Electronic Supporting Information

Amphiphilic, phosphonic acid-capped cadmium selenide quantum dots sensitize a thiomolybdate catalyst for hydrogen production

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SUPPORTING INFORMATION TABLE OF CONTENTS

Materials and Methods

General Considerations. All chemicals and solvents were purchased from commercial sources and used without further purification unless otherwise noted. Acetonitrile used in the synthesis of the tetraethyleneglycol monomethyl ether phosphonic acid ligand was dried on a Glass Contour Solvent Purification System (Pure Process Technology, LLC) and stored over activated 4 Å molecular sieves (Fisher Scientific) prior to use. Deuterated solvents (toluene-d_8, D_2O) for nuclear magnetic resonance spectroscopy were purchased from Cambridge Isotope Laboratories and used as received.

QD Characterization: ^{1}H NMR spectra were recorded at room temperature on a 400 MHz Bruker AVANCE spectrometer or a 500 MHz Bruker AVANCE spectrometer locked on the signal of deuterated solvents. All chemical shifts are reported relative to the chosen deuterated solvent as a standard. 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 as calculated using the first excitonic absorbance transition as described by Yu *et al*.[1] Photoluminescence (PL) spectra were measured with a modular fluorometer system (Acton Research) with a photomultiplier tube detector.

Synthesis of OA-Capped CdSe QDs: CdSe quantum dots were synthesized and purified following the procedure of Hens and coworkers.[2] In a dry 100 mL 3-neck round bottom flask, 514 mg of CdO (Sigma-Aldrich, ≥99.99%) was added to 3 mL of oleic acid (Sigma-Aldrich, ≥99%) and 10 mL of 1-octadecene (Sigma-Aldrich, 90%). The flask was placed under N_2 and heated to 270 °C with a heating mantle while vigorously stirring until the solution became clear. During the heating process, the selenide precursor was prepared with 680 mg of selenium powder (Sigma Aldrich, 100 mesh, 99.99%) and 10 mL of 1-octadecene (Sigma Aldrich, 90%) and stirred until well-mixed. Once the flask reached 270 °C, the temperature was set to 240 °C and 1 mL of Se precursor was rapidly injected. The color changes of the solution indicated the growth of QDs. The flask was lifted from the heating mantle and cooled until the temperature reading was approaching 258 °C, then the flask was put back onto the heating mantle and once the temperature dropped to 240 °C, the solution was left to grow for 30 seconds. The solution was further cooled until 210 °C and the flask was moved from the heating mantle to a water bath until room temperature. The reaction solution was separated into 6 test tubes, and 45 mL of ethanol was added in each. The test tubes were centrifuged at 5000 rpm for 15 minutes to produce clear supernatants and orange pellets. The clear supernatant was discarded, and the orange pellets were dissolved in a minimum volume of hexane and added with 45 mL of ethanol to repeat the washing procedure, and the final orange pellet was dissolved in 15 mL of hexane.

Synthesis of tetraethyleneglycol monomethyl ether phosphonic acid (TEGPA): Synthesis of tetraethyleneglycol monomethyl ether phosphonic acid (TEGPA) was carried out via literature procedure.[3] In a flame-dried 25 mL Schlenk flask, 187 µL (2.00 mmol) of $POCl_3$ (Sigma-Aldrich, 99.999%) and 10 mL of acetonitrile was added in the glove box. The Schlenk flask was then transferred to the Schlenk line where 399 µL (2.0 mmol) of tetraethyleneglycol monomethyl ether (Sigma Aldrich, 95%) was added dropwise while the flask was under N_2. The reaction mixture was stirred continuously at room temperature overnight. The next day, 5 mL of distilled water was added to the solution and heated to 55 °C under N_2 for 1 hour. After heating, the mixture was dried under high vacuum for 1 hour. The crude product was purified using column chromatography with an eluent ratio of dichloromethane (DCM), ethanol (EtOH), and water in a ratio of 65:30;5. 541.9 mg (94%) of pure product was obtained as a viscous yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 4.54 – 3.28 (m, 16H), and 3.16 (s, 3H).

