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Supporting Information:

Light-Driven Hydrogen Production with CdSe Quantum Dots and a Cobalt Glutathione Catalyst

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Electrochemical Investigation of $Co_x(MPA)_y$

Materials and Methods

Chemicals: All chemicals and solvents were used without further purification unless otherwise stated. Tri-n-octylphosphine (TOP, 97%), selenium shot (≥99.99%), tetradecylphosphonic acid (TDPA, 97%), trioctylphosphine oxide (TOPO, 99%), hexadecylamine (HDA, 98%), L-glutathione reduced (GSH, 98%), 3-mercaptopropionic acid (MPA, ≥99%), tetramethylammonium hydroxide pentahydrate (≥97%), α-lipoic acid (>99%), nickel chloride ($NiCl_2$, 98%), and TraceSelect nitric acid (HNO_3, ≥69.0%) were all purchased from Sigma-Aldrich. Anhydrous cadmium acetate ($Cd(acetate)_2$, 99.9%) was purchased from Strem Chemical Company, Inc. Acetone, hexanes, methanol, chloroform, ethyl acetate, ethyl ether, sodium borohydride, dichloromethane, and magnesium sulfate were purchased from Fisher Scientific. Sodium bicarbonate and ascorbic acid (AA) were purchased from EMD Chemicals, Inc. Cobalt chloride hexahydrate ($CoCl_2 \cdot 6H_2O$, 98.0 – 102.0 %) and sodium hydroxide (NaOH, 99%) were purchased from JT Baker, and hydrochloric acid (HCl) was from BDH chemicals. Pure ethanol (200 proof) was purchased from Koptec. The following analytical inductively coupled plasma-mass spectrometry (ICP-MS) standards in dilute HNO_3 were purchased from Inorganic Ventures: 10 ppm cadmium, 10 ppm cobalt, and 10 ppm indium.

CdSe Quantum Dot (QD) Synthesis: CdSe QDs were synthesized by a procedure modified from Talapin *et al.*[1] Prior to synthesis, Cd-TOP and TOP-Se were prepared in an inert glovebox. A solution of 1 M TOP-Se was made by mixing 0.32 g Se pellets and 4 mL TOP in the glovebox. Cd-TOP (0.28 M) was prepared by mixing 0.38 g $Cd(acetate)_2$ and 6 mL TOP. The solutions were stirred overnight at 60 °C, until clear and colorless.

In a 100 mL, 3-neck flask, the following were combined: 0.17 g TDPA, 2.3 g HDA, and 7.7 g TOPO. The mixture was degassed for 30 minutes at 100 °C by evacuating the flask to a pressure below 30 mT. Under N_2 atmosphere, 1.8 mL of the prepared TOP-Se solution was added to the flask, and the mixture was heated to 310 °C. Next, 2.5 mL Cd-TOP was swiftly injected into the flask, and the temperature was immediately cooled to 260 °C. The QDs were allowed to grow for 6-7 minutes, at which point the flask was cooled to room temperature with cool air to quench the reaction. The crude reaction mixture was divided between 2- 50 mL falcon tubes. To each tube, 5 mL hexanes, 25 mL acetone, and 10 mL methanol were added. The QDs were centrifuged for 15 min, and the clear, colorless supernatant was discarded. The resulting QD pellets were suspended in 5 mL hexanes. To remove residual TOPO, the QDs were centrifuged for 10 minutes, and then, the clear supernatant with CdSe QDs was decanted and saved. The resulting QD colloid was stored in a glovebox under N_2 until use. Prior to photocatalysis experiments, the native organic ligands were exchanged with GSH, MPA, or dihydrolipoic acid (DHLA), conferring water-solubility to the QDs.

CdSe-GSH Ligand Exchange: First, a solution of GSH (0.5 g), NaOH (0.4 g), and methanol (20 mL) was stirred vigorously 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 N_2 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.*[2]

CdSe-MPA Ligand Exchange: The MPA ligand exchange procedure was adapted from Zhang, *et al.*[3] First, 75 nmol of CdSe QDs in hexanes were added to a 50 mL falcon tube, and additional hexanes were added to a total volume of 5 mL. 20 mL methanol was added, and the mixture was centrifuged for 15 minutes, precipitating the QDs from solution. After the clear, colorless supernatant was discarded, the QD pellet was resuspended in 6 mL chloroform. A separate solution with 85 μL MPA, 250 μL nanopure water, and 830 μL methanol was adjusted to pH 11 with the addition of 20% NaOH (290 μL). The QD colloid in chloroform and MPA solution were combined and stirred at 600 RPM for 35 minutes under ambient conditions. Then, 8.5 mL nanopure water was added, and the solution was stirred for an additional 20 minutes at 800 RPM. Following stirring, the solution separated into two phases, and the top aqueous layer containing MPA-capped CdSe QDs was decanted and transferred to a 50 mL falcon tube, and 35 mL acetone was added. The mixture was centrifuged for 20 minutes, precipitating the QDs. The clear, colorless supernatant was decanted, and the QD pellet was resuspended in 300-500 μL of nanopure water.

