Electronic Supporting Information:

Robust Photocatalytic Hydrogen Generation from CdSe Nanoplatelets

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Table of Contents

Materials and Methods

Materials

Technical grade oleic acid (OA, 90%), technical grade 1-octadecene (ODE, 90%), selenium powder (Se, 99.99% trace metal basis, -100 mesh), cadmium acetate dihydrate ($Cd(Ac)_2 \cdot 2H_2O$, 98%), cadmium nitrate tetrahydrate ($Cd(NO_3)_2 \cdot 4H_2O$, 98%), sodium myristate (≥99%), 3-mercaptopropionic acid (MPA, ≥99%), tetramethylammonium hydroxide pentahydrate (TMAHP, ≥97%), methyl acetate (≥98%), ethyl acetate (≥99.5%), and nickel chloride ($NiCl_2$, 98%) were purchased from Sigma-Aldrich. L-ascorbic acid (AA, crystalline/certified ACS), methanol absolute (ACS grade, 99.8%) hexane (certified ACS), and ethyl ether anhydrous (certified ACS) were purchased from Fisher Scientific. Ethanol (900 proof) was purchased from VWR.

Cadmium Myristate Synthesis

Sodium myristate (5 g) was added to methanol (500 mL) and sonicated until fully dissolved. As a separate solution, $Cd(NO_3)_2 \cdot 4H_2O$ (3 g) was added to methanol (200 mL) and stirred until fully dissolved. Then, the prepared $Cd(NO_3)_2 \cdot 4H_2O$ solution was added dropwise (~1 drop/second) to the stirring sodium myristate solution at room temperature, forming a white precipitate. This proceeded for a total of 2 hours until all of the $Cd(NO_3)_2 \cdot 4H_2O$ solution was added. The precipitate was collected using vacuum filtration and washed generously with methanol. The washed precipitate was then dried under vacuum overnight until solid and stored in a nitrogen-filled glovebox.

4.5-ML CdSe NPL Synthesis

Colloidal 4.5-ML CdSe NPLs were synthesized via a modified hot injection method adapted from Yoon et al.[1] Cadmium myristate (680 mg), Se (48 mg), and ODE (60 mL) were added to a 250 mL 3-neck round bottom flask and stirred under N_2 at room temperature. The solution was then heated to 120°C and degassed for 30 minutes. After degassing, the solution was then returned to N_2 and heated to 240°C. At 210°C, $Cd(Ac)_2 \cdot 2H_2O$ was swiftly added to the flask. The temperature was maintained at 240°C for 8-9 minutes. After the growth period, the flask was cooled to 185°C, at which point 6 mL OA was added. The flask was then cooled to room temperature using a water bath. Once cooled, 15 mL hexane was added, and the solution was centrifuged at 3000 rpm for 10 minutes. The supernatant was subsequently discarded, and the pellet was redispersed in 5 mL hexane and left to sit undisturbed for 2 hours. After this period, the solution was centrifuged at 6000 rpm for 10 minutes and the supernatant was recovered. If the resulting solution needed further purification (observed via fluorimetry), minimal methyl acetate was added until the solution became turbid and then was centrifuged at 5670 x g for 3 minutes. The pellet was redispersed in 5 mL total hexane and was washed with methyl acetate until purified. The resulting NPL solution was solubilized in hexane and stored in the dark.

MPA Ligand Exchange for Pristine NPLs

Methanol (180 mL) and TMAHP (2.93 g) were combined in a 400 mL beaker and mixed until TMAHP was fully dissolved. MPA (2.69 mL) was added to this solution and mixed well. A volume of 140 mL of the prepared solution was added to a 250 mL 3-neck round bottom flask. The flask was then immersed in an ice water bath to cool down for at least 15 minutes before proceeding. A stock solution of NPLs in hexane (1.5 mL, 80 nM) was then diluted to a total of 3 mL of hexane and added to the solution dropwise with shaking in between to allow for adequate dispersion. The reaction proceeded on ice for a total of 5 minutes and then was washed with ethyl ether (2.33:1) and ethyl acetate (0.66:1). The solution was then centrifuged at 4500 rpm for 20 minutes. The pellet was recovered and dried before redispersing in nanopure water (2 mL total volume). The resulting solution was stored in the dark and used for subsequent experiments.

