

Photoelectrochemical Generation of Hydrogen from Water Using a CdSe Quantum Dot-Sensitized Photocathode

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Materials

Nickel(II) chloride hexahydrate, potassium chloride, and hexamethylenetetramine were purchased from Sigma-Aldrich and used without further purification. Indium tin oxide (ITO) glass was purchased from Delta Technologies Limited and cut to a size of 3 cm × 0.5 cm for PEC experiments. All solvents were used without further purification unless otherwise stated.

Experimental

Synthesis of trioctylphosphine oxide capped CdSe¹ and (nBu₄N)[Co(bdt)₂]² were done following literature procedures. (nBu₄N)[Co(bdt)₂] stock solution was prepared by dissolving 0.0217 g of (nBu₄N)[Co(bdt)₂] complex in 10 mL of acetonitrile. Ni(DHLA)_x complex was prepared by simple mixing of Ni(NO₃)₂·6H₂O (3.0 mg, 0.01 mmol) dissolved in 10 mL of pH 6 electrolyte solution with DHLA (5.0 mg, 0.024 mmol). It should be noted that we used freshly prepared solutions of Ni(DHLA)_x for all experiments because Ni(DHLA)_x forms a relatively insoluble precipitate with time. TOPO ligands on CdSe were exchanged with S₃-caps³ and the resultant QDs were suspended in slightly basic water (pH ~8.0) prior to use.

NiO film preparation. Single sided ITO glass was washed with acetone, soap water and ethanol for 10 min each respectively. NiO films were grown according to the procedure reported in literature.⁴ Briefly, a growth solution was prepared by mixing nickel nitrate hexahydrate [Ni(NO₃)₂·6H₂O] with hexamethylenetetramine in distilled water. ITO glasses were immersed in this solution and heated at 90 °C for 12 min. Next, they were washed thoroughly with water and dried at room temperature. Then, these films were heated to 320 °C in a furnace for 30 minutes. These films were characterized by SEM and XRD techniques. (figure S3)

NiO-S₃-cap-CdSe film preparation. NiO films were placed in solutions of S₃-cap-CdSe solution for 24 hours. These films were washed with water, dried and UV/Vis was obtained. To quantify the amount of CdSe nanoparticles adsorbed on to NiO, they were detached from NiO film to the solution by using aqueous trifluoroacetic acid. From the absorption spectra of the solution it was determined that approximately 10⁻⁸ mols of CdSe QDs were attached to the surface of NiO layer. The amount of CdSe QDs adsorbed was further confirmed by measuring the decrease in the concentration of the original S₃ cap - CdSe solution.

Characterization by absorption spectroscopy. UV-VIS absorption spectra were taken on a Perkin-Elmer Lambda 950 UV/Vis/NIR spectrophotometer.

Scanning electron microscopy (SEM). Sample surfaces were characterized by field emission scanning electron microscopy (SEM, Zeiss Auriga). Prior to analysis samples were grounded, to prevent charging. Conductive carbon tape was affixed to the ITO surface and to the microscopy stub, bypassing the electrically insulating glass substrate thereby providing an outlet for electrons

X-ray diffraction. For phase analysis of NiO films Philips X'Pert MPD (Multi-Purpose Diffractometer) system was used. The x-ray source was a long-fine-focus, ceramic x-ray tube with Cu anode. Normal operating power was 40 kV, 30 mA (or less than 1.8 kW).

IPCE measurement. IPCE measurements were performed using a 300 W xenon lamp and a grating monochromator (Spex Fluoromax-P fluorimeter). The incident photon flux was calibrated using a OPHIR PD300-UV-SH ROHS power meter.

PEC experiments. A custom built, air-tight three-compartment electrochemical cell was used for PEC experiments. Pt mesh was used as the auxiliary electrode and Ag/AgCl (Sat KCl) was used as the reference electrode. Electrolyte solution used was 0.1M KCl with pH 6 hexamethylenetetramine (HMTA) /HCl buffer in 1:1 CH₃CN: H₂O solution. This electrolyte solution was used for all experiments unless otherwise mentioned. The samples were then degassed using a mixture of 20% CH₄ in N₂ with the CH₄ being used later as an internal reference for GC analysis. The cells were irradiated from the side with high power Philips Lumi Luxeon Star Hex green (λ_{max} 520 nm) 700 mA LEDs. The light power of each LED was set to 0.15 W and measured with an L30 A Thermal sensor and Nova II power meter (Ophir- Spiricon LLC). The samples were stirred using IKA™ squid stirrer.

pH measurements. The pH of the 1:1 CH₃CN: H₂O mixtures were measured directly with a digital pH meter.