TEGPA Ligand Exchange Procedure with OA-capped CdSe QDs: In a dry 50 mL 3-neck round bottom flask, 5 mL of 80 µM samples of OA capped QDs in Hexane was added. Then, 27.7 mg (150 equivalent) of TEGPA ligand was measured and dissolved in 5 mL of methanol (Sigma Aldrich, 99.8%), and added to the flask. The flask was put under N_2 and heated to 45°C and refluxed for 10 mins while vigorously stirring.

The solution was then separated into 2 test tubes and 40 mL of hexane was added into each tube. The test tubes were centrifuged at 6000 rpm for 8 minutes to produce clear supernatants and orange pellet. The clear supernatants were discarded, and the pellet was dried using N_2 and dissolved in desired polar solvents such as DMF and DMSO.

Preparation of Systems for Photocatalysis: A fresh 50-mL stock solution of 2 M ascorbic acid was prepared and adjusted to pH 4.0 with minimal NaOH (<5 mL) in water purified by a Millipore system. A 2-mL stock solution of 1 mM $\mathbf{[Mo_3S_{13}]^{2-}}$ was prepared in water purified by a Millipore system. A **CdSe-TEGPA** stock solution was prepared by ligand exchange into DMF as described prior. The components were mixed at the desired concentration and additional DMF and water were added to achieve the correct solvent ratio and concentrations for photochemical experiments. This 5.0-mL solution was housed in 41-mL vials with a headspace of 36 mL. The vials were sealed with gas-tight septa and purged with 80%/20% N_2/CH_4 (Airgas) as an internal standard for 15 min through the liquid and 5 min through the headspace. All vials were placed in a custom-built temperature-controlled block connected to a Thermotek circulating water bath at 15 °C and illuminated through the base of the vials by green (530 nm) light-emitting diodes (Philips LumiLED Luxeon Star Hex 700 mA LEDS mounted on 20-mm star-shaped CoolBases). A L30A thermal sensor and a Newport Power Meter (1918-C) were used to measure each LED's power individually before and after the experiment. Each LED power at 530 nm was adjusted to 0.015 W $\pm$ 0.003 W prior to each experiment. The block was mounted on a Thermo-Scientific MaxQ orbital shaker which allowed for continuous shaking at 100 rpm.

Transmission Electron Microcopy Images: The oleic acid-capped CdSe QDs (**CdSe-OA**) in hexane were weighed out into six 50 mL Polypropylene tubes and excess ethanol was added and centrifuged at 5000 rpm for 10 mins, and the supernatant was discarded and the pellet was redispersed in minimal hexane and the washing procedure was repeated another five times; **CdSe-TEGPA** after ligand exchange was first washed with excess hexane and centrifuged at 6000 rpm for 6 mins, and the pellet was redispersed in minimal methanol and the washing was repeated one more time; the clear supernatant was discarded and the pellet was redispersed in minimal ethyl acetate and excess diethyl ether was added and centrifuged at 6000 rpm for 6 mins, and the pellet was redispersed in minimal ethyl acetate and the washing step was repeated one more time and the final pellet was dispersed in diethyl ether. Both QDs samples were drop casted onto the TEM grid.

Powder XRD: Powder samples were affixed to a Nylon loop (0.1 mm ID) with a light coating of viscous oil. X-ray diffraction data were collected on a Rigaku XtaLAB Synergy-S diffraction system equipped with a HyPix-6000HE HPC detector. CuKα radiation (λ = 1.54184 Å) was generated by a PhotonJet-S microfocus source at 50 kV, 1 mA. At RT (293 K) and with a sample-to-detector distance of 34 mm, two combination ω-φ "Gandolfi" scans were performed, each for 300 s: 1) ω from -62.00 to 31.00 degrees and φ rotated through 720 degrees, at θ = -42.18 and κ = 70.00 degrees; 2) ω from -30.00 to 61.00 degrees and φ rotated through 720 degrees, at θ = 41.17 and κ = -70.00 degrees.

Inductively Coupled Plasma Mass Spectrometry: For the supernatant samples, 0.1 mL supernatant liquid was added to 15 mL polypropylene tubes and 2% nitric acid was added to a final volume of 10 mL. These were subsequently diluted 100-fold before analysis. QD samples were weighed out in 50 mL polypropylene tubes. 1mL of concentrated trace metal grade nitric acid was added, then the tubes were placed in a boiling water bath at 100 °C for 1 hour to ensure total dissolution of the quantum dots. Ultra-pure water was added to a final volume of 20 mL, and the samples were diluted 100-fold for Cd QD's and not diluted for the Mo QD's, then analyzed for the desired elements by a Perkin Elmer 2000C ICP-MS. Calibrations were run at 2,4, and 10 ppb Co, and Mo. Samples were run in KED more at 4ml/min helium flow.

