

## **Electronic Supplementary Information**

**For**

# **A biomimetic self-assembly Cobaloxime@CdS/rGO hybrid for boosting photocatalytic H<sub>2</sub> production**

Jun-Chao Hu, Shanshan Sun, Mingde Li,\* Wu Xia, Jin Wu, Hongfang Liu, Feng Wang\*

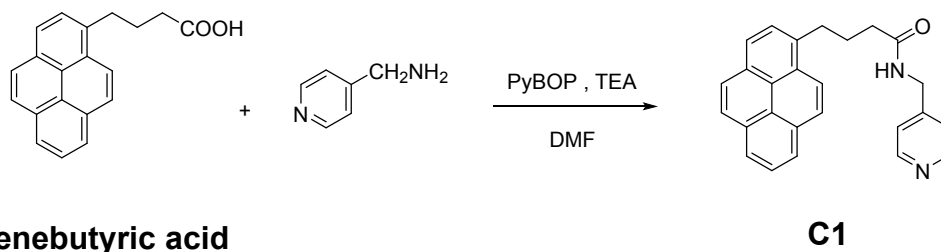
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## 1. Chemicals and synthesis

Dimethylglyoxime, N-Methylpyridin-4-amine, 1-Pyrenebutyric acid, Benzotriazol-1-yl-oxytripyrrolidinophosphonium hexafluorophosphate (PyBoP), Cobalt chloride hexahydrate ( $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ ), Cadmium acetate dihydrate ( $\text{Cd}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ ) and Triethylamine (TEA) were purchased from commercial suppliers (Sinopharm chemical reagent co., LTD and Sigma-Aldrich) and used without further purification. All solvents of analytical grade were purchased from commercial suppliers and used without further purification.

### ▪ The synthesis of CoPe

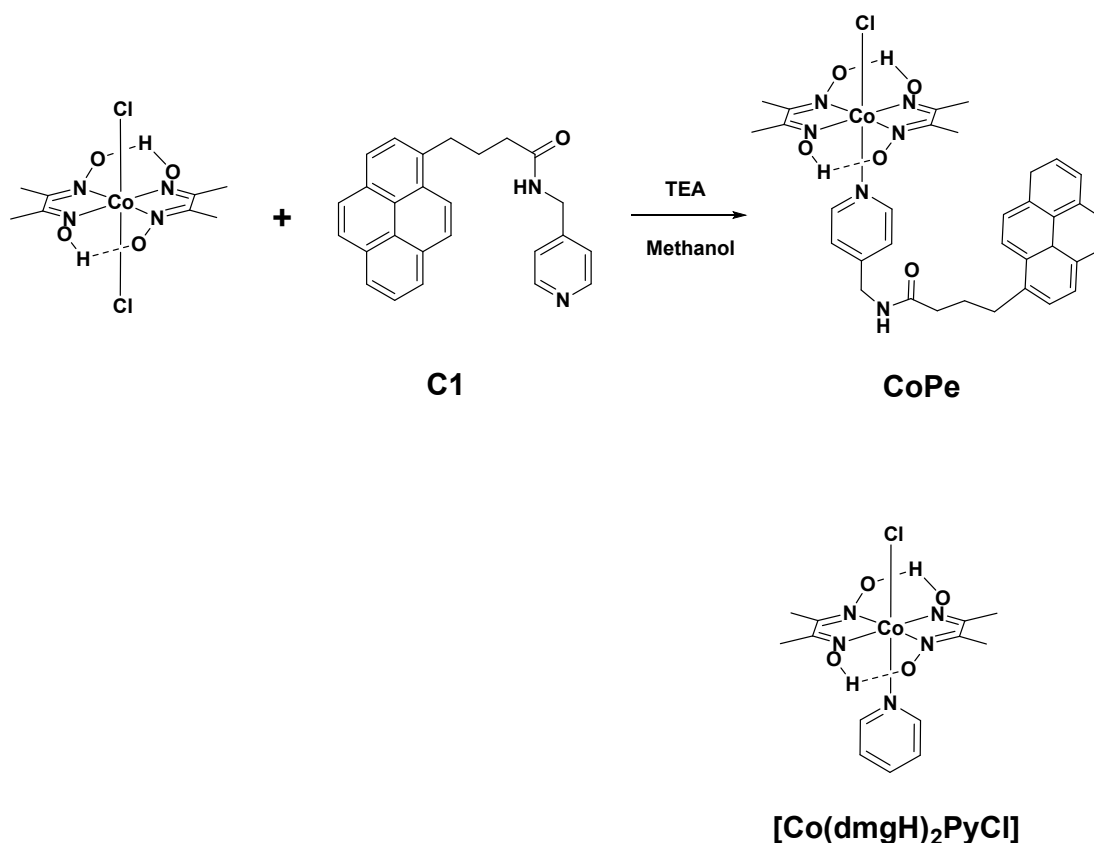
**[Co(dmgh<sub>2</sub>)(dmgh)Cl<sub>2</sub>]:** The [Co(dmgh<sub>2</sub>)(dmgh)Cl<sub>2</sub>] was synthesized using a previously reported method.<sup>[1]</sup> Briefly,  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  (1.09 g, 4.58 mmol) and dimethylglyoxime (1.10 g, 9.48 mmol) were dissolved in 20 ml of acetone, then the solution was stirred for 5 minutes and bubbled by air pump and stirring for another 40 min to form green [Co(dmgh<sub>2</sub>)(dmgh)Cl<sub>2</sub>].