H₂ measurements. The amounts of hydrogen evolved were determined using a Shimadzu GC-17A gas chromatograph with a 5Å molecular sieve column (30 m, 0.53 mm) and a TCD detector, and were quantified by a calibration plot to the internal CH₄ standard.

Cyclic Voltammetry. Cyclic Voltammetry (CV) measurements of the metal-DHLA complexes were performed with a CHI 680 D potentiostat using a one-compartment cell with a glassy carbon working electrode, glassy carbon auxiliary electrode, and SCE reference electrode. The electrolyte for electrochemistry in 1:1 CH₃CN/H₂O was 0.1 M potassium chloride. Argon was used to purge all samples.

Faraday efficiency calculation. Faraday efficiency= (moles of H₂ produced)/(moles of electrons/2)

Conversion of potentials to reversible hydrogen electrode

All potentials reported in this paper were converted to reversible hydrogen electrode (RHE) using following equation:

$$V_{\text{RHE}} = [V_{\text{Ag/AgCl}} + (\text{pH} \times 0.059) + 0.196] \text{ V}$$

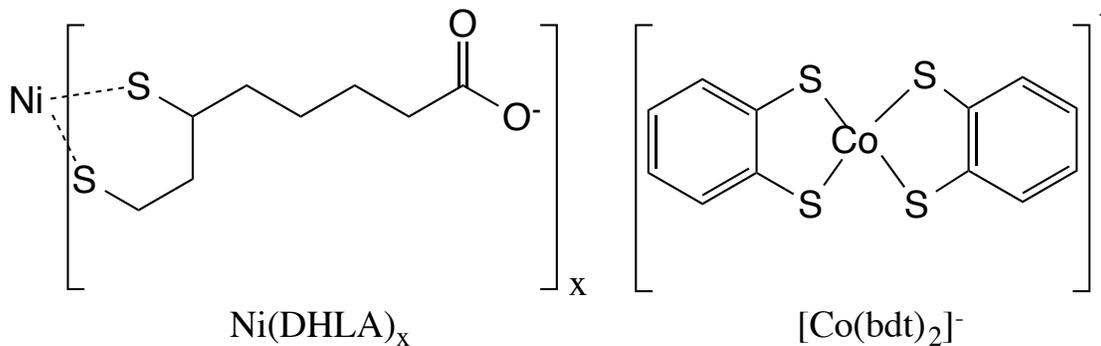


Figure S1: Chemical structures of the molecular catalysts.

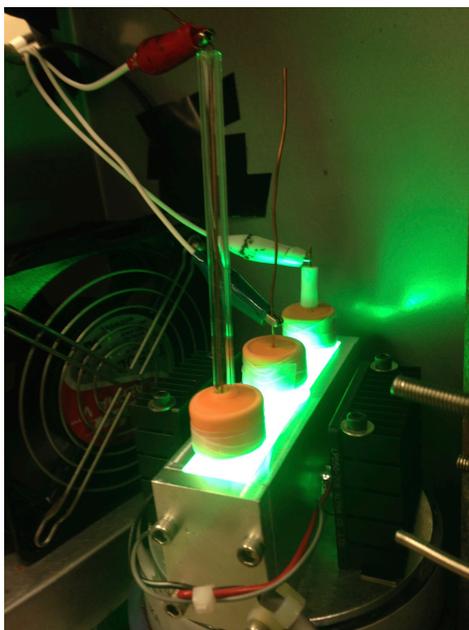


Figure S2: PEC experimental setup used for the study

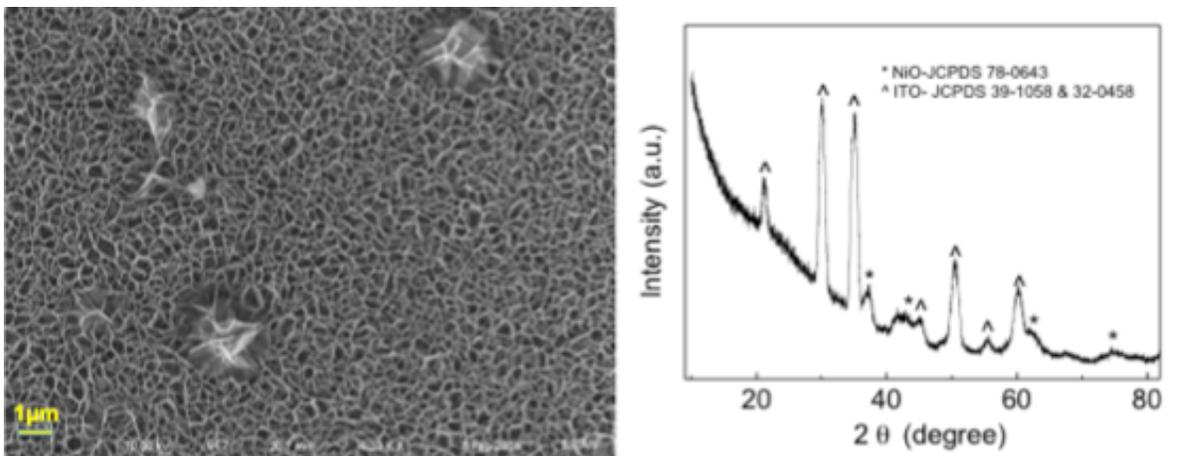


Figure S3: (a) SEM of ITO-NiO film (thickness $0.75(\pm 25) \mu\text{m}$) (b) XRD of ITO-NiO film