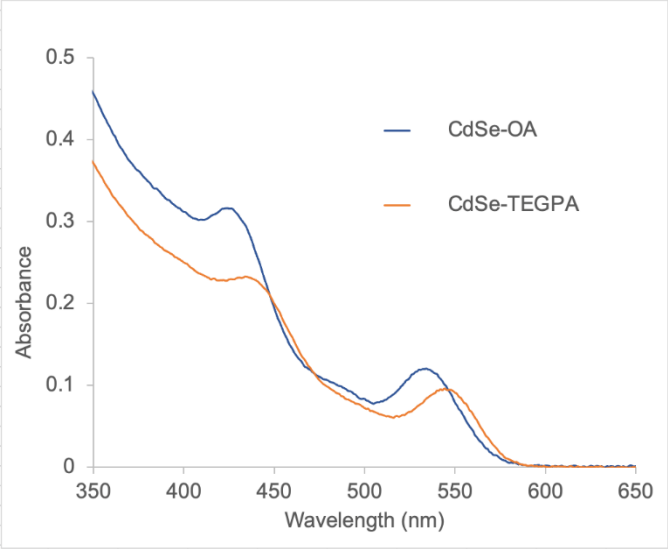

Figure S1. Electronic absorbance spectra of CdSe QDs capped with oleic acid (**CdSe-OA**, λ_{max} 520 nm) and tetraethyleneglycol monomethyl ether phosphonic acid (**CdSe-TEGPA**, λ_{max} 529 nm). Spectra collected in hexanes (**CdSe-OA**) and dimethylformamide (**CdSe-TEGPA**) at room temperature (~22 ºC).

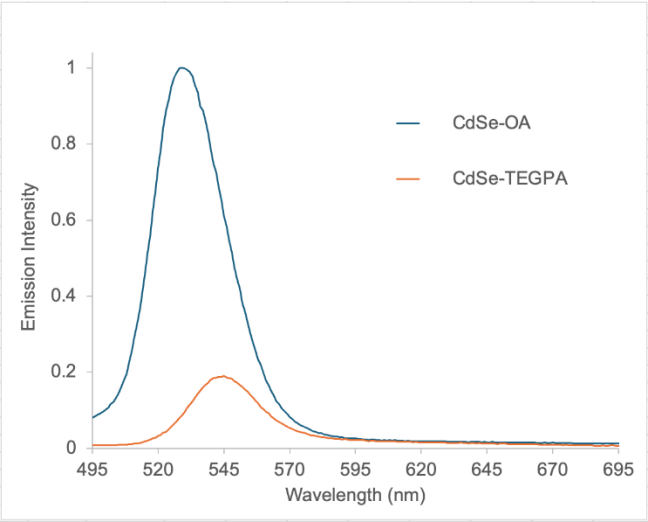

Figure S2. Steady-state photoluminescence spectrum of CdSe QDs capped with OA (λ_{max} 529 nm) and TEGPA (λ_{max} 544 nm). Spectrum collected in hexanes (**CdSe-OA**) and dimethylformamide (**CdSe-TEGPA**) at room temperature (~22 ºC).