MPA Ligand Exchange for Etched NPLs

This procedure is identical to the above pristine NPL protocol except the reaction was run for a total of 45 minutes.

MPA Ligand Exchange for Dot-Like NPLs

This procedure is identical to the above pristine NPL protocol except the entire prepared solution (180 mL) was added to the flask and the reaction was run for a total of 45 minutes.

CdSe NPL Optical Characterization

Colloidal 4.5-ML CdSe NPLs were characterized using a PerkinElmer Lambda 950 UV/Vis/NIR spectrophotometer and a home-built fluorometer for absorbance and photoluminescence spectra, respectively. The fluorometer setup was comprised of a 450 W xenon arc lamp, a SpectraPro 150 monochromator system for excitation, and a SpectraPro 300i monochromator and PMT detector for emission detection.

NPL concentration was determined using the absorbance spectrum via Beer's Law:

$$A = bC\varepsilon, \quad (1)$$

where A is absorbance, b is path length, C is concentration, and ε is molar absorptivity. Molar absorptivity for 4.5-ML CdSe NPLs was determined using the calculated absorption cross section from Rodà et al. in the following equation:

$$\varepsilon = \frac{\sigma \times N_A}{\ln(10) \times 10^3}, \quad (2)$$

where σ is the absorption cross section and N_A is Avogadro's number.[2]

Transmission Electron Microscopy (TEM)

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. NPL lateral dimensions were determined through TEM imaging and sizing via ImageJ.

Reduction Potential Calculations

The reduction potential for 4.5-ML CdSe NPLs was determined to be −1.67 ± 0.06 V vs $Fc^{+/0}$ (−1.27 ± 0.06 V vs NHE) by Sinai et al. via circular voltammetry (CV) experiments.[3] The oxidation potential can be determined from this by adding the reduction potential to the band gap of the NPLs. However, due to the large exciton binding energy as calculated by Shornikova et al. (270 meV), this needs to be considered in these calculations.[4] Li et al. previously calculated these values for 4.5-ML CdSe NPLs with heavy-hole (hh) peak absorption at ~516 nm.[5] The following calculations were adjusted for 4.5-ML CdSe NPLs with hh peak absorption at 530 nm.

To determine the contribution of the electron and hole to the binding energy of the NPLs, their effective masses were used in the following equation:

$$\frac{E_e}{E_h} = \frac{m_h^*}{m_e^*} = \frac{0.45m_0}{0.13m_0} = 3.46E_h \tag{3}$$

where E_e is the contribution of the electron to the binding energy, E_h is the contribution of the hole to the binding energy, m_h^* is the effective hole mass and m_e^* is the effective electron mass in 4.5-ML CdSe NPLs, and m_0 is the free electron mass. The effective masses were used from Li et al.[5]

Once the ratio was determined above, E_e and E_h were calculated by plugging the solution to (3) into the following equation:

$$E_{ex} = E_g + E_h + E_e \tag{4}$$

where E_{ex} is the exciton binding energy (2.34 eV) and E_g is the band gap of the bulk material (1.7 eV). Once calculated, these values were subtracted from the conduction band (CB) and valence band (VB) edge positions of bulk CdSe (-4.0 eV and -5.7 eV, respectively) and converted to V vs NHE to determine the final CB and VB positions presented in Figure S3.

Photocatalysis Experiments

A 1.6 mM solution of Ni-DHLA (based on Ni^{+2}) was prepared by adding 4.5 mg of $NiCl_2$ to a 1:1 mixture of nanopure water and ethanol and mixing until fully dissolved. DHLA (6 µL) was then added to the solution and mixed well before purging with N_2 for 2 hours.

A solution of 1 M AA was also prepared by adding 8.8 g of L-ascorbic acid to 45 mL of nanopure water and stirring until fully dissolved. The pH of the solution was adjusted using a 10 M NaOH solution to reach a final pH of 4.5. Nanopure water was added to the solution to reach a final volume of 50 mL.