Figure S4: SEM of NiO film: before CdSe QD deposition(left) after CdSe deposition(right). Notice the smoothness of the surface of NiO has disappeared upon QD deposition

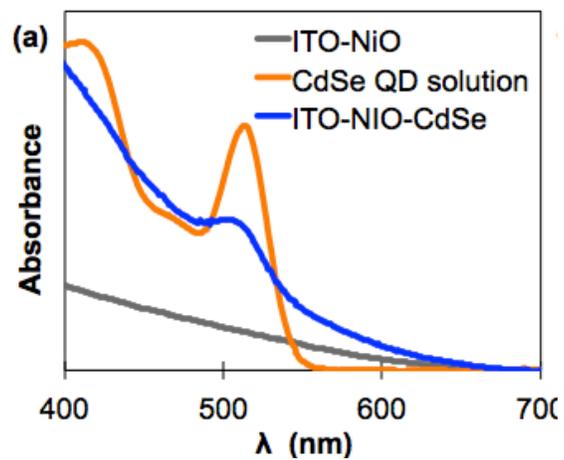


Figure S5: UV-Vis spectra of S_3 -cap-CdSe solution, ITO-NiO and NiO- S_3 -cap-CdSe thin films

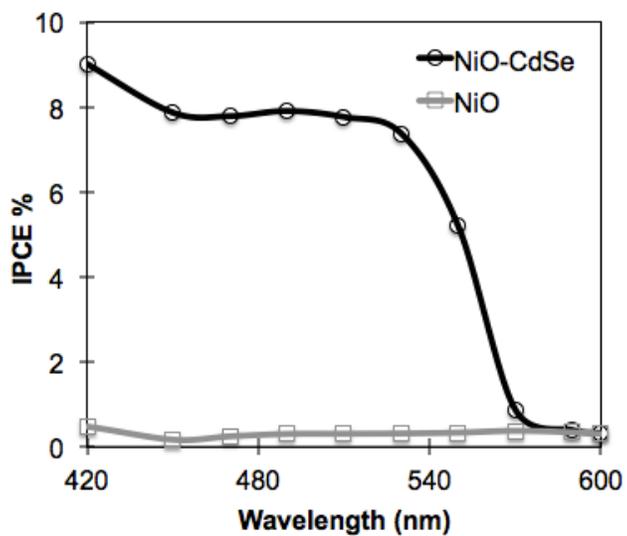


Figure S6: IPCE spectra of NiO- S_3 -cap-CdSe and NiO film

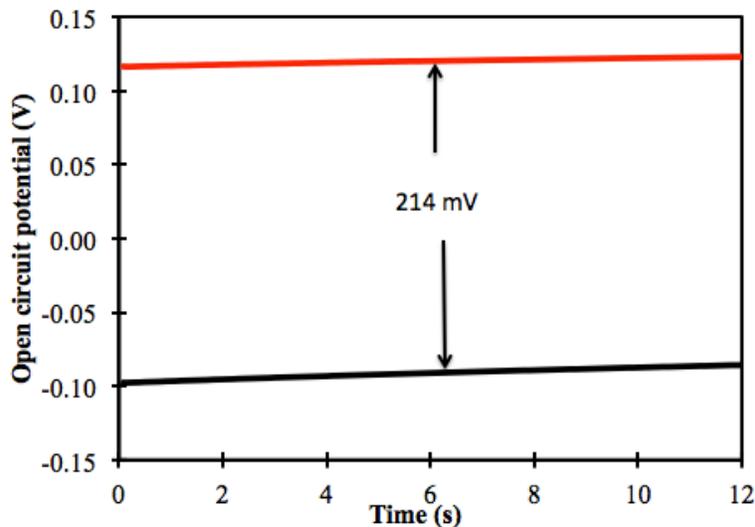


Figure S7: Open circuit potential (OCP) vs. Ag/ AgCl (1 M KCl) under dark (black line) and illuminated (red line, 150 mW light intensity) conditions. The difference in magnitude of the two values shows photocathode has a photovoltage of 214 mV.