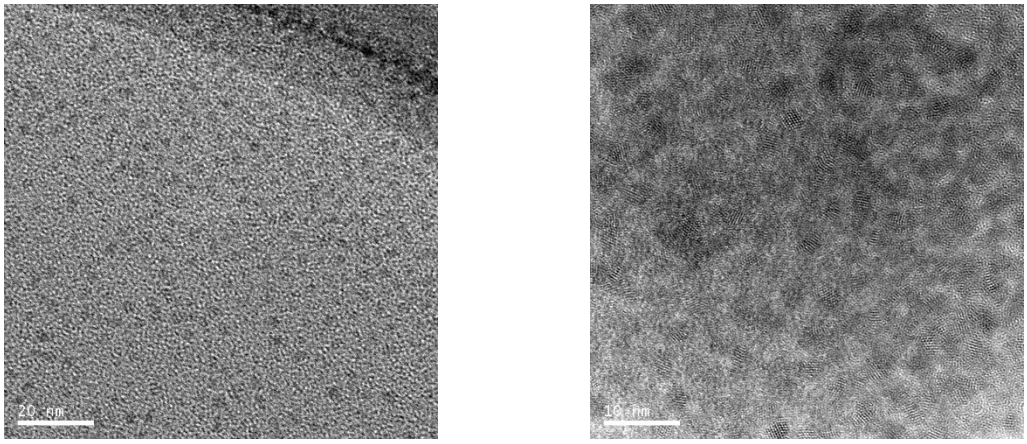

Figure S3. Transmission electron microscopy (TEM) micrographs of CdSe-OA QDs (left panel) and CdSe-TEGPA QDs (right panel). TEM imaging was executed on a FEI TECNAI F-20 field emission microscope at an accelerating voltage of 200 kV using -400 mesh ultrathin lacey carbon grids.

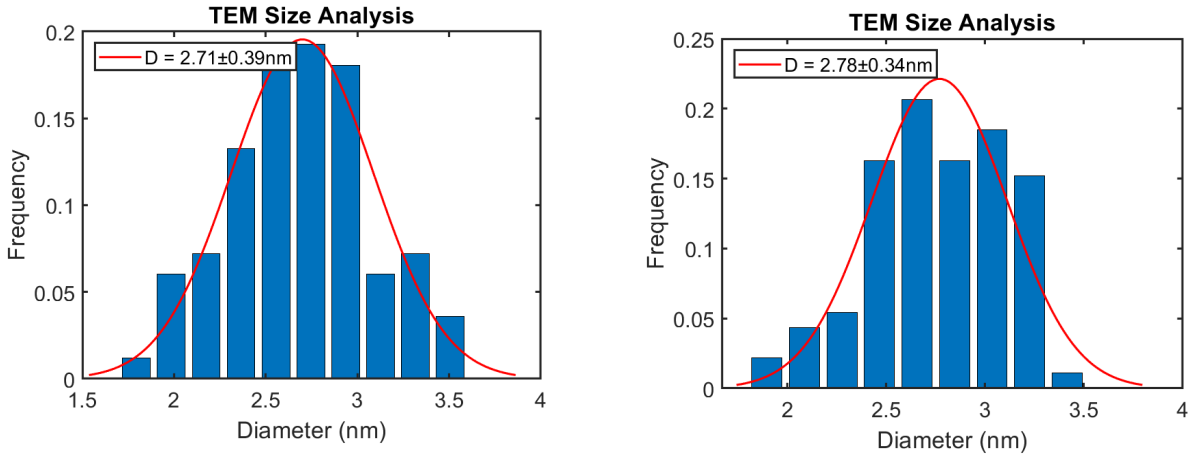

Figure S4. QD diameters were determined through sizing of TEM micrographs via ImageJ. The average size of the CdSe-OA QDs (left) and CdSe-TEGPA QDs (right) were 2.71 ± 0.39 nm and 2.78 ± 0.34 nm, respectively.