Optical QD Characterization: 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.*[4] Photoluminescence (PL) spectra were measured with a modular fluorometer system (Acton Research) with a photomultiplier tube detector.

Transmission Electron Microscopy (TEM): For TEM, QD samples were spotted on lacey carbon grids with 300 mesh copper supports (Ted Pella, Inc.). All micrographs were recorded on a FEI Tecnai F-20 field emission microscope with a 200 kV accelerating voltage.

Energy Dispersive X-Ray (EDX) Spectroscopy: All EDX spectra were recorded with FEI Tecnai F-20 field in scanning-transmission electron microscopy (STEM) mode.

Photocatalytic H_2 Production: H_2 evolution experiments were performed as described previously.[5-7] Briefly, in a 40-mL scintillation vial, CdSe QDs (1 μM), $CoCl_2 \cdot 6H_2O$ (1 μM), and AA (0.5 M) were combined in 5 mL of water, and the pH was adjusted to 4.5 by the addition of NaOH. Vials were fitted with septum caps, each with a pressure transducer to monitor changes in the headspace pressure in real time, and the sample block was cooled to 15 °C. After purging vials with a gas mixture of N_2/CH_4 (79:21) to 1 atm, each vial was illuminated from below by a light-emitting diode (Philips LumiLED Luxeon Star Hex green 700 mA LEDs) at 525 nm. The LED power was set to 21 ± 2 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, and pressure changes were recorded with a free scale semiconductor sensor (MPX4259A series). After 48 hours of illumination, the amount of H_2 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 H_2 evolved was quantified with a calibration curve, using CH_4 as an internal standard. Uncertainty reported in the manuscript for both H_2 generation and turnover numbers were determined by the standard deviation of 10 measurements for experiments with CdSe-GSH and 6 measurements for experiments with CdSe-MPA. These experiments utilized CdSe QD samples from multiple syntheses and ligand exchanges.

Determination of External Quantum Yield (QY) for H_2 Production: The external QY for hydrogen production (Φ_{H2}) describes the amount of H_2 produced relative to the number of photons absorbed by the QDs, taking into account the two photons required for the formation of one H_2 molecule. k describes the rate of H_2 production (moles of H_2 per second), and q_p describes the photon flux.

$$\Phi_{H_2} = \frac{2k}{q_p} \tag{S1}$$

The photon flux (moles of photons per second) was calculated using the following equation:

$$q_p = \frac{n}{t} = \frac{P_{abs} \times \lambda}{c \times h \times A} \tag{S2}$$

λ, in units of meters, is taken to be the wavelength of light from the LED source (525 nm), c is the speed of light, h is Planck's constant, and A is Avogadro's number. The power of light absorbed by the QDs, P_{abs}, was determined by relating absorbance to transmittance with Beer's law to determine the power of light exiting the sample (P_f) following illumination:

$$A_{525} \times b = log_{10}\frac{P_0}{P_f} \tag{S3}$$

Which can be rearranged to

$$P_f = \frac{P_0}{10^{A_{525} \times b}} \tag{S4}$$

A_{525} is the absorbance of 1 μM CdSe QDs at 525 nm and b is the path length in centimeters. P_0 describes the initial power of the LED illumination source, which was measured as described in the Experimental Methods section of the manuscript. Then, the difference between P_0 and P_f, was calculated, giving P_{abs}:

$$P_0 - P_f = P_{abs} \tag{S4}$$

The reported external QY for H_2 production was determined after 48 hours of illumination, and the uncertainty was estimated from the standard deviation of 10 experiments. A sample calculation is shown below.

Sample calculation for a photocatalysis cell containing 1 μM CdSe-GSH and 1 μM $CoCl_2$:

Moles of H_2 generated = 0.000566 mol
t (time) = 48 hours = 172,800 sec
P_0 = 26.2 mW
A_{525} = 0.082145
b = 1 cm
λ = 525 nm

$$k = \frac{H_2(mol)}{t(s)} = \frac{0.000566}{172800} = 3.28 \times 10^{-9} mol/s$$

$$P_f = \frac{P_0\,(W)}{10^{A_{525} \times b}} = \frac{0.0262}{10^{0.082145 \times 1}} = 0.0217\ W$$

$$P_{abs} = P_0 - P_f = 0.0262 - 0.0217\ W = 0.0045\ W = 0.0045 \frac{J}{s}$$

Then, by combining equations S1 and S2:

$$\Phi_{H_2} = \frac{2k}{q_p} = \frac{2k \times c \times h \times A}{P_{abs} \times \lambda}$$

$$\Phi_{H_2} = \frac{2\left(3.28 \times 10^{-9} \frac{mol}{s}\right) \times \left(3 \times 10^{8} \frac{m}{s}\right) \times (6.63 \times 10^{-34} J \cdot s) \times \left(6.022 \times 10^{23} \frac{1}{mol}\right)}{\left(0.0045\ \frac{J}{s}\right) \times (5.25 \times 10^{-7} m)} = 33.1\%$$