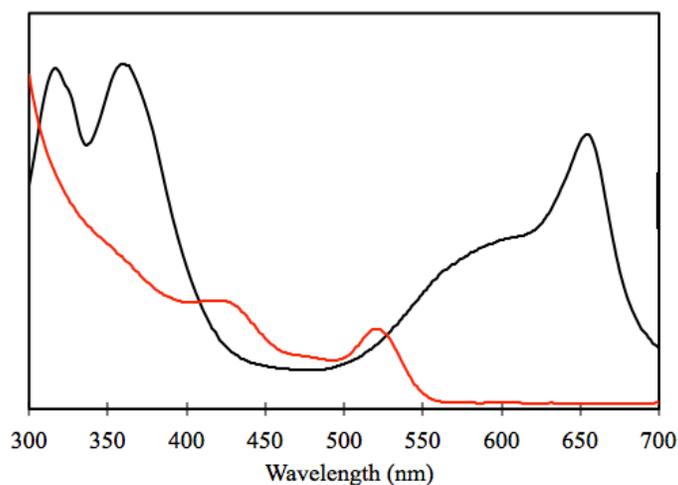


Figure S8: UV/Vis spectra of CdSe quantum dots (red) and $[\text{Co}(\text{bdt})_2]^-$ (black) in 1:1 $\text{CH}_3\text{CN}:\text{H}_2\text{O}$ solution. Molar extinction coefficients for CdSe quantum dots and $[\text{Co}(\text{bdt})_2]^-$ at 520 nm wavelength are $64000 \text{ M}^{-1}\text{cm}^{-1}$ and $3000 \text{ M}^{-1}\text{cm}^{-1}$ respectively

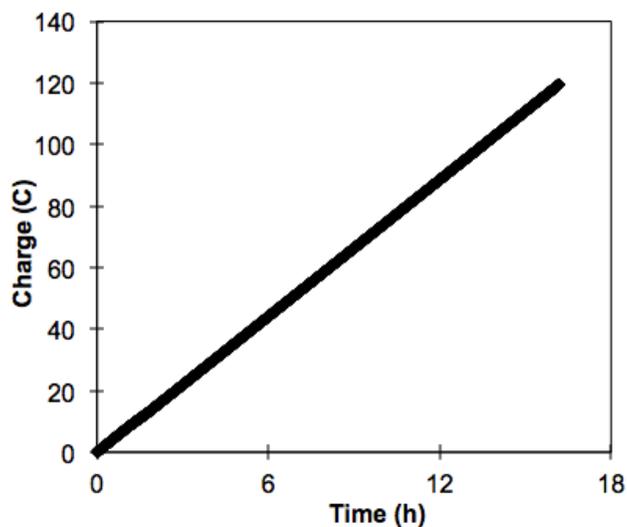


Figure S9: Charge vs. time curve of NiO-S₃-cap-CdSe photocathode with [Co(bdt)₂]⁻ (185µM) at -0.28 V vs. RHE in 1:1 CH₃CN:H₂O with 0.1M KCl with pH 6 HMTA /HCl buffer.

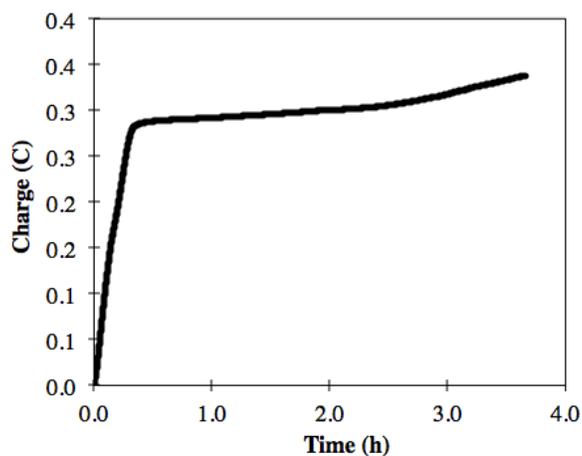


Figure S10: Charge vs. time for NiO-S₃-cap-CdSe with [Co(bdt)₂]⁻. Controlled potential electrolysis at -0.28 V versus RHE in pH 2 0.1M KCl in 1:1 CH₃CN: H₂O solution.

