

## Supplemental Information

### Light-Driven Hydrogen Production from Aqueous Solutions based on a New Dubois-Type Nickel catalyst

Yulu Zhou, Sizhuo Yang, and Jier Huang\*

\*Corresponding Authors:

[jier.huang@marquette.edu](mailto:jier.huang@marquette.edu)

#### 1. Chemicals and Materials

Phenylphosphine was purchased from Sigma-Aldrich. The rest chemicals and solvents were purchased from VWR. All chemicals were used as received without further purification.

#### 2. Standard Characterization

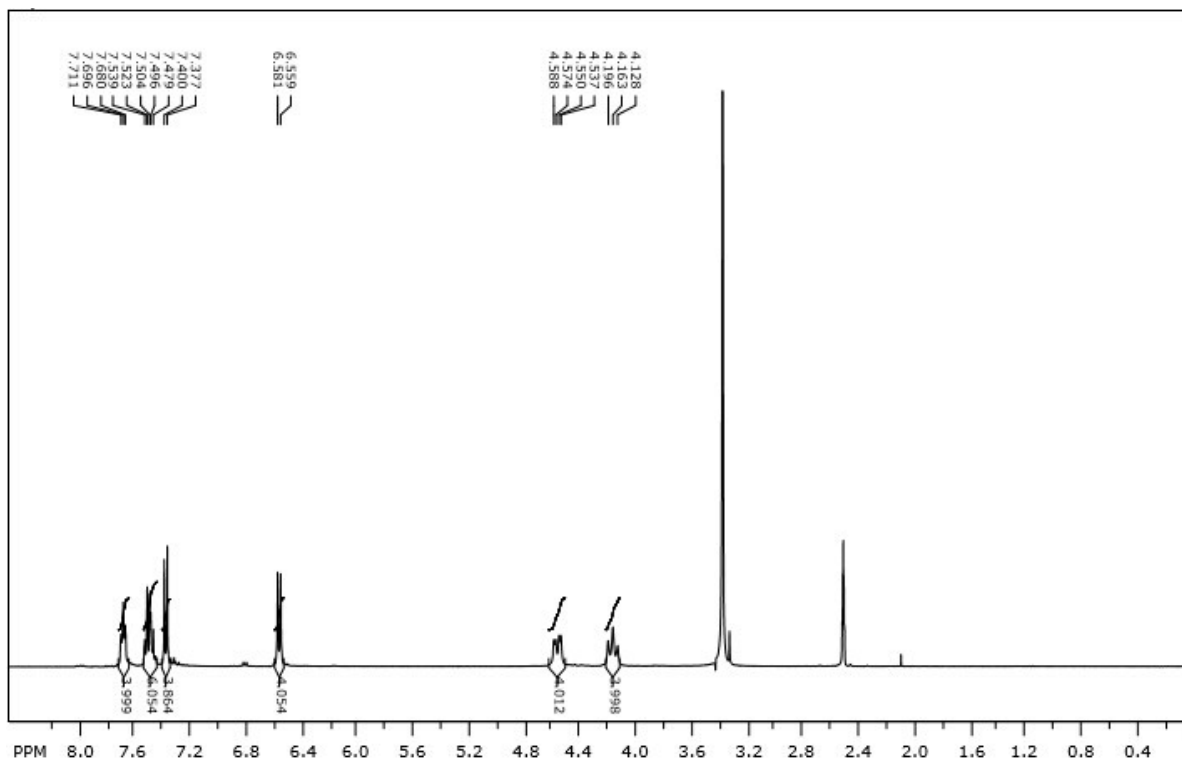
UV-Visible absorption spectra were taken using an Agilent 8453 spectrometer. Steady state and time-resolved emission spectra were measured using a PTI QM40. NMR experiments were carried out on VNMRS 400. Mass spectra were measured on Shimadzu LCMS-2020. Elemental analysis were measured by Midwest Microlab LLC. Cyclic voltammetry was carried out at BASi Epsilon Electrochemical Workstation (BASi Version E2-000000).