Photocatalysis Redispersion Experiment: To determine if the active Co catalyst is on the QD surface or free in solution, a redispersion photocatalysis experiment was completed. First, a photocatalysis experiment was run under the following conditions: 1 μM CdSe-GSH, 1 μM $CoCl_2$, 0.5 M AA, pH 4.5 for 48 hours (λ_{ex}=525 nm). After the headspace of each vial was sampled via GC, the contents of each vial were transferred to a centrifuge tube, and the samples were centrifuged for 10 minutes. Then, the clear supernatant was carefully decanted and filtered with a 0.5 μm syringe filter. The precipitated pellet containing QDs was allowed to dry before resuspending in nanopure water. Once separated, both the collected supernatant solution QD pellets were prepared as described below.

The separated supernatants were prepared for a photocatalysis experiment under two sets of experimental conditions. First, fresh AA (0.5 M) was added to the separated supernatant (5 mL), and the pH was adjusted to 4.5 with a 10 M solution of NaOH. In another vial, both fresh AA and 1 μM CdSe-GSH QDs were added to the separated supernatant. Likewise, the resuspended CdSe QD pellets were also prepared under two different experimental conditions, both to a total volume of 5 mL: (1) with the addition of only fresh AA (0.5 M), pH 4.5 and (2) with the addition of both AA (0.5 M) and fresh $CoCl_2$ (1 μM), pH 4.5. With the four experimental conditions described above, a photocatalysis experiment was run for 48 hours under illumination (λ_{ex}=525 nm). At the conclusion of the experiment, the amount of H_2 evolved was again quantified by GC analysis. Uncertainty values reported in the manuscript were determined by the standard deviation of 2-3 measurements, all following a single QD synthesis and ligand exchange to GSH.

ICP-MS: After photocatalysis, ICP-MS was used to quantify the amount of cadmium and cobalt in both the supernatant and precipitated QD pellet. Because of the concentration requirements for ICP-MS analysis, the standard photocatalysis conditions were adjusted as follows: 1 μM CdSe-GSH, 7 μM $CoCl_2$, and 0.01 M AA, pH 4.5. The total solution volume for each vial was 5 mL. After 48 hours of irradiation with 525 nm LEDs, the samples were prepared for ICP-MS by first combining the contents two identical experiment vials in a 50 mL falcon tube, for a total volume of 10 mL. Then, 30 mL of ethanol was added to the falcon tube, and the sample was centrifuged at 4500 RPM until the QDs precipitated from solution. The clear, colorless supernatant was transferred to a clean falcon tube, and the QD pellet was gently dried with a warm sand bath, until any trace solvent was evaporated. To prepare the supernatant solution for ICP-MS, the solvent was evaporated under N_2 flow with gentle heating in a water bath at approximately 90 °C. Then, the falcon tube was set in a warm sand bath to evaporate any final traces of solvent.

Once both the supernatant and QD pellet were dried thoroughly. The samples were digested in 200 µL of concentrated HNO_3 for 2 days. Once completely digested, the samples were diluted with nanopure water to a 2% HNO_3 concentration. These samples were then diluted for ICP-MS in a 2% HNO_3 stock solution and spiked with a small concentration of indium. The amount of cadmium and cobalt was quantified with a calibration curve. The calibration curve standards were prepared in a 2% HNO_3 matrix with cobalt, cadmium and indium standards. In both the samples and standards, indium served as an internal standard.

***Ex situ* Catalyst Preparation and Characterization:** Ex *situ* catalyst formation was done by combining 2 mL of 20 mM $CoCl_2.6H_2O$ in water (adjusted to pH 4.5, the pH at which photocatalysis is run, with 100 mM HCl) and 4 mL of 20 mM ligand (GSH or MPA) in water (adjusted to pH 4.5 with 1 M NaOH) in a closed vial. These samples were prepared under N_2, and the mixture was stirred for 48 hours. UV-Vis absorption spectra of the resulting complexes were taken in a quartz cell using a Shimadzu UV-2401PC Spectrophotometer.

An attempt was made to purify the resulting cobalt GSH complexe ($Co_x(GSH)_y$) by adapting a procedure previously used for a cobalt tripeptide complex, $Co(III)GGH(H_2O)_2$.[8] A light brown solution obtained after mixing $CoCl_2$ and GSH for 48 hours, as described above, was lyophilized, yielding a brown solid. This product was redissolved in ~1 mL of water and was subsequently chromatographed on a Bio-Gel P2 resin (Bio-Rad) loaded in a 1.2 x 12 column with water as the eluent. Fractions were collected in 800-1000 µL volumes. A similar procedure was run on the $Co_x(MPA)_y$ complex. As described in the main text, gel filtration altered the catalytic activity of the reaction mixtures, indicating that even this gentle purification method perturbed the active catalytic speices.