Photocatalysis vials were prepped by adding AA (0.5 M), Ni-DHLA (variable concentration), MPA-CdSe NPLs (218 nM, 0.2 OD), and nanopure water (final volume 5 mL) into a 40 mL scintillation vial sealed with a septum. The vials were then purged with an 80:20 N_2/CH_4 mixture as an internal standard for 30 minutes. The vials were then placed in a custom temperature-controlled shaker (15°C with 100 rpm shaking) illuminated through the base of the vials with LEDs (Philips LumiLED Luxeon Star Hex green 700 mA LEDs) that emit at 514 nm (~15 mW). Gas chromatography was used to quantify H_2 produced.

Turnover Number (TON) Calculations

Per Particle (TON (NP))

The TON (NP) describes the moles of H2 produced per mole of nanoparticle in solution. This is calculated according to the following equation:

(5) $$TON\ (NP) = \frac{H_2(mol)}{NP\ (mol)}$$

Per Catalyst (TON (Cat))

The TON (Cat) describes the moles of H_2 produced per mole of catalyst in solution. This is calculated according to the following equation:

(6) $$TON\ (NP) = \frac{H_2(mol)}{Cat\ (mol)}$$

Quantum Efficiency (QE) Calculations:

The quantum efficiency (ΦH_2) of our given system relates the amount of H_2 produced at a given rate (moles H_2 per second, k) to the number of photons absorbed by the nanoparticles at a given wavelength (photon flux, q_p), as described by the equation below:

$$\Phi H_2 = \frac{2k}{q_p} \tag{7}$$

noting that the equation accounts for the two photons required to make one molecule of H_2.

Photon flux is calculated using the following equation:

$$q_p = \frac{n}{t} = \frac{P_{abs} \times \lambda}{c \times h \times A} \tag{8}$$

P_{abs} describes the power (W) of the light absorbed by the QDs at 530 nm (based on position of excitonic peak). This was determined by measuring the power of the LED with a blank sample (standard vial with 5 mL nano pure water) and with a sample containing the nanoparticles of a specified concentration (1 μM for the QDs and 2.18 nM for the NPLs), then subtracting them to get a final power absorbed value. The power was measured using a Newport power meter (Model 1918-C). λ describes the wavelength of light emitted by the LEDs (530 nm), c is the speed of light, h is Planck's constant, and A is Avogadro's number. Calculations were performed at the 48-hour mark for the QD system and the 45-hour mark for the NPL system and are reported in Table S1.

Figures and Tables

	TON (mol H_2/mol particle)	TON (mol H_2/mol Ni-DHLA)	QE (%)
CdSe QDs	147,000 ± 800	3,700 ± 20	30 ± 1
CdSe NPLs	6,616,763 ± 483,000	92 ± 7	11 ± 1

Table S1. Calculated TON and QE of MPA-CdSe NPLs and QDs for photocatalytic H_2 production. MPA-CdSe QDs were at a 1 μM concentration with 0.5 M AA and 40 μM Ni-DHLA loading and were irradiated for 48 hours with 514 nm LEDs. MPA-CdSe NPLs were at 218 nM (0.2 OD) with 0.5 M AA and 500 μM Ni-DHLA loading and were irradiated for 45 hours with 514 nm LEDs.