**Scheme S1.** The synthetic route for C1

**C1:** 1-Pyrenebutyric acid (144 mg, 0.5 mmol) was suspended in dry DMF (10 mL) under a  $\text{N}_2$  atmosphere, and then TEA (2.0 mL) was added dropwise. The solution was stirred for 12 h at room temperature (r.t.). Then PyBoP (0.52 g, 1.0 mmol) was dissolved DMF (5 ml) and injected to the stirring solution. N-Methylpyridin-4-amine (0.06 g, 1.0 mmol) was dissolved DMF (3 ml) and injected to the solution. After 3 h stirring at r.t., most of solvent was removed by vacuum distillation, saturated saline was added and the aqueous layer was extracted with DCM. The

combined organic layers were washed with brine, dried over  $\text{Na}_2\text{SO}_4$ , and evaporated in vacuo to dryness. The crude product was further purified by column chromatography on silica gel with  $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{OH}$  mixture solvent to give **C1** as yellow solid (yield 63.4%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.46(d,  $J = 5.28$ , 2H), 8.27-7.97(m, 8H), 7.82(d,  $J = 7.76$  Hz, 1H), 7.06(d,  $J = 5.08$  Hz, 2H), 5.89(s, 1H), 4.36(d,  $J = 5.92$  Hz, 2H), 3.39 (t,  $J = 7.08$  Hz, 2H), 2.31-2.20 (m, 4H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  172.95, 149.89, 147.67, 135.68, 131.50, 130.96, 130.08, 128.88, 127.57, 127.45, 126.89, 126.05, 125.19, 125.11, 125.05, 124.94, 124.91, 123.38, 122.35, 42.34, 35.81, 32.73, 27.37. MS (ESI,  $m/z$ ): Calcd. For  $\text{C}_{26}\text{H}_{22}\text{N}_2\text{O}$   $[\text{M}+\text{H}]^+$ : 379.17; found, 379.16.



**Scheme S2.** The synthetic route for **CoPe** and the structure of  $[\text{Co}(\text{dmgH})_2\text{PyCl}]$

**CoPe:** The Green  $[\text{Co}(\text{dmgH}_2)(\text{dmgH})\text{Cl}_2]$  (0.1 g, 0.277 mmol) and TEA (192  $\mu\text{L}$ ) were added to alcohol (10 mL), the solution was stirred for 10 minutes, and then **C1** (0.1 g, 0.277 mmol) were added to the solution, a brown precipitate of

**CoPe** was formed during the stirring. The mixture was stirred for another 1 hours until the green precipitate disappeared completely. The brown **CoPe** was obtained by filtration, washed with alcohol, and dried at 40 °C under vacuum (yield 91.4%). MS (ESI, m/z): Calcd. For  $C_{34}H_{36}ClCoN_6O_5$   $[M+Na]^+$  : 725.1660; found: 725.1628.

- **The synthesis of CdS/rGO**

The CdS@rGO composite was synthesized according to literatures' methods.<sup>[2]</sup> Shortly, GO (2.69 mg) was dispersed in DMSO (100 ml) by ultrasonication for 1h to prepare a homogeneous solution. To a 100 mL of the above solution, Cd(Ac)<sub>2</sub>·2H<sub>2</sub>O (265.6 mg, 1 mmol) was added and dissolving by stirring. The solution was transferred to a 50 mL Teflon-lined autoclave and held at 180 °C for 12 h. After that, the formed precipitates from the mixture were allowed to be collected by centrifugation, and then rinsed with acetone and ethanol several times to remove residue of DMSO. The final product was dried in an oven at 60 °C for 12 h.