Electrochemical Methods: Cyclic voltammetry (CV) measurements were performed on a CH Instruments electrochemical analyzer (CHI620D). A three-electrode configuration was used, consisting of a platinum wire counter electrode (CH Instruments), Ag/AgCl (1 M KCl) reference electrode (CH Instruments), and a hanging mercury drop working electrode (HMDE) from BASi. All CV measurements were completed in 5 mL solutions of 0.5 M AA with 1 M KCl in water at pH 4.5, which was adjusted by the addition of 5 M NaOH. For both the crude complexes ($Co_x(GSH)_y$ and $Co_x(MPA)_y$), which were lyophilized and redissolved in ~1 mL of water, and the $Co_x(GSH)_y$ fractions collected from the P2 size-exclusion column, the sample concentrations were unknown. However, the fractions were considerably more dilute compared to the crude samples. All measurements were performed under N_2, and all potentials are reported vs. Ag/AgCl (1 M KCl), unless otherwise specified.

Constant potential electrolysis (CPE) experiments were performed using a 620E potentiostat. In a three-compartment cell, Ag/AgCl (1 M KCl) served as a reference electrode, a glassy carbon rod was the counter electrode, and mercury (surface area of approximately 1.5 cm^2 and using an insulated platinum wire as an electrode lead) was the working electrode. The electrodes were separated by glass frits (P5 porosity with 1.0 - 1.6 µm pores). A total of 5 mL of solution containing 0.5 M AA and 1 M KCl in water at pH 4.5 was added to each compartment. The cell was purged with 80% N_2/20% CH_4 prior to electrolysis experiments. The CH_4 served as an internal standard for gas chromatography (GC) detection.

The equation used for Faradaic efficiency calculations is as follows:

$$Faradaic\ efficiency\ (\%) = \frac{96485\,\frac{C}{mol} \times 2 \times mol\ H_2\ (GC) \times 100\%}{Q_T\ (CPE)}$$

To calculate moles of H_2 formed, known amounts of H_2 were injected into GC to develop a calibration curve based on the ratio of H_2:CH_4. This ratio was linearly correlated to the amount of H_2.

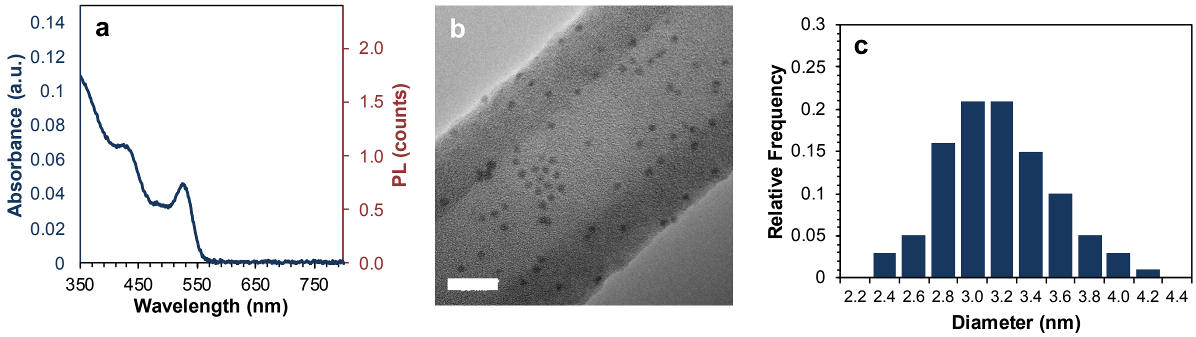


Figure S1. Absorbance and PL spectra of CdSe QDs (a) directly after synthesis show well-defined first exciton absorbance and emission features. The corresponding brightfield TEM (b) and histogram (c) show an average QD diameter of 3.26 ± 0.37 nm, determined by measuring 100 particles. The scale bar in (b) is 20 nm.

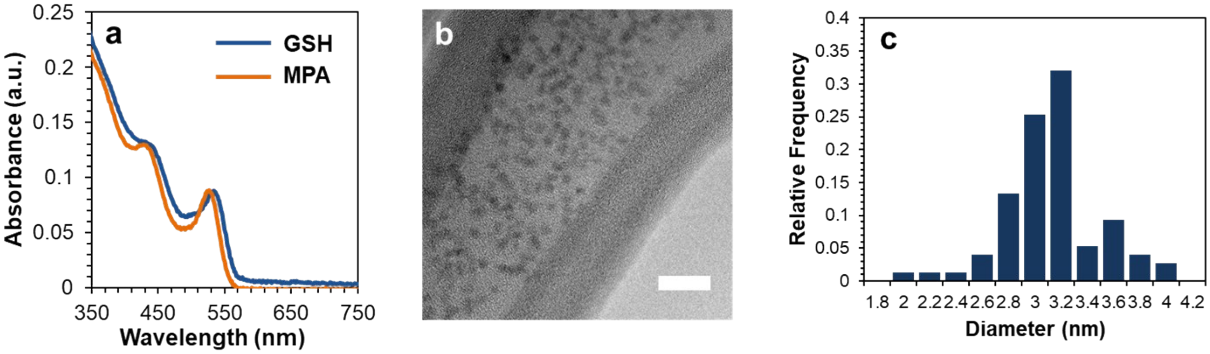


Figure S2. Absorbance spectra of CdSe-GSH and CdSe-MPA QDs (a) directly after ligand exchange. The corresponding brightfield TEM (b) and histogram (c) show an average QD diameter of 3.22 ± 0.36 nm from the average measurement of 75 nanoparticles. The scale bar in (b) is 20 nm.