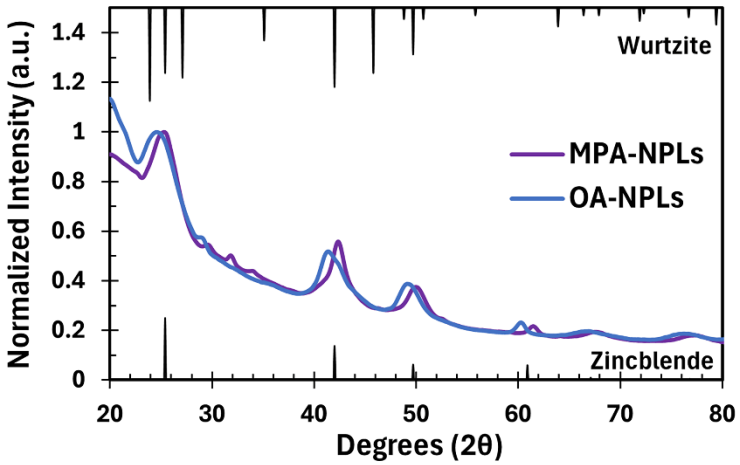

Figure S1. Powder XRD spectra of NPLs before and after ligand exchange with MPA. Both spectra show NPLs exhibit zinc-blende crystal structure. Peak shifts toward higher angles indicate uniform lattice strain across the NPLs.[6] References used are for bulk wurtzite (00-008-0459) and zinc-blende (00-019-0191) CdSe.

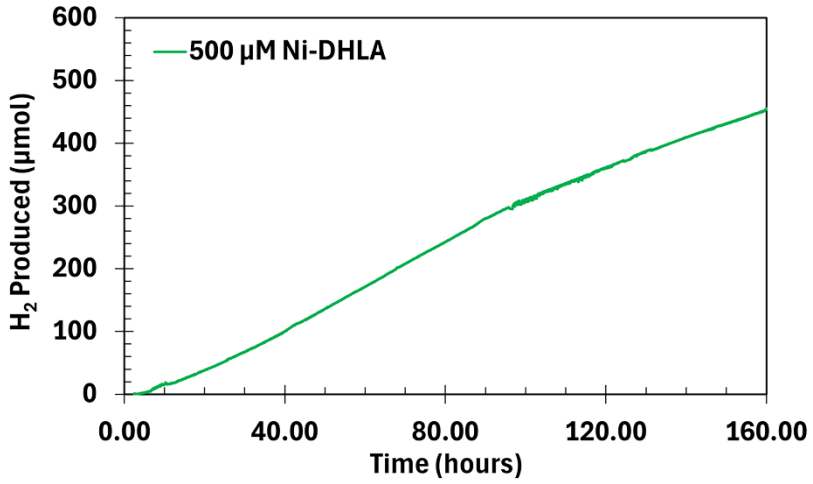

Figure S2. Hydrogen produced from 218 nM MPA-CdSe NPLs with 0.5 M AA and 500 µM of Ni-DHLA, irradiated with 514 nm LEDs for 160 hours. Activity slows at the 90-hour mark but does not plateau within the 160-hour period.