#### 3. The Synthesis and Characterization of $\text{P}_2^{\text{Ph}}\text{N}_2\text{C}_6\text{H}_4\text{PSO}_3\text{Na}$ .

Phenylphosphine (330 mg, 3.0 mmol) was added dropwise to a suspension of paraformaldehyde (180 mg, 6.0 mmol) in 5 mL of ethanol under  $\text{N}_2$  protection. The mixture was kept stirring for 12 h, after which a solution of sodium salt of sulfonic acid (586 mg, 3 mmol) in water (2 mL) was

added into the mixture. A white precipitate was formed after stirring overnight. The white precipitate was filtered out under vacuum, which is followed by washing with 2 mL of ethanol three times. This precipitate was confirmed to be  $P_2PhN_2C_6H_4PSO_3Na$  with  $^1H$  NMR,  $^{13}C$  NMR,  $^{31}P$  NMR and ESI-MS.

$^1H$  NMR (400 MHz, DMSO- $d_6$ ):  $\delta$  7.70 (t, 4H,  $J = 6.2$  Hz, Ph); 7.51 (m, 6H, Ph); 7.39 (d,  $J = 9.2$  Hz, 4H, Ph); 6.57 (d,  $J = 8.8$  Hz, 4H, Ph); 4.56 (dd,  $J = 5.4$  Hz,  $J = 15.0$  Hz, 4H, PCH $_2$ N); 4.16 (t,  $J = 13.6$  Hz, 4H, PCH $_2$ N).  $^{13}C\{^1H\}$  NMR (100.5 MHz, DMSO- $d_6$ ):  $\delta$  145.5 (s, Ph), 135.8 (s, Ph), 132.9 (d,  $J = 18.9$  Hz, Ph), 129.5 (s, Ph), 129.010 (s, Ph), 129.0095 (d,  $J = 6.4$  Hz, Ph), 126.5 (s, Ph), 111.1 (s, Ph), 55.5 (d,  $J = 14.0$  Hz, NCH $_2$ P).  $^{31}P\{^1H\}$  NMR (162 MHz, DMSO- $d_6$ ):  $\delta$  -49.4 (CH $_2$ PPhCH $_2$ ). ESI-MS (H $_2$ O, negative):  $m/z$  for  $[M-Na]^-$  635.05,  $m/z$  for  $[M-2Na]^{2-}$ , 306.05,  $m/z$  for  $[M-2Na+H]^-$  613.05.