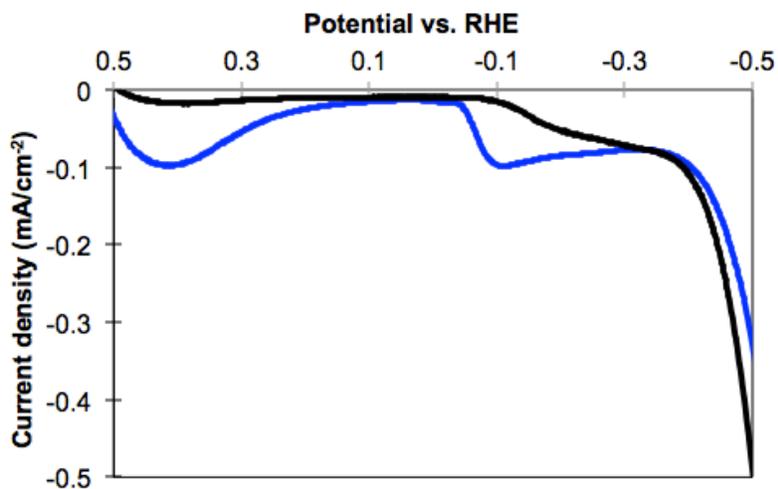


Figure S11: Linear sweep voltammograms of ITO- NiO-S₃-cap-CdSe film before (black) and after (blue) photoelectrocatalytic reaction.

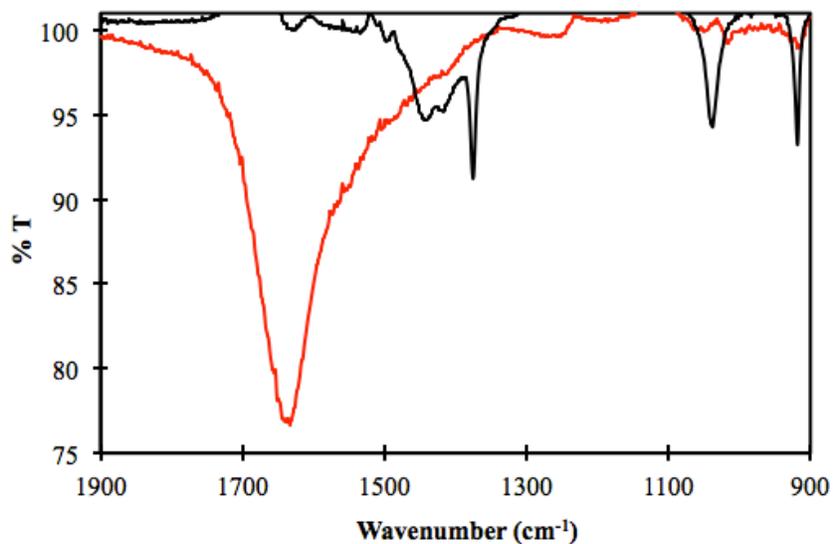


Figure S12: FT-IR spectra of S₃-cap-CdSe quantum dots dissolved in water (red line) and (nBu₄N)[Co(bdt)₂] complex in acetonitrile (black line).

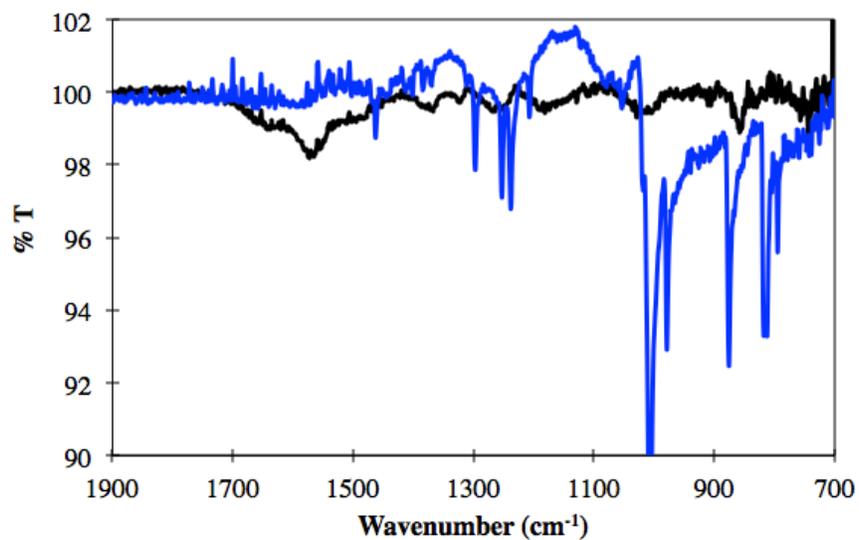


Figure S13: FT-IR spectra of ITO- NiO-S₃-cap-CdSe film before (black) and after (blue) photoelectrocatalytic reaction.