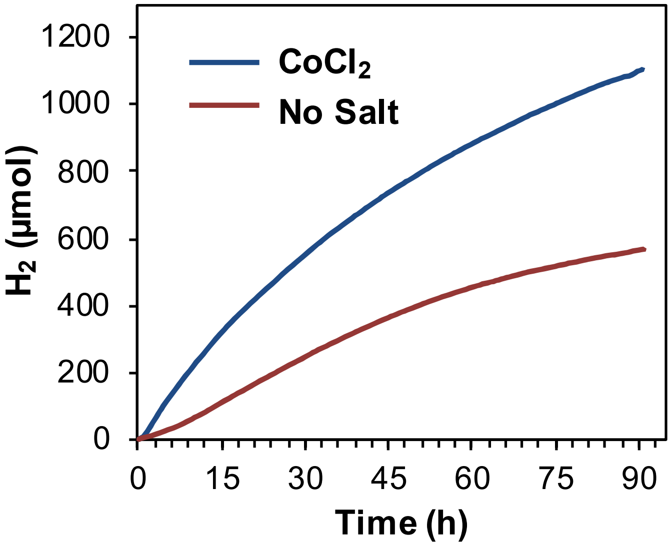
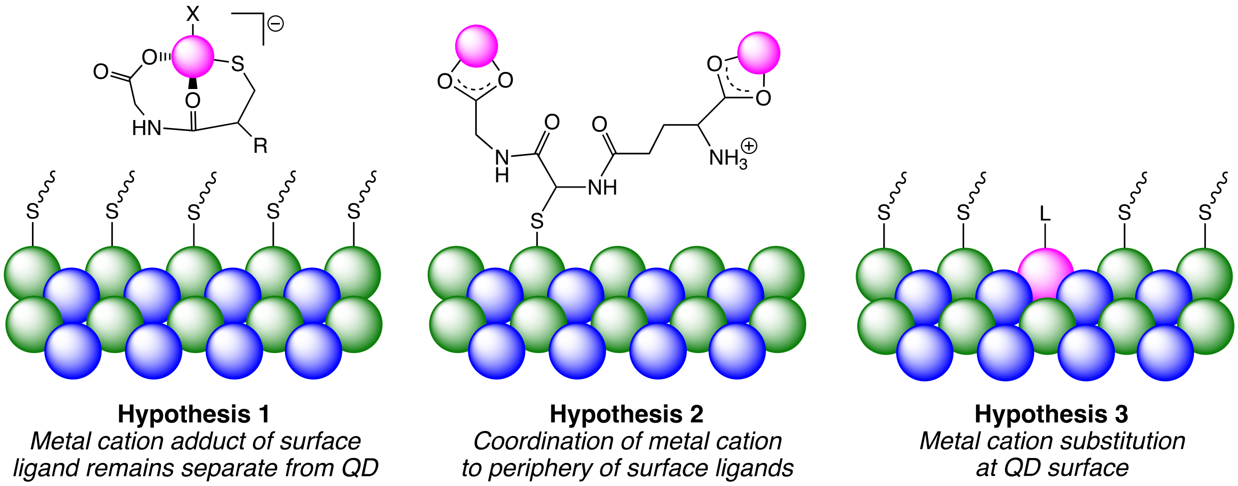


Figure S3. Photocatalytic H_2 generation over 91 h with CdSe-GSH QDs (1 µM) and AA (0.5 M) with the addition of $CoCl_2$ (1 µM, blue) or no added metal salt (red) in water, pH 4.5 (λ_{ex}=525 nm).



Hypothesis 1
Metal cation adduct of surface ligand remains separate from QD

Hypothesis 2
Coordination of metal cation to periphery of surface ligands

Hypothesis 3
Metal cation substitution at QD surface

Figure S4. Proposed modes for interaction of cobalt ions with CdSe-GSH quantum dots. Note that many metal-ligand coordination modes are possible and the drawn binding modes represent potential methods for interaction.