**Figure S1**  $^1H$  NMR for  $P_2PhN_2C_6H_4PSO_3Na$

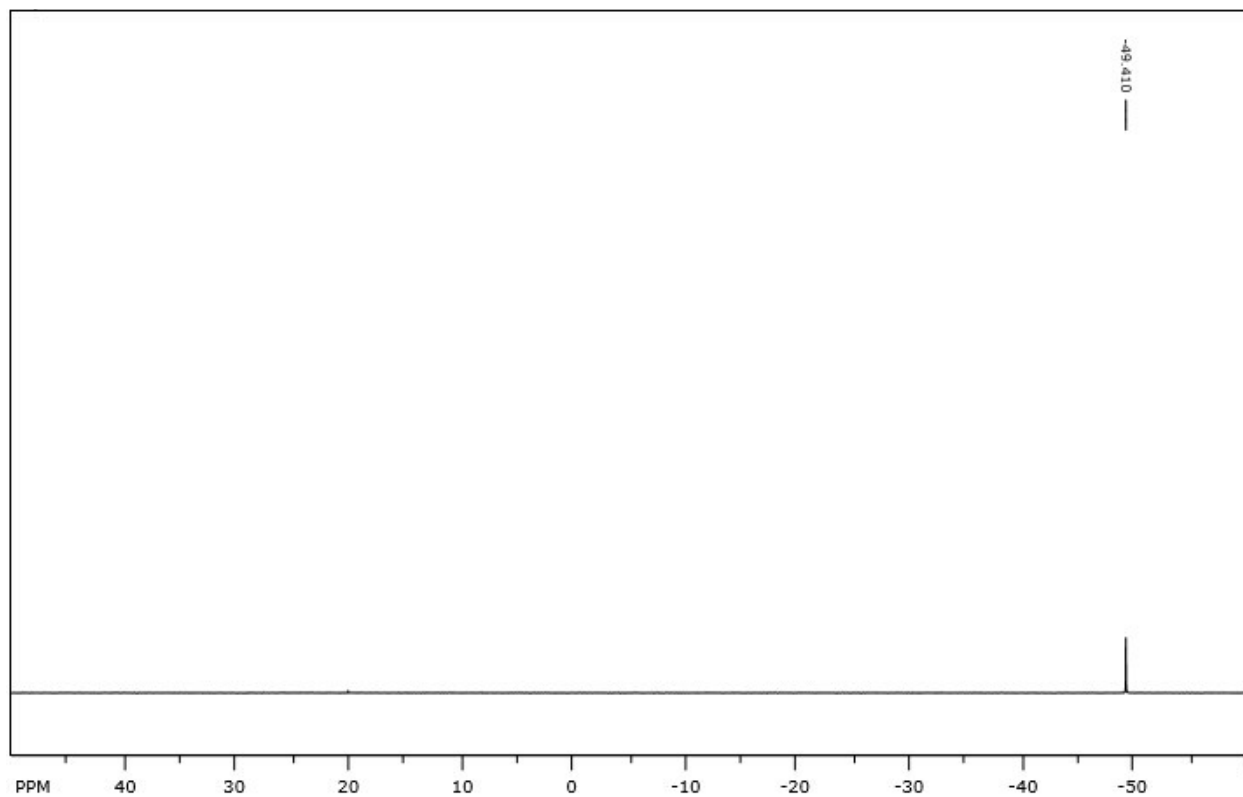
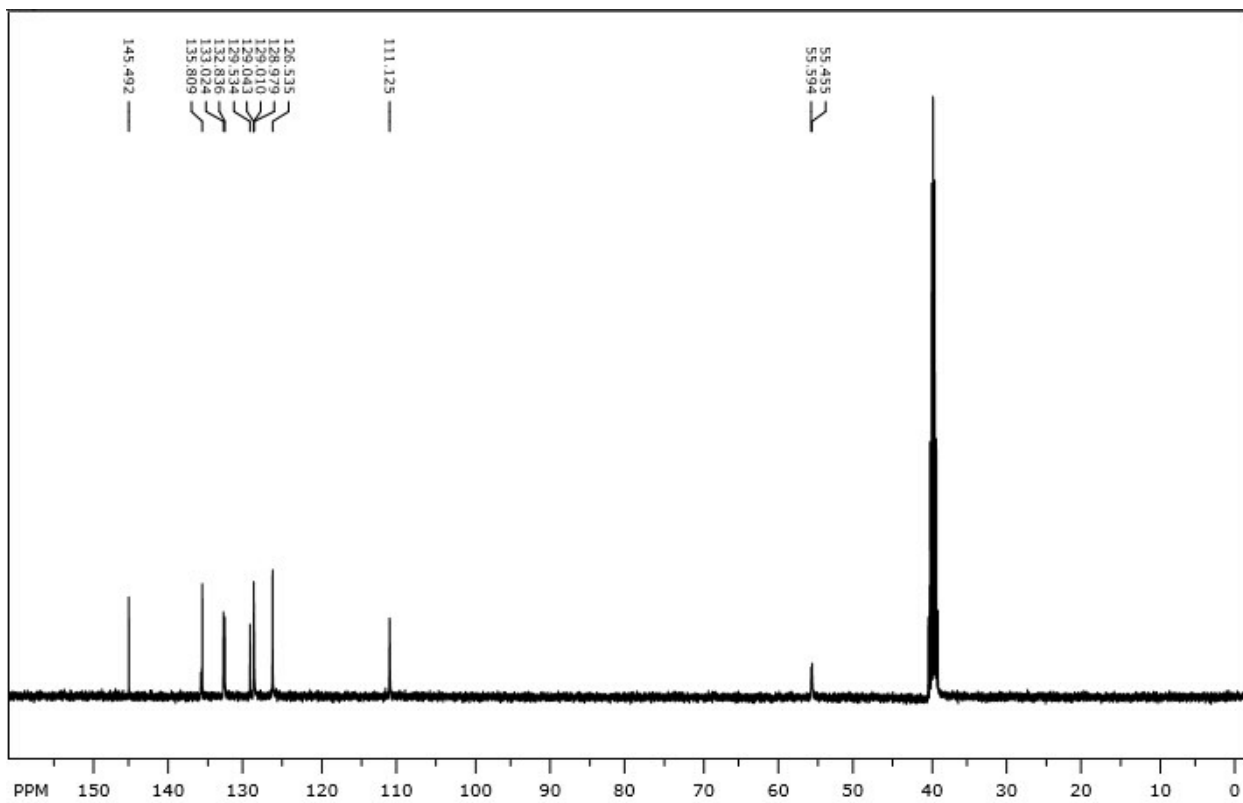