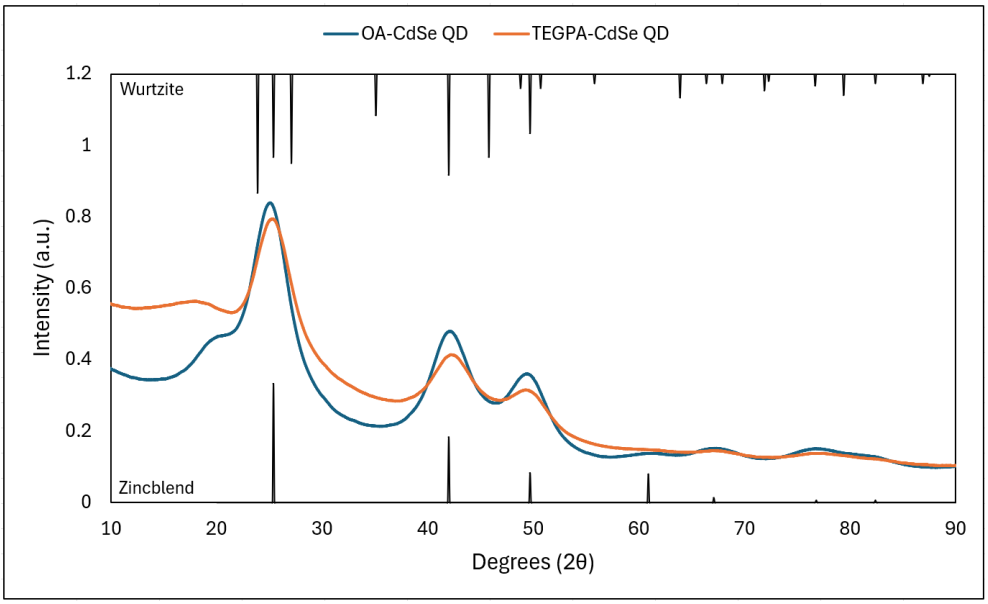

Figure S5. Corresponding XRD patterns of CdSe-OA (blue) and CdSe-TEGPA (orange). The simulated standard XRD pattern of bulk wurtzite (Ref ICDD Code: 00-008-0459) and bulk zincblende (Ref ICDD Code: 00-019-0191) are shown for comparison. Both CdSe-OA and CdSe-TEGPA QDs show similar diffraction patterns, suggesting that the ligand exchange process happened without altering the crystal structure. The slight variation in peak intensities and positions between the two QDs samples are indicative of different surface ligands binding to the surface that leads to changes in crystalline orientation and size.

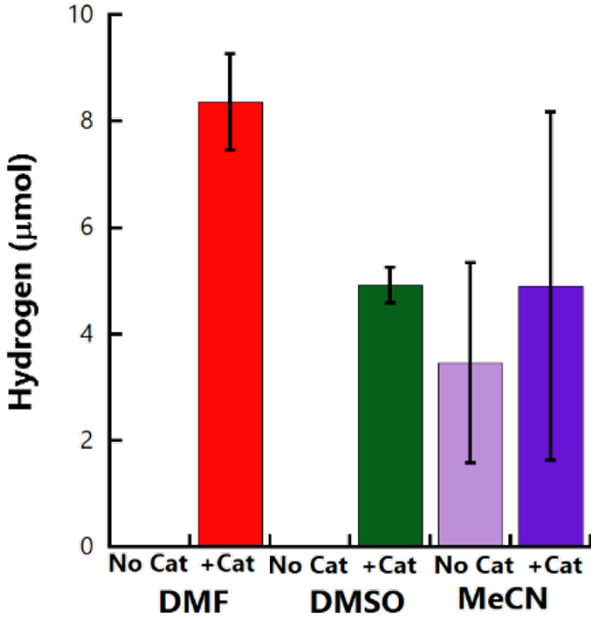

Figure S6. Photocatalytic hydrogen evolution (24 hr) using different organic solvents in a 9:1 ratio with water. 1.0 μM **CdSe-TEGPA**, and 100 mM ascorbic acid in the presence (+Cat) and absence (No Cat) of 10 μM $\mathbf{[Mo_3S_{13}]^{2-}}$.