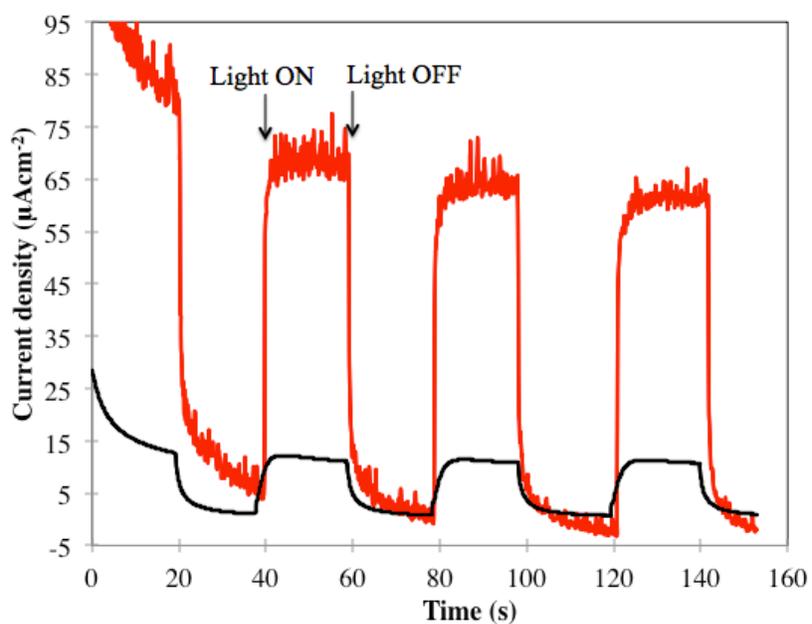


Figure S14: Photoresponse of ITO- NiO-S₃-cap-CdSe QD film (black) and ITO- NiO-S₃-cap-CdSe film with added [Co(bdt)₂]⁻ (red).

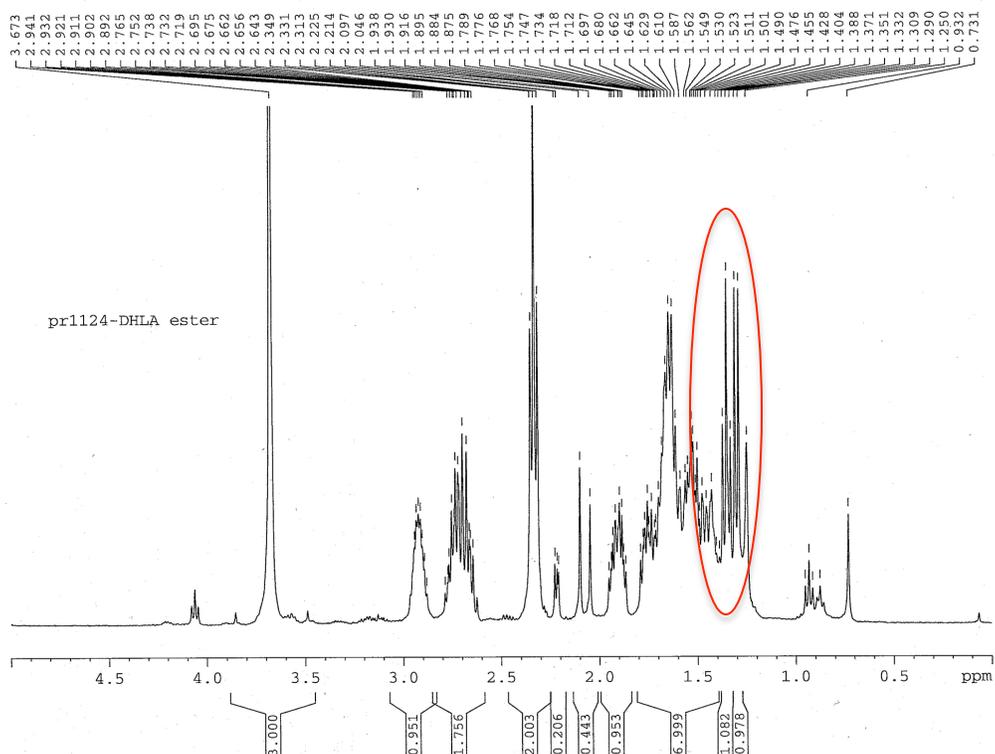


Figure S15: ^1H NMR of DHLA ester. Red circle highlights protons attached to the S atoms