Figure S2  $^{31}\text{P}$  NMR for  $\text{P}_2\text{PhN}_2\text{C}_6\text{H}_4\text{SO}_3\text{Na}$



**Figure S3.  $^{13}\text{C}$  NMR for  $\text{P}_2^{\text{Ph}}\text{N}_2^{\text{C}_6\text{H}_4\text{PSO}_3\text{Na}}$**

#### **4. The Synthesis and Characterization of $\text{Na}_4[\text{Ni}(\text{P}_2^{\text{Ph}}\text{N}_2^{\text{C}_6\text{H}_4\text{SO}_3^-})_2(\text{BF}_4)_2]$**

$\text{P}_2^{\text{Ph}}\text{N}_2^{\text{C}_6\text{H}_4\text{PSO}_3\text{Na}}$  (328 mg, 0.5 mmol) and  $\text{Ni}(\text{CH}_3\text{CN})_6(\text{BF}_4)_2$  (120 mg, 0.25 mmol) were mixed in a round bottom flask, which is followed by purging with  $\text{N}_2$  for 30 min. After that, 5 mL of  $\text{H}_2\text{O}$  was added to the solution, which made the solution turn red immediately. The mixture solution was kept stirring overnight, after which a purple precipitate was formed. The mixture was then condensed to one third under vacuum, after which 10 mL of ethanol was added. The precipitate was filtered out under vacuum, washed with 2 mL of ethyl ether for three times, and finally dried under vacuum. 342 mg of purple product was collected with a yield of 88.3%. The structure of the product was confirmed by  $^1\text{H}$  NMR,  $^{31}\text{P}$  NMR, and element analysis.

$^{31}\text{P}\{^1\text{H}\}$  NMR (162 MHz,  $\text{D}_2\text{O}$ ):  $\delta$  18.1 (very broad signal,  $\text{CH}_2\text{PPhCH}_2$ ), -2.3 (very broad signal,  $\text{CH}_2\text{PPhCH}_2$ );  $^1\text{H}$  NMR (400 MHz,  $\text{D}_2\text{O}$ ):  $\delta$  7.48-6.76 (broad signal, m, 36H, Ph); 4.12-3.79 (broad signal, m, 16H, Ph); Anal. Calcd for  $\text{Na}_4[\text{Ni}(\text{P}_2^{\text{Ph}}\text{N}_2^{\text{C}_6\text{H}_4\text{SO}_3^-})_2(\text{BF}_4)_2] \cdot 6\text{H}_2\text{O}$ : C, 40.58; H, 3.89; N, 3.38; S, 7.74; Found: C, 40.31; H, 3.94; N, 3.51; S, 7.99.