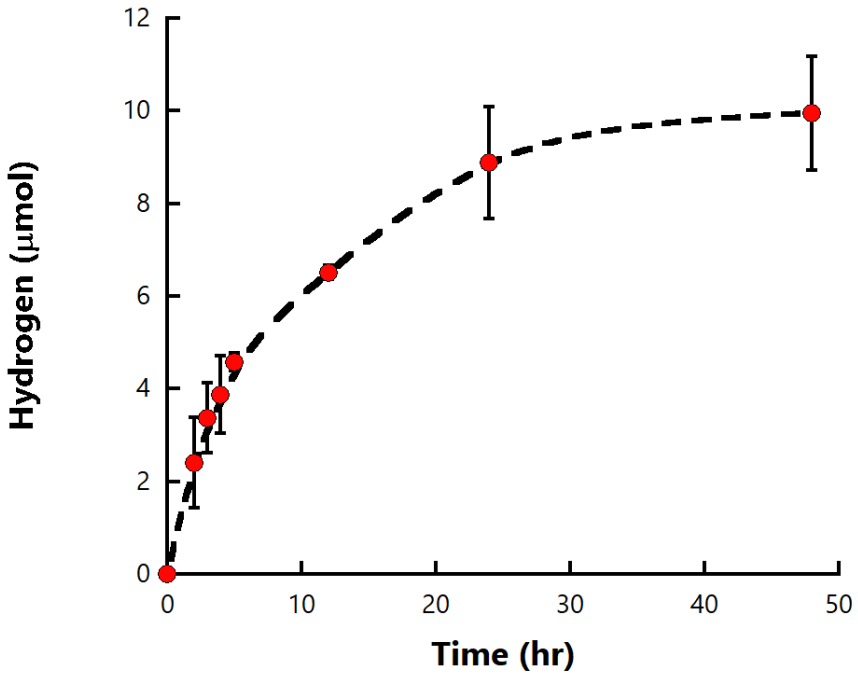

Figure S7. Time-course photocatalytic hydrogen evolution with 1.0 μM **CdSe-TEGPA**, 10 μM **$[Mo_3S_{13}]^{2-}$** and 100 mM ascorbic acid in DMF:water (9:1 solvent mixture by volume).

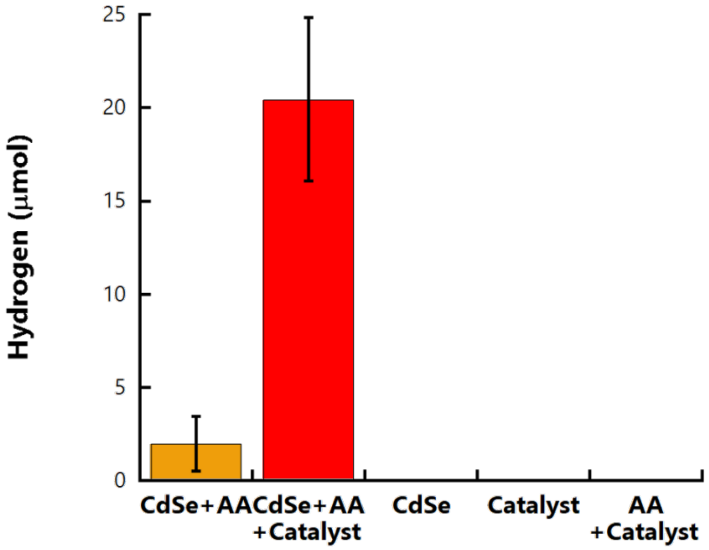

Figure S8. Photochemical H_2 evolution (24 hr) demonstrating activity with and without all components. 1.0 μM **CdSe-TEGPA** (**CdSe**), 10 μM **$[Mo_3S_{13}]^{2-}$** (**Catalyst**) and 200 mM ascorbic acid (**AA**) in DMF:water (9:1). 530 nm LED irradiation, 31 °C, 100 rpm.

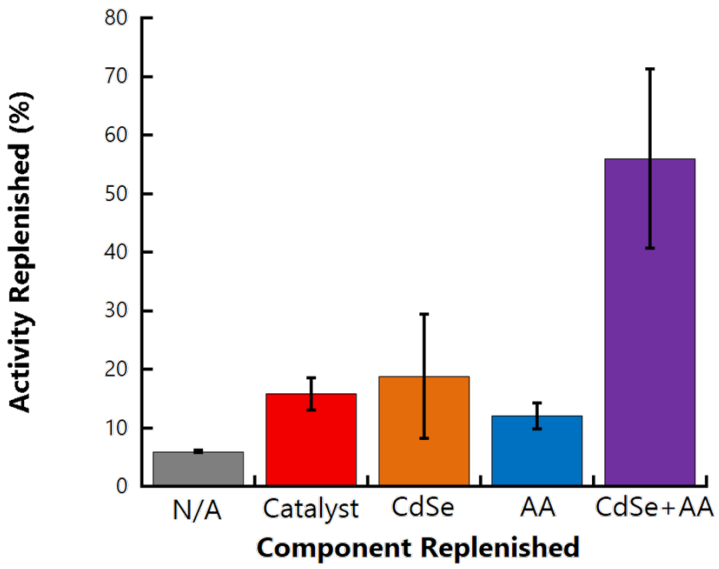

Figure S9. Photocatalytic hydrogen evolution after component replenishment. After 24 hr photocatalysis experiment, excess component was added to the reaction mixture and photocatalysis was run for an additional 24 hr. Initial reactions contained 1.0 μM **CdSe-TEGPA**, 10 μM **$[Mo_3S_{13}]^{2-}$** and 100 mM ascorbic acid in DMF:water (9:1 ratio).