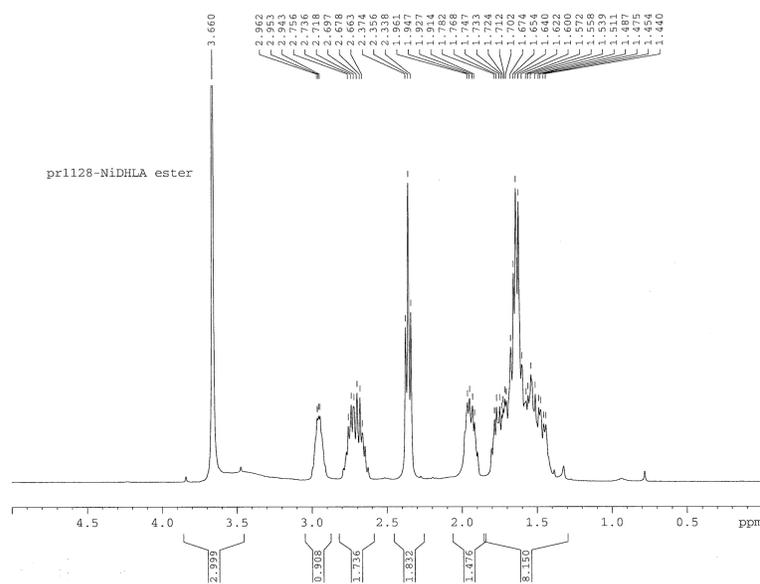


Figure S16 ^1H NMR of Ni(DHLA-ester) $_x$ complex. Notice the disappearance of the protons attached to S atoms. (DHLA-methyl ester was used as the ligand instead of DHLA because of improved solubility of the complex in NMR solvents.)

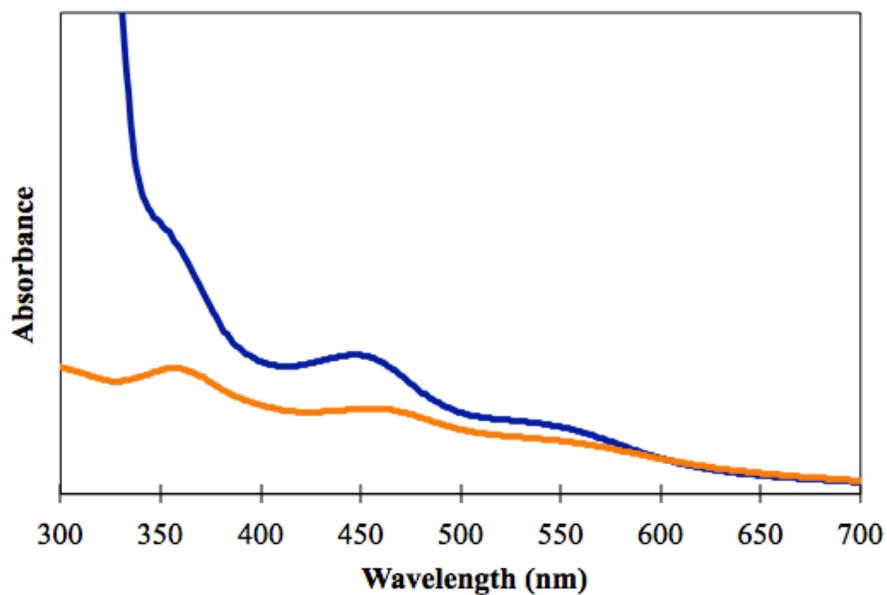


Figure S17: UV/Vis spectra of Ni(DHLA)_x complex (blue) and Ni(DHLA-ester)_x complex (orange) in 1:1 acetonitrile and water solution. Notice that both complexes have same set of peaks indicating both have similar electronic structure.

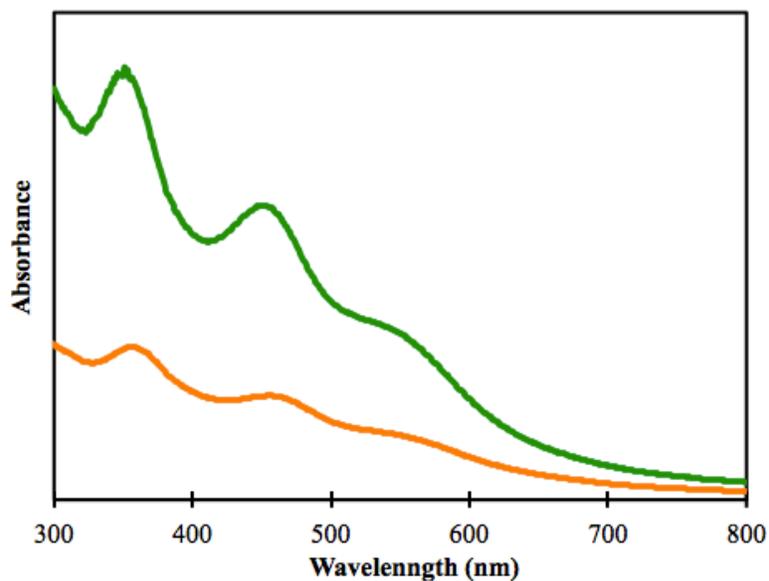


Figure S18: UV/Vis spectra of Ni(DHLA)_x complex (orange) and Ni(propane-dithiol)_x complex (green) in 1:1 acetonitrile and water solution and toluene respectively. Notice that both complexes have same set of peaks indicating both have similar electronic structure.