#### **5. The Synthesis of CdSe QDs.**

20.5 mg (0.16 mmol) of CdO was mixed with 197.7 mg (0.7 mmol) oleic acid (OA) and 4.8 g (19 mmol) of 1-octadecene (1-ODE) in a 50 mL three-neck flask. The mixture was heated to  $300^\circ\text{C}$  under  $\text{N}_2$  for 30 min, and then injected with a solution of 7.9 mg (0.1 mmol) of Se dissolved in 125.4 mg (0.62 mmol) of tributylphosphine (TBP) and 1.0 g (4 mmol) of 1-ODE. The mixture solution was then cooled to  $260^\circ\text{C}$  and maintained at  $260^\circ\text{C}$  for 30 s. The mixture was washed with 10 mL of acetone and methanol for 3 times by centrifuging successively. The resulting CdSe

QDs were re-dispersed in 5 mL of toluene. For ligand exchange, a 5 mL of CdSe QDs nanocrystals solution was mixed with a solution of 3-mercaptopropionic acid (MPA) at a fixed concentration of 5 mM (MPA 123 mg, 0.3 mL of H<sub>2</sub>O, 1 mL of MeOH), which was kept stirring overnight. The QDs were precipitated out by acetone. The resulting ligand-exchanged QDs is redispersed in 20 mL of H<sub>2</sub>O.

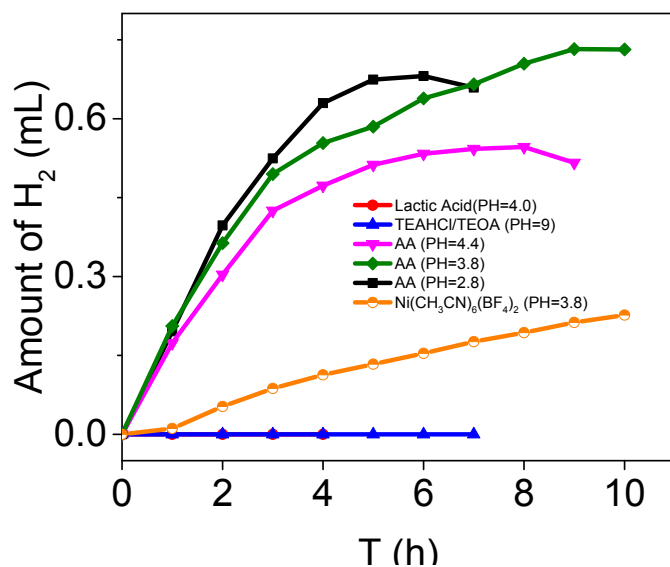
## **6. Electrochemical Experiments.**

In a typical experiment, a 0.1 mM solution of NiS in H<sub>2</sub>O was prepared in an electrochemical cell with three electrode system. A platinum electrode, platinum wire, and Ag/AgCl electrode (3 M NaCl) were used as working, counter, and reference electrode, respectively. 0.1 M KCl was used as electrolyte. The solution was degassed with N<sub>2</sub> for 60 min. Cyclic voltammogram was collected under a scan rate of 20 mV s<sup>-1</sup>.

## **7. Photochemical Hydrogen Generation**

In a general process, a certain amount of NiS stock solution ( $4.0 \times 10^{-3}$  M in H<sub>2</sub>O) was added to a vial first, followed by adding varying QDs stock solution ( $1.37 \times 10^{-5}$  M in H<sub>2</sub>O). The volume was then adjusted to 1.0 mL with water. Finally, 1.00 mL of ascorbic acid stock solution (0.2 M in H<sub>2</sub>O, pH 2.05 (NaOH)) was added, bringing the total volume to 2.0 mL. The vial was sealed, degassed with nitrogen, and transferred to photolysis apparatus. All photochemical hydrogen evolution experiments were performed in 9 mL vials and were run in a photolysis apparatus and irradiated from side. The apparatus consists of a model GPS-4303 Gwinstek laboratory DC power supply and a model M505L3 Thorlabs LED. The LED's nominal wavelength is 505 nm and the minimum power output is 400 mW. The power of the 505 nm LED was set to 22 mW measured by a Newport 843-R power meter. After irradiation, 200  $\mu$ L of the headspace of the vial was