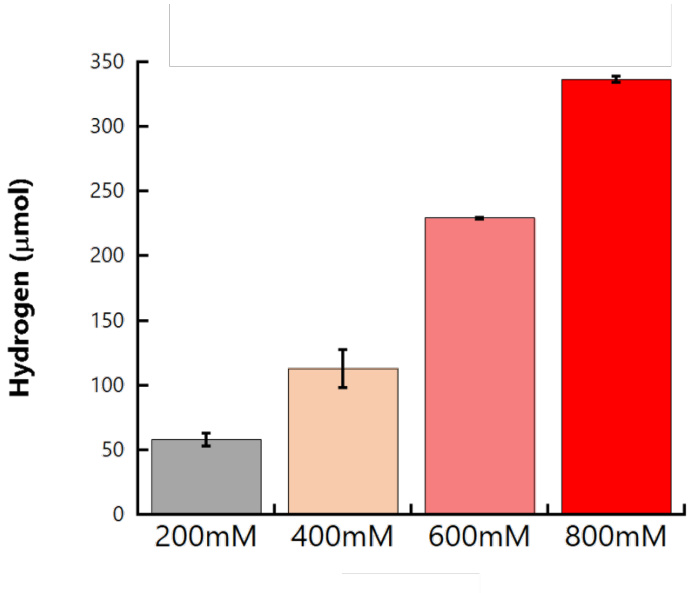

Figure S10. Photochemical hydrogen evolution (48 hr) with **CdSe-TEGPA** (1.0 μM), **$[Mo_3S_{13}]^{2-}$** (10 μM) and ascorbic acid (200 -800 mM) in DMF:water (6:4) 530 nm LED irradiation, 31 °C, 100 rpm .

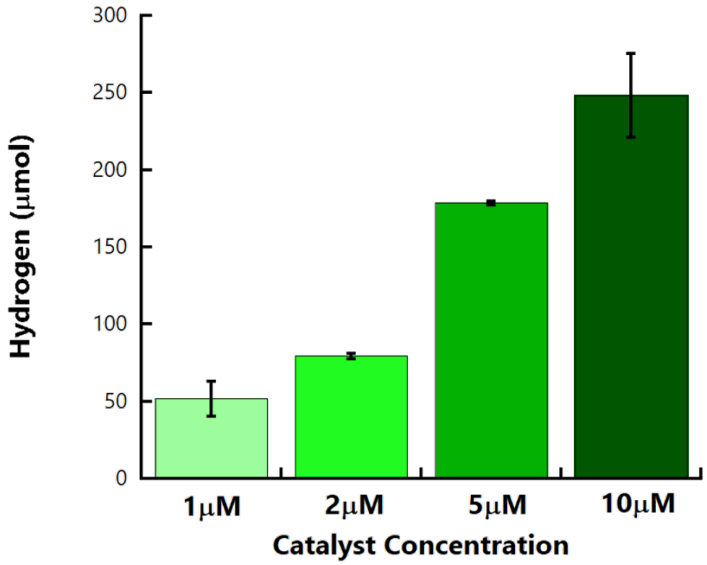

Figure S11. Photochemical hydrogen evolution (48 hr) with **CdSe-TEGPA** (1.0 μM), **$[Mo_3S_{13}]^{2-}$** (1.0 - 10 μM, concentration shown in legend) and ascorbic acid (800 mM) in DMF:water (6:4) 530 nm LED irradiation, 31 °C, 100 RPM.