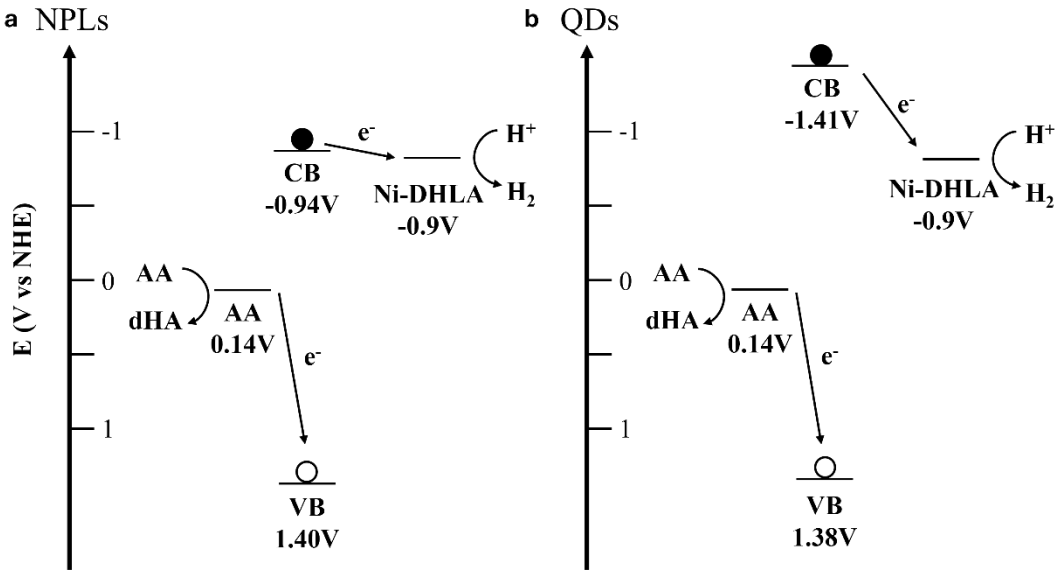

Figure S3. Reduction potential diagram of (a) 4.5-ML CdSe-NPLs (16 x 16 nm) and (b) CdSe QDs (2.6 nm) in conjunction with Ni-DHLA and AA in relation to proton reduction. The reduction potentials of AA,[7,8] Ni-DHLA,[7] and CdSe QDs[9] were determined from literature while those of CdSe NPLs were calculated (see *Redox Potential Calculations* above).

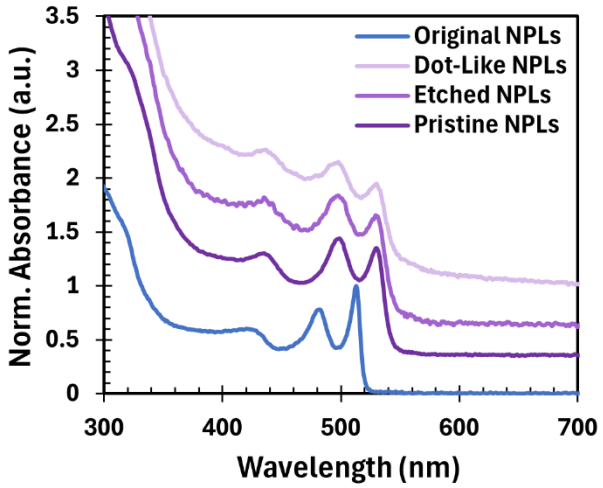

Figure S4. Absorbance spectra of NPLs with increasing levels of etching (ligand exchanges outlined in Materials and Methods section). With increasing concentration of base and time of reaction, the hh and lh peaks become broadened and their intensities decrease, with the hh peak intensity decreasing greater relative to the lh peak. The hh peak position upon ligand exchange was red-shifted by ~15 nm; however, between different ligand exchanges, the hh peak position remained the same, indicating only lateral etching. Pristine NPLs are classified based on minimal peak broadening and relative intensity changes in the absorbance spectrum compared to as-synthesized NPLs as well as observation of edge preservation in TEM imaging.

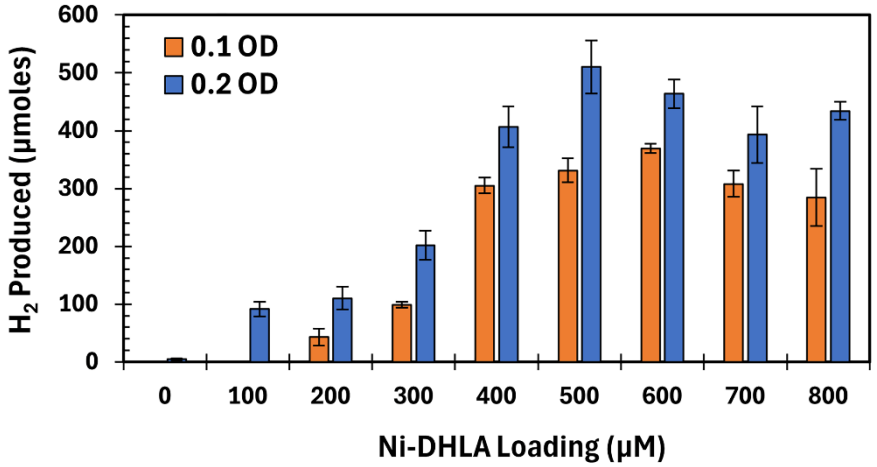

Figure S5. Different NPL loadings were tested based on optical density (OD). MPA-CdSe NPLs of different ODs, 0.5 M AA, and variable Ni-DHLA co-catalyst loadings (0-800 µM) were combined in aqueous solution and irradiated with 514 nm LEDs for 90 hours. The NPLs at a lower OD (0.1) produced less hydrogen at all co-catalyst loadings.

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