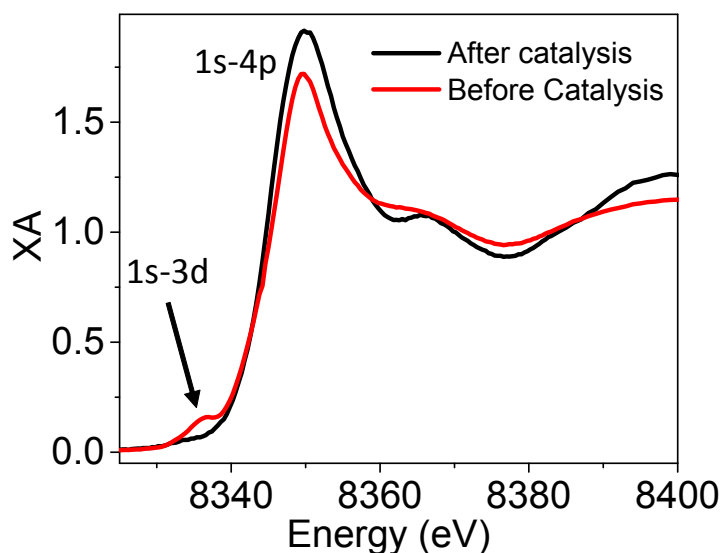
analyzed using a Agilent 490 micro gas chromatograph (5 Å molecular sieve column) to quantify the amounts of hydrogen evolved using a 2% hydrogen standard gas calibration curve.



**Figure S4.** Comparison of H<sub>2</sub> generation rate for different photocatalytic systems by varying the sacrificial electron donor/proton source and the value of pH. The H<sub>2</sub> generation profile using Ni(CH<sub>3</sub>CN)<sub>6</sub>(BF<sub>4</sub>)<sub>2</sub> was also presented for comparison.

## 8. X-ray absorption spectroscopy

The steady-state XAS experiments were performed at 12BM-B of the Advanced Photon Source at Argonne National Laboratory. The samples were oriented at standard 45° incident angle to give equal X-ray footprint and penetration depth at each sample thickness for fluorescence mode detection with 13-element germanium solid-state detector. Three ion chambers were configured to detect incident X-ray flux, transmission through the sample, and then transmission through a Ni reference foil for energy calibration.

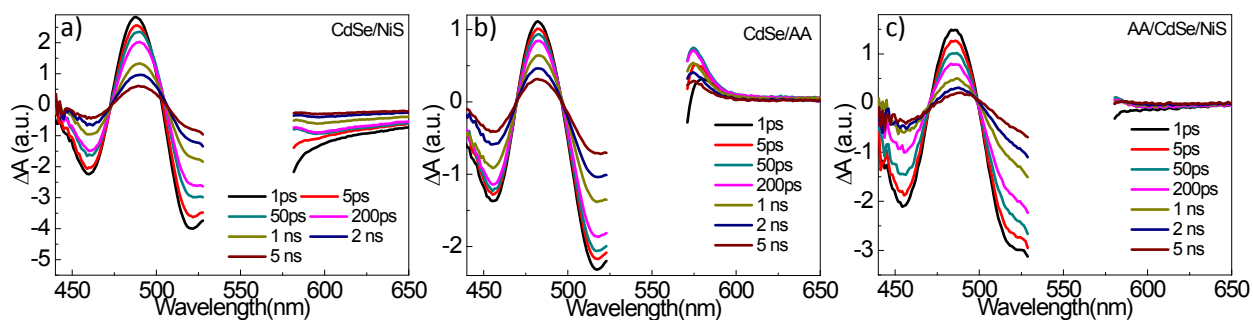


**Figure S5.** The comparison of X-ray absorption near edge structure spectra of NiS based photocatalytic system before and after catalysis.