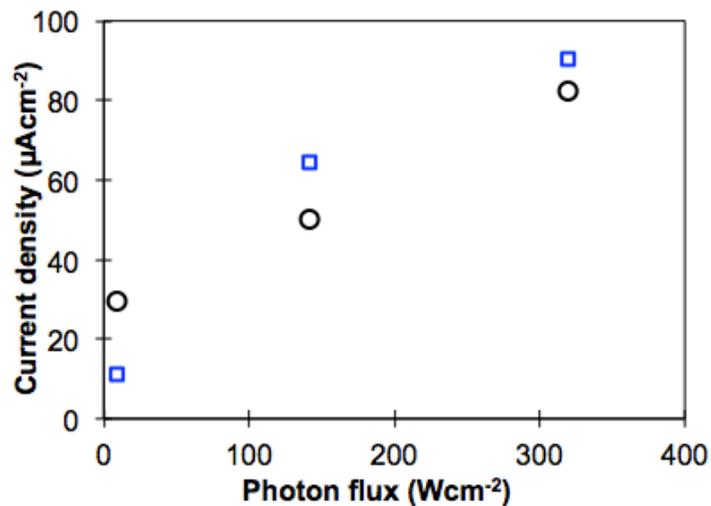


Figure S19: Current density vs. photon flux for NiO-S₃-cap-CdSe with [Co(bdt)₂]⁻ before (black circles) and after (blue squares) the PEC experiment.

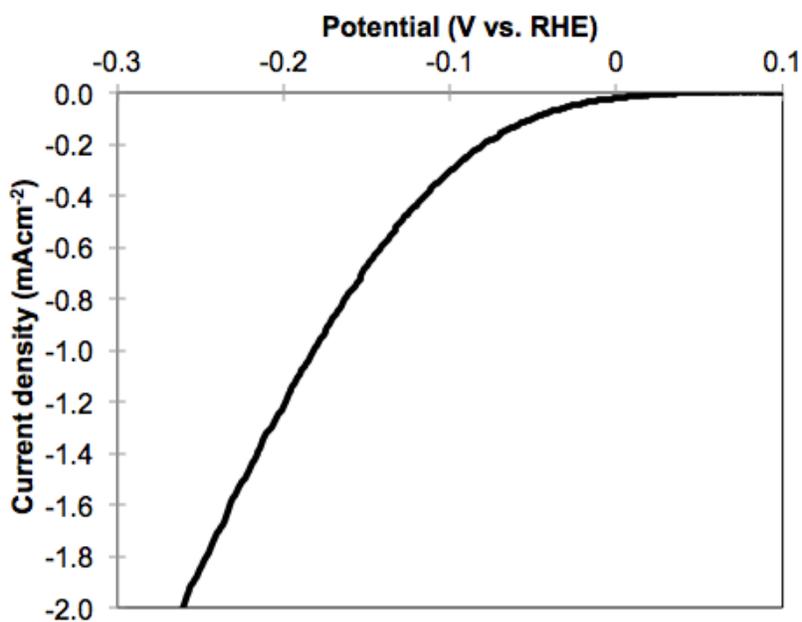


Figure S20: Current density vs. applied potential for NiO-S₃-cap-CdSe with [Co(bdt)₂]⁻

Table S1: A table of the concentration of [Co(bdt)₂]⁻ vs. amount of hydrogen produced

Catalyst concentration (mM)	μmols of H ₂ produced in 3 h
0.368	4.1
0.277	32.1
0.185	83.8
0.092	5.5
0.046	0.1

Table S2: A table of the pH of NiO-S₃-cap-CdSe with [Co(bdt)₂]⁻ system vs. Faradic efficiency for H₂ production. (Citric acid /sodium citrate buffer solutions in 1:1 H₂O/CH₃CN mix were used for pH 2-5 measurements. For pH 6 and 7 HMTA/HCl buffer and Na₂HPO₄/NaH₂PO₄ (in pure water) buffer were used respectively.

pH	Faradic efficiency %	pH	Faradic efficiency %
2	100 % (Electrode dissolves)	5	10±2
3	40±1	6	100±2
4	4±1	7	4±3*

*We believe that drastic change in Faradic efficiency from pH 6 to 7 is due to the poor solubility of the molecular catalyst in 100% water at pH 7.

References

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2. McNamara, W. R.; Han, Z.; Alperin, P. J.; Brennessel, W. W.; Holland, P. L.; Eisenberg, R. *J. Am. Chem. Soc.* **2011**, *133*, 15368-15371.
3. Das, A.; Han, Z.; Haghghi, M. G.; Eisenberg, R. *Proc. Natl. Acad. Sci. U.S.A.* **2013**, *110*, 16716-16723.
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