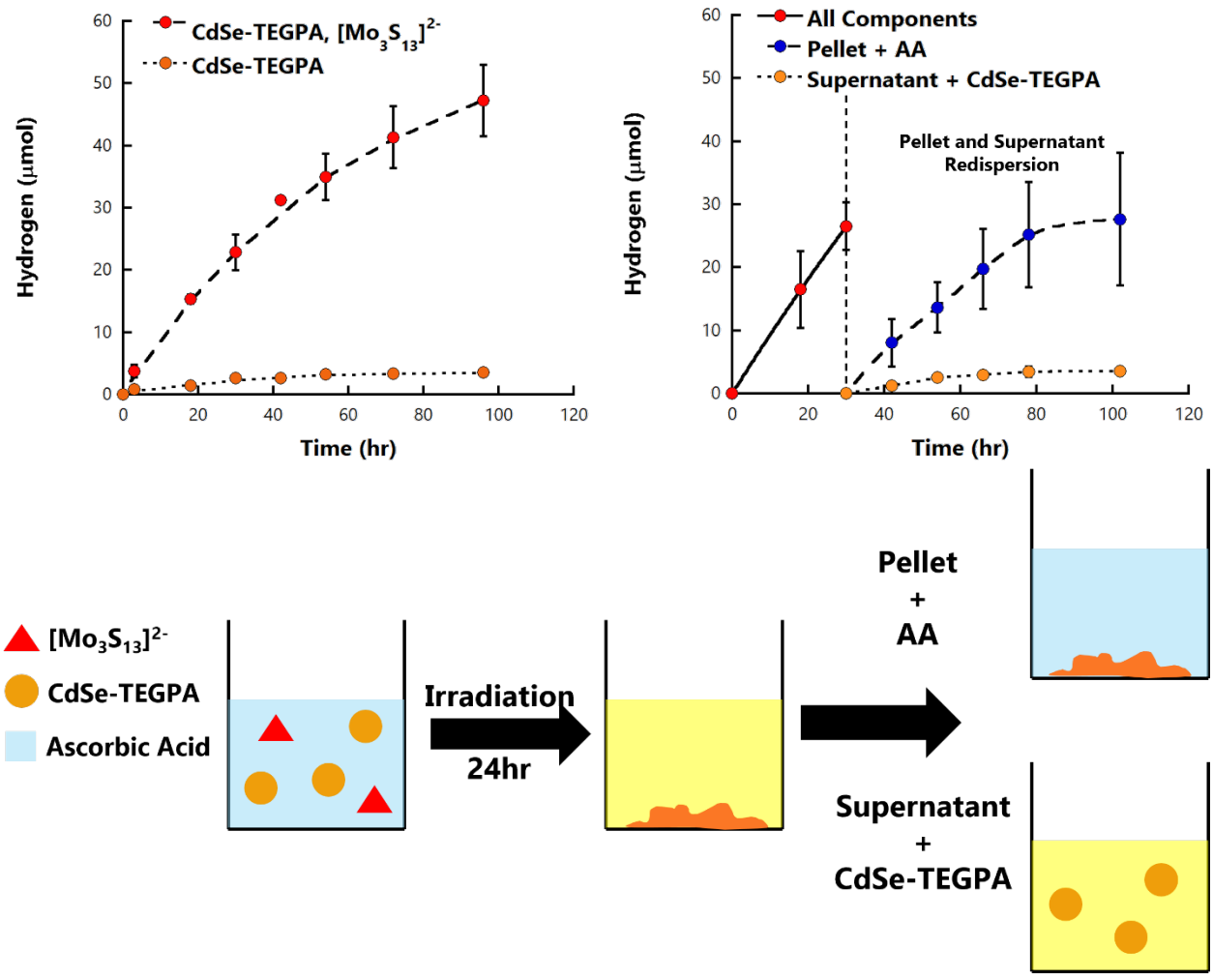

Figure S12. (Top) Photochemical H_2 evolution with 1.0 μM **CdSe-TEGPA** , 10 μM **$[Mo_3S_{13}]^{2-}$** and 200 mM ascorbic acid in DMF:water (6:4). 530nm LED irradiation, 31°C, 100 rpm. Pellet and supernatant were isolated after 30 hr irradiation. 200 mM ascorbic acid in DMF:water (6:4) was added to the pellet. 1.0 μM **CdSe-TEGPA** was added to the supernatant. Samples were irradiated for a further 96 hr to evaluate hydrogen produced. (Bottom) Schematic outlining the redispersion experiment described above.

Table S1. ICP-MS Analysis of the pellet and supernatant post-photocatalysis.

Sample	[Cd] (ppb)	[Mo] (ppb)	Total Cd (%)	Total Mo (%)
Pellet	79300	691	92.6%	86.2%
Supernatant	6320	110	7.4%	13.8%

References

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[3] N. Möller, A. Rühling, S. Lamping, T. Hellwig, C. Fallnich, B. Jan Ravoo, F. Glorius. “Stabilization of high oxidation state upconversion nanoparticles by N-heterocyclic carbenes” *Angew. Chem. Int. Ed.* 2017, **56**, 4356-4360.