## 9. Femtosecond absorption spectroscopy

The femtosecond absorption spectrometer is based on a regenerative amplified Ti-Sapphire laser system (Solstice, 800nm, < 100 fs FWHM, 3.5 mJ/pulse, 1 KHz repetition rate). The tunable pump is generated in TOPAS which has output with tunable wavelength ranging from 254 nm to 1100

nm. The tunable UV-visible probe pulses are generated by white light generation in a Sapphire window (430-750 nm) on a translation stage. The femtosecond transient absorption is performed in Helios ultrafast spectrometer (Ultrafast Systems LLC). The sample cuvette path length was 2 mm.



**Figure S6.** Femtosecond absorption spectra of CdSe/NiS (a), CdSe in the presence of AA (b), CdSe/NiS in the presence of AA (c).

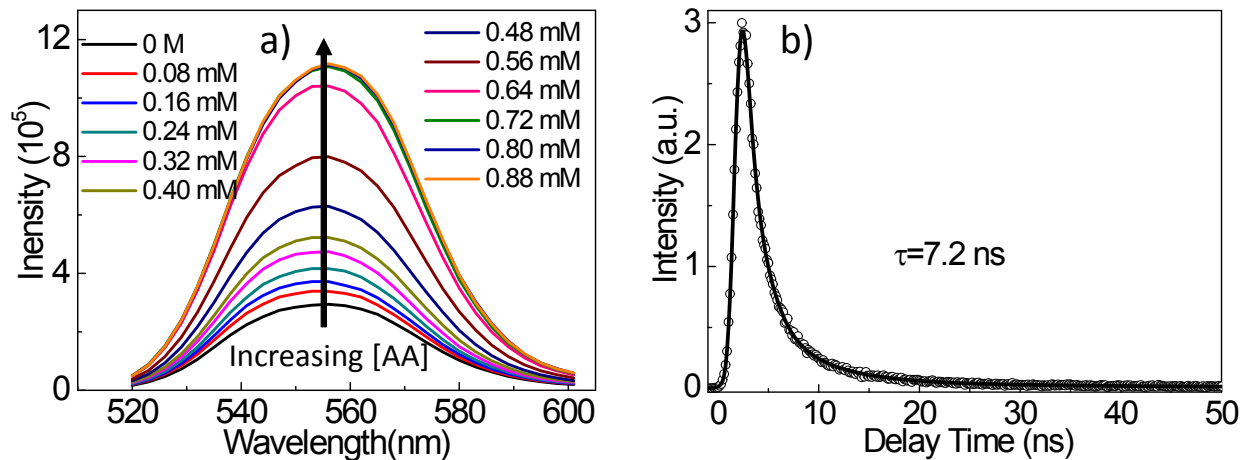
## 10. Emission Quenching by AA

A various amount of ascorbic acid (0.2 M in H<sub>2</sub>O) was added to CdSe QDs solution in a quartz cuvette. The solution was degassed with N<sub>2</sub>. The emission of CdSe QDs was collected after excitation at 400 nm. The hole transfer dynamics was modeled using Stern-Volmer equation:

$$I_0 / I = 1 + k_q \tau [AA] \quad (1)$$

Where  $I_0$  and  $I$  are the emission intensity of CdSe QDs in the absence and presence of AA;  $\tau$  is the electron-hole lifetime of CdSe QDs in the absence of AA, which is 7.2 ns obtained from TCSPC measurement (Figure S8b);  $k_q$  is the quenching rate constant. Plotting  $I_0 / I$  as a function of  $[AA]$  yields a linear plot that can be fitted by equation 1, from which we obtained  $k_q$ .





