_0 - P_{QD} \quad (S10)$$

Photon flux, q_p , measures the moles of photons per second. It can be calculated by relating this equation to the power absorbed during the experiment. P_{abs} (W), power absorbed, was calculated by subtracting the power when quantum dots were present, PQD, from the initial power of the LED, P_0 , measured by a Newport power meter (Model 1918-C) as described in the experimental methods. λ is the wavelength measured (525 nm), c is the speed of light (m/s), h is Planck's constant (J s), and A is Avogadro's constant (mol^{-1}). The uncertainty in each quantum yield calculation (example following) is representative of standard deviations from three concurrent reactions.

Example Calculation:

H_2 Generated in 48 Hours: $98 \mu mol = 9.8 \times 10^{-5} mol$

Time: 48 hours = 172,800 seconds

Power Absorbed: 0.0028 W

Wavelength: 525 nm

$$k = \frac{H_2(mol)}{t(s)} = \frac{(9.8 \times 10^{-5} mol)}{172,800 s} = 5.7 \times 10^{-10} mol/s$$

$$q_p = \frac{[(0.0028 \frac{J}{s}) \times (525 \times 10^{-9} m)]}{[(3 \times 10^8 \frac{m}{s}) \times (6.626 \times 10^{-34} Js) \times (6.022 \times 10^{23} mol^{-1})]}$$

$$= 1.23 \times 10^{-8} mol/s$$

$$\Phi_{H_2} = \frac{2 \times (5.7 \times 10^{-10} mol/s)}{(1.23 \times 10^{-8} mol/s)}$$

$$\Phi_{H_2} = 9.3 \%$$

Quantum Yield Calculation Results Tabulated:

[Quantum Dot]	[Cluster] (μM)	k (mol/s)	P_{abs} (W)	QY
CdSe-GSH, 1 μM	0	6.37×10^{-10} ($\pm 2.4 \times 10^{-10}$)	0.0036 (± 0.0007)	8.0% ($\pm 2.4\%$)
CdSe-GSH, 1 μM	100	1.29×10^{-10} ($\pm 2.1 \times 10^{-10}$)	0.0033 (± 0.0003)	18% ($\pm 4.5\%$)
CdSe-Cys, 1 μM	0	5.86×10^{-10} (1.49×10^{-10})	0.0054 (± 0.0009)	4.9% ($\pm 1.3\%$)
CdSe-Cys, 1 μM	100	7.04×10^{-10} ($\pm 8.53 \times 10^{-11}$)	0.0067 (± 0.001)	5.0% ($\pm 1.6\%$)
CdSe-MPA, 1 μM	0	2.87×10^{-10} ($\pm 6.71 \times 10^{-11}$)	0.0091 (± 0.0006)	1.4% ($\pm 0.3\%$)
CdSe-MPA, 1 μM	100	2.74×10^{-10} (5.22×10^{-11})	0.0082 (± 0.002)	1.7% ($\pm 0.7\%$)

Total Hydrogen and TON Tabulated:

[Quantum Dot]	[Cluster] (μM)	Total H_2 (μmol)	TON (per nanocrystal)
CdSe-GSH, 1 μM	0	110 ± 42	$22,000 \pm 8,400$
CdSe-GSH, 1 μM	100	222 ± 37	$44,600 \pm 7,400$
CdSe-Cys	0	106 ± 22	$21,200 \pm 4,400$
CdSe-Cys	100	128 ± 20	$25,600 \pm 4,000$
CdSe-MPA	0	50 ± 11	$10,000 \pm 2,200$
CdSe-MPA	100	48 ± 10	$9,600 \pm 2,000$

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