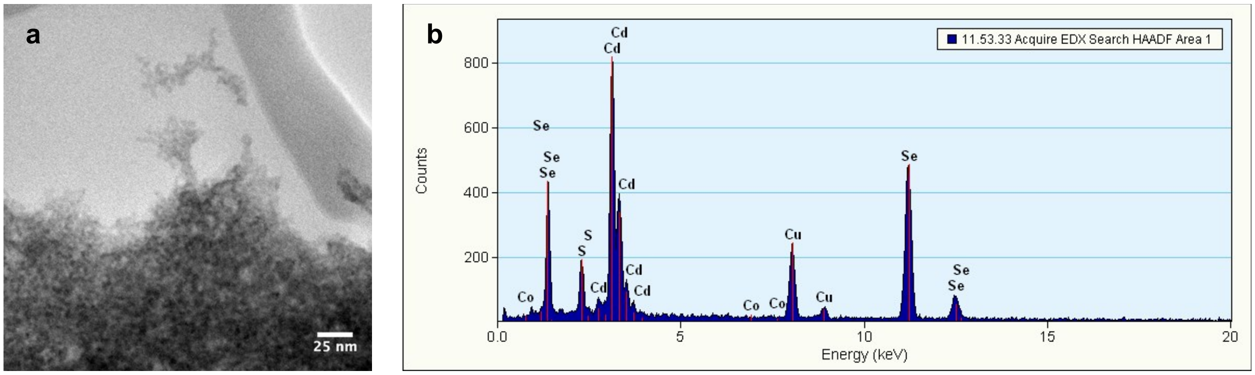


Figure S5: Brightfield TEM of CdSe-GSH QDs after photocatalysis under standard conditions in the presence of $CoCl_2$ (a). While QDs do show signs of aggregation following photocatalysis, the micrograph shows no signs of Co particle formation around or on the QD surface. (Scale bar is 25 nm). The corresponding EDX spectrum (b) shows negligible Co signal, while both Cd and Se signals are strong, as expected from the QDs. SI Table 1 provides the corresponding average weight percent for each element. Cu signal is observed from the Cu TEM grids.

Table S1. Average Weight Percent for Co, Cd, Se, and Cu in CdSe-GSH QDs after Photocatalysis

Element (X-Ray)	Average Wt. Percent
Co (K)	0.10%
Cd (L)	23.6%
Se (K)	32.5%
Cu (K)	12.4%

Following photocatalysis, CdSe-GSH QD samples were analyzed by EDX spectroscopy. The values reported here are the average weight percent for Co (K), Cd (L), Se (K), and Cu (K) characteristic x-rays. Values were averaged over 13 measurements. As shown, the Co (K) signal is significantly small, suggesting the active Co catalyst species is likely not on the QD surface. The observed Cu signal is from the TEM grids.

Table S2. Co and Cd Concentrations Found in the QD Pellet and Supernatant

Sample	[Co] ppm	[Cd] ppm	% Total Co	% Total Cd
QD Pellet	0.0078	10.8679	2.4%	98.1%
Supernatant	0.3249	0.2145	97.6%	1.9%

ICP-MS analysis on the separated QD pellet and supernatant following photocatalysis reveal that 98.1 % of the Cd was detected in the QD pellet, while 97.6% of the Co was detected in the supernatant. This result strongly supports a freely diffusing, solution-based cobalt catalyst in the photocatalytic system. Samples were prepared as described in the Materials and Methods section.

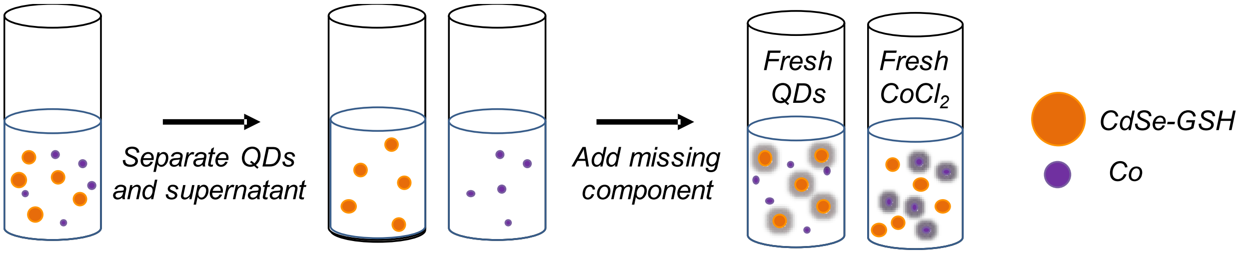


Figure S6. Illustration of the CdSe QD redispersion experiment described in the Materials & Methods. Following 48 h of illumination, the photocatalytic solution containing CdSe-GSH and $CoCl_2$ is separated via centrifugation. The supernatant is collected, and the resulting QD pellet is resuspended in water. These samples are illuminated for 48 h, and the H_2 generation is measured via GC. Additionally, either the fresh CdSe-GSH QDs are added to the separated supernatant *or* fresh $CoCl_2$ is added to the resuspended QDs, and the photocatalytic activity of these solutions are tested, as well.