**Figure S7.** (a) The emission spectra of CdSe QDs with different concentrations of AA. (b) Fluorescence decay of CdSe QDs in H<sub>2</sub>O after 400 nm excitation. Emission was collected at 555 nm by TCSPC measurement.

### 10. Estimation of Energy Transfer Rate from CdSe QDs to AA

We estimated the energy transfer rate from excited CdSe QDs to AA using Förster resonant energy transfer (FRET) model described elsewhere.<sup>1,2</sup> The Förster radius ( $R_0$ ) is the distance at

which energy transfer is 50% efficient and is given by:  $R_0 = [8.8 \times 10^{23} \cdot \kappa^2 \cdot n^{-4} \cdot \eta \cdot J(\lambda)]^{\frac{1}{6}}$  Å

(S1)

Where  $\kappa^2$  = dipole orientation factor

$\eta$  = fluorescence quantum yield of the donor in the absence of the acceptor

$n$  = refractive index of the solvent

$$J(\lambda) = \int F_D(\lambda) \varepsilon_A(\lambda) \cdot \lambda^4 d\lambda \quad (\text{S2})$$

= spectral overlap integral (cm<sup>3</sup>M<sup>-1</sup>)

where  $F_D(\lambda)$  = fluorescence emission intensity of donor as a fraction of the total integrated intensity and  $\varepsilon_A(\lambda)$  = extinction coefficient of acceptor.

According to the emission spectrum of CdSe QDs and absorption extinction coefficient of NiS, the obtained  $J(\lambda)$  is  $4.7 \times 10^{-15} \text{ cm}^3 \cdot \text{M}^{-1}$ . If NiS is directly attached to the surface of CdSe QDs through  $\text{SO}_3^-$  group, the orientation of optical dipoles is fixed in NiS molecules but is random in CdSe QDs, which is similar to the previously reported nanoparticle/dye hybrid<sup>3,4</sup> and gives rise to the orientation factor around 1/2. In contrast, if NiS is not attached to CdSe QDs, then dipole orientations of both components are random which gives the orientation factor 2/3.

Using  $\kappa^2 = \frac{1}{2}$  or  $\kappa^2 = \frac{2}{3}$ ,  $\eta = 0.003$ ,  $n = 1.330$  (water), the calculated Förster radius is 11.2 or 11.8 Å.

The time constant for FRET is given by the equation:

$$t = \tau_D \left( \frac{r}{R_0} \right)^6 \quad (\text{S3})$$

Where  $\tau_D$  and  $r$  are the donor lifetime in the absence of the acceptor (7.2 ns) and the distance separating the donor and acceptor, respectively. If NiS is attached to the surface of CdSe QDs through  $\text{SO}_3^-$  group, the distance of donor and acceptor is given by the sum of the distance of Ni atom to  $\text{SO}_3^-$  (12.52 Å) and the radius of CdSe QDs (23 Å).<sup>5</sup> Therefore, the upper limit of the FRET time is 5.5  $\mu\text{s}$ , corresponding to the directly attached CdSe/NiS hybrid. This FRET rate is slower than ET process with magnitude of orders, suggesting that ENT in the current system is negligible.

- (1) Wu, K.; Chen, Z.; Lv, H.; Zhu, H.; Hill, C. L.; Lian, T. *J. Am. Chem. Soc.* **2014**, *136*, 7708.
- (2) Förster, T. *Ann. Phys. (Berlin)* **1948**, *437*, 55.
- (3) Van der Meer, B. W.; Coker, G.; Chen, S.-Y.; *Resonance Energy Transfer: Theory and Data*, Wiley-VCH, New York, **1994**.
- (4) Hardzei, M.; Artemyev, M.; Molinari, M.; Troyon, M.; Sukhanova, A.; Nabiev, I. *ChemPhysChem* **2012**, *13*, 330.
- (5) Yu, W. W.; Qu, L. H.; Guo, W. Z.; Peng, X. G. *Chem. Mater.* **2003**, *15*, 2854.