Table S3. Experimental Conditions and Yields of H_2 for the Photocatalysis Redispersion Experiment

Sample	Contents	H_2 (μmol)
Before Separation		
$CoCl_2$	CdSe-GSH (1 μM), $CoCl_2$ (1 μM), AA (0.5 M)	428
QDs (No Salt)	CdSe-GSH (1 μM), AA (0.5 M)	98
After Separation		
QD pellet & AA	Redispersed QDs, AA (0.5 M)	82
Supernatant & AA	Separated solution, AA (0.5 M)	0
QD pellet, fresh $CoCl_2$, AA	Redispersed QDs, $CoCl_2$ (1 μM), AA (0.5 M)	222
Supernatant, fresh QDs, AA	Supernatant, CdSe-GSH (1 μM), AA (0.5 M)	194

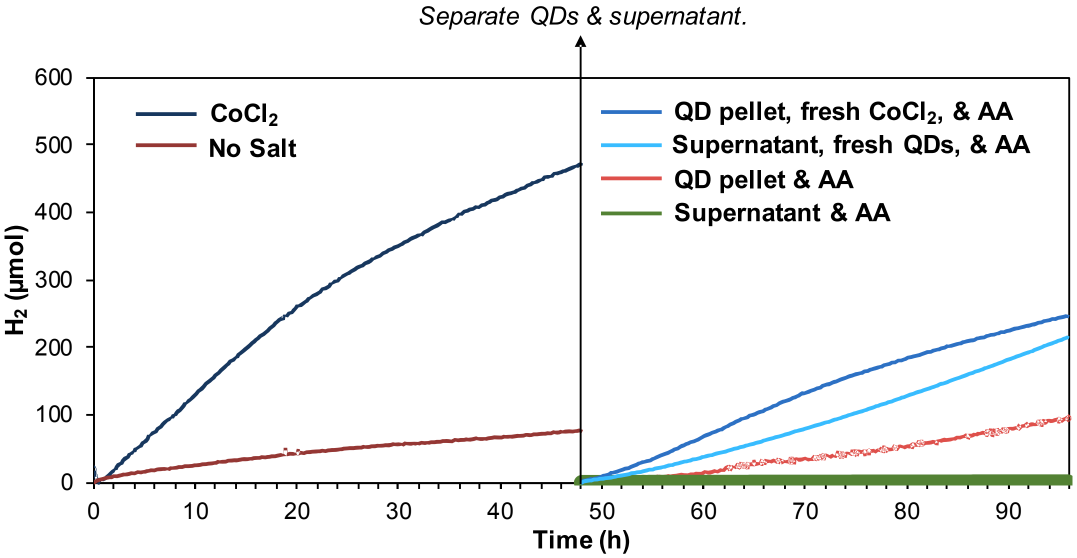


Figure S7: Photocatalytic H_2 production before (*left*) and after (*right*) separation and redispersion. As shown, only the systems with both the CdSe-GSH QDs and a Co^{2+} salt or supernatant (blue curves) exhibit yields of H_2 greater than the baseline H_2 production from CdSe-GSH QDs alone (red and orange curves). This behavior is consistent with a freely diffusing, molecular proton reduction catalyst.

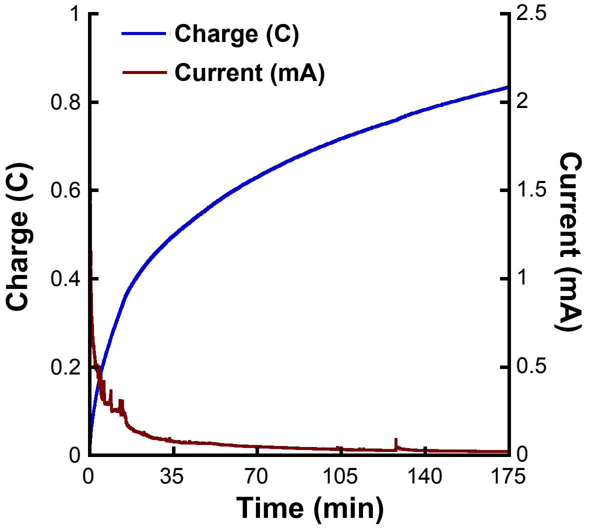


Figure S8: Controlled potential electrolysis at −1.10 V vs Ag/AgCl (1 M KCl) over 175 minutes of 333 µM $CoCl_2$ and 666 µM GSH ("$Co_x(GSH)_y$") in 0.5 M AA/1 M KCl in water, pH 4.5. The experiment was carried out under a nitrogen atmosphere in the presence of methane (80% N_2/20% CH_4). The total accumulated charge is shown as a blue line (left axis) and the current is shown as a red line (right axis).

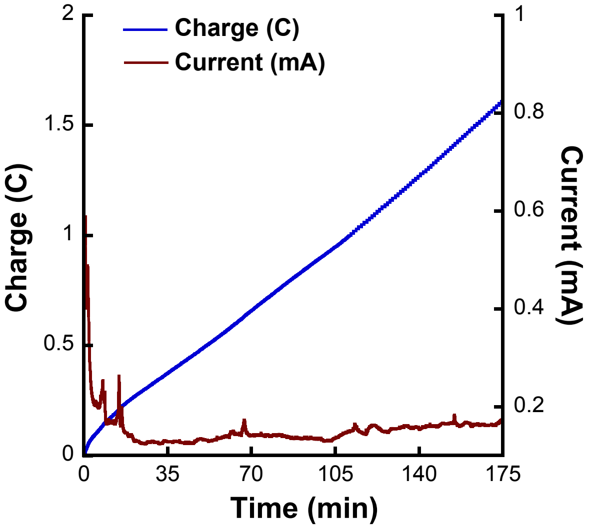


Figure S9: Controlled potential electrolysis at −1.03 V vs Ag/AgCl (1 M KCl) over 175 minutes of 333 µM $CoCl_2$ and 666 µM MPA ("$Co_x(MPA)_y$") in 0.5 M AA/1 M KCl in water, pH 4.5. The experiment was carried out under a nitrogen atmosphere in the presence of methane (80% N_2/20% CH_4). The total accumulated charge is shown as a blue line (left axis) and the current is shown as a red line (right axis).

Table S4: Tabulated results from controlled potential electrolysis experiments (listed in Figure S8, Figure S9). Hydrogen is quantified via gas chromatography and Faradaic efficiency is calculated from total charge passed after subtracting the charge and hydrogen generated from a background scan (background collected at −1.10 V vs Ag/AgCl (1 M KCl) over 175 minutes from 0.5 M AA/1 M KCl in water, pH 4.5).

Catalyst	Total Charge Passed (C)	Hydrogen (μmol)	Faradaic Efficiency (F.E.)
$Co_x(GSH)_y$	0.834	2.36	89%
$Co_x(MPA)_y$	1.63	4.89	71%
Background	0.399	0.357	-

Table S5: Photocatalytic H_2 generation over 48 hours with components listed, prepared at concentrations relevant to catalysts discussed in the main text. Trials contain GSH (1 μM), AA (0.5 M), MPA (1 μM), $CoCl_2$ (1 μM), $Co_x(GSH)_y$ (1 μM), and $Co_x(MPA)_y$ (1 μM) in water at pH 4.5, as listed in the table. The amount of H_2 was determined based on the lower limit of detection in our analyses.

Conditions	Hydrogen (μmol)
AA (0.5 M), **$CoCl_2$** (1 μM)	< 0.01
GSH (1 μM), **AA** (0.5 M), **$CoCl_2$** (1 μM)	< 0.01
MPA (1 μM), **AA** (0.5 M), **$CoCl_2$** (1 μM)	< 0.01
$Co_x(GSH)_y$ (1 μM), **AA** (0.5 M)	< 0.01
$Co_x(MPA)_y$ (1 μM), **AA** (0.5 M)	< 0.01

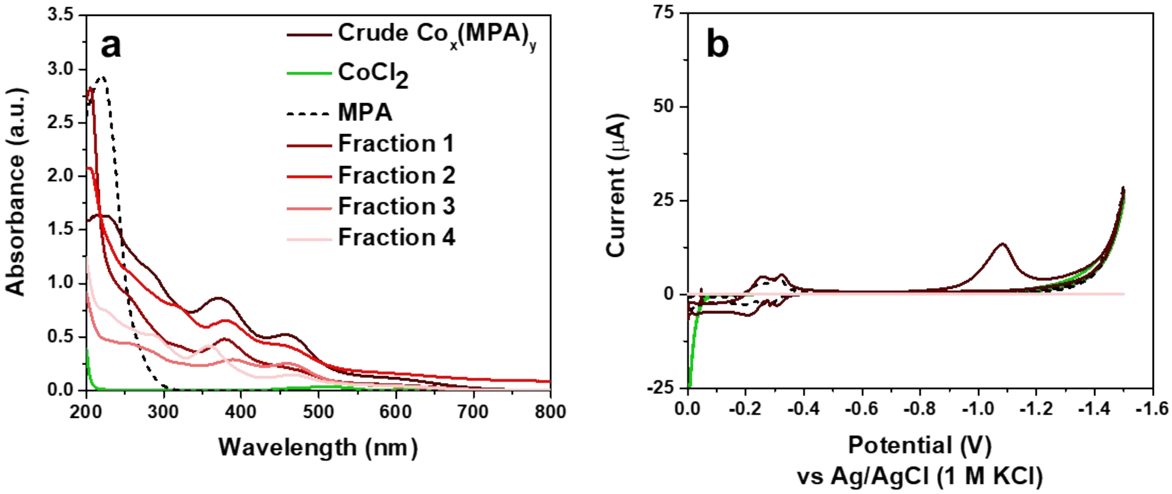


Figure S10: (a) Absorbance spectra of $Co_x(MPA)_y$ before and after column purification. Fractions 1-4 refer to the fractions collected from the P2 size-exclusion column. (b) CVs (100 mV/s) of the corresponding $Co_x(MPA)_y$ samples in 0.5 M AA/1 M KCl in water, pH 4.5, with a hanging mercury drop working electrode, Ag/AgCl (1 M KCl) reference electrode, and Pt wire counter electrode. For both the crude sample, which was lyophilized and dissolved in ~1 mL of water, and fractions 1-4, which are more dilute in comparison, exact concentrations are unknown.

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