## 2. Instruments and methods

<sup>1</sup>H NMR spectra were recorded using a Bruker Avance III 400 MHz instrument with tetramethylsilane (TMS) as an internal standard. The X-ray diffraction quality crystal of **CoPe** was obtained by slow evaporation of a CHCl<sub>3</sub>/Et<sub>2</sub>O solution. X-ray diffraction data of **CoPe** were collected on an Apex Duo CCD diffractometer with Mo K $\alpha$  radiation (= 0.71073 Å). Empirical absorption corrections were applied using the multi-scan algorithm. The structure was solved by direct methods and refined by full-matrix least-squares on F<sup>2</sup> with anisotropic thermal parameters for all non-hydrogen atoms with the SHELXTL-2014 program. In this structure as it was not possible to see clear electron-density peaks in difference maps which would correspond with acceptable locations for the H atoms bonded to the half-occupancy water oxygen O5 atom, the refinement was completed with no allowance for these water H atoms in the model. The CCDC number of **CoPe** is 1858729. Field emission transmission electron microscope (FTEM) images were recorded on a Talos F200X (operated at an accelerating voltage of 200kV). The Raman spectra were recorded on a LabRAM HR800 Raman system using a light source with a wavelength of 532 nm. FT-IR spectra were performed on a VERTEX-10 (BRUKER, USA). Powder X-ray diffraction (XRD) was performed on an Empyrean X-ray diffractometer with monochromatized Cu K $\alpha$  radiation (1  $\frac{1}{4}$  1.5418 Å). UV-vis diffuse reflectance spectra (DRS) was carried out on a UV-3600 spectrophotometer employed with a lab-sphere diffuse reflectance accessory in the range of 200–800 nm. UV-vis spectra in solution were measured on UV-2600. The pH value measurements were determined with a Model PHS-3C meter (Mettler Toledo FE28, Swiss).

Cyclic voltammetry (CV) was recorded on CHI 760E electrochemical workstation. A three-electrode-system was used for the CV measurements; a glass carbon electrode, a platinum wire, and a Ag/AgNO<sub>3</sub> electrode were applied as working electrode, counter electrode, and reference electrode, respectively. The working electrode was polished with a 0.05  $\mu$ m alumina paste and sonicated for 15 min before use. The electrolyte solution is 0.1 M [nBu<sub>4</sub>N]PF<sub>6</sub> in DMF under at a scan rate of 100 mVs<sup>-1</sup>. The potentials are reported vs. NHE using Fc/Fc<sup>+</sup> couple as an internal standard (0.72 V vs. NHE in DMF).

Photocurrent density measurements were conducted using an electrochemical analyser (CHI 660E). The photocathode materials were

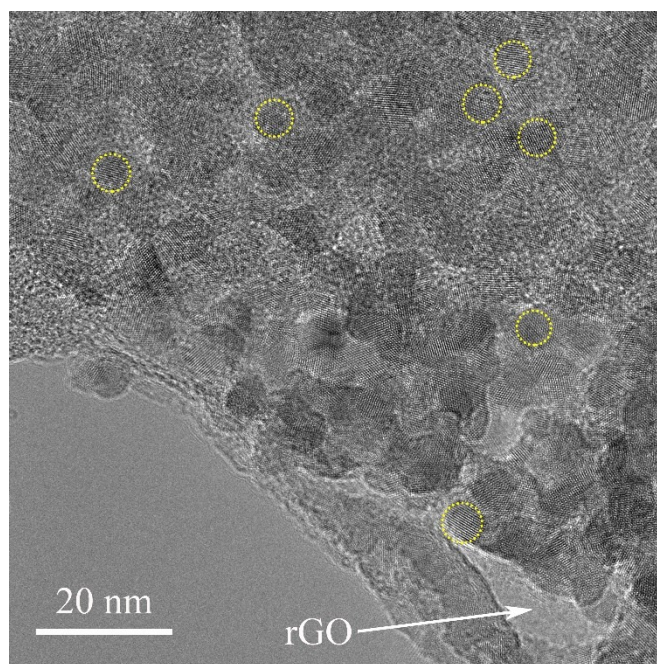
evaluated with a three-electrode configuration. The photocathode, a saturated calomel electrode (SCE), and a platinum electrode were used as working, reference, and counter electrodes, respectively. 0.1 M Na<sub>2</sub>SO<sub>4</sub> aqueous solutions were used as electrolytes. Irradiation of the electrode with 420 filter ( $\lambda > 420\text{nm}$ ;  $120\text{mW cm}^{-2}$ ) was conducted using a solar simulator (CEL-S500R3, Aulight). The gaseous reaction products were analysed using gas chromatography (GC; GC-7900, Techcomp) with a thermal conductivity detector (TCD), a flame ionization detector (FID) and Ar as the carrier gas.

The fs-TA spectra were measured using a femtosecond regenerative amplified T<sub>i</sub>: sapphire laser system in which the amplifier was seeded with 80 fs laser pulses from an oscillator laser system. The laser probe pulse was produced by utilizing ~12.5% of the amplified 800 nm laser pulses to generate a white-light continuum (410–780 nm) by a Sapphire crystal. Then, this probe beam was split into two parts before traversing the sample. One probe beam passed through the sample, while the other probe laser beam passed through the reference spectrometer to monitor the fluctuations of the probe beam intensity. For the experiments in this study, a solution sample was measured in a 2 mm path length quartz cuvette. The sample was excited by a 400 nm pump beam, and the power was approximately 0.48 mW. To obtain the time constant of the different intermediates, a sum of convoluted exponentials function was used to fit a kinetic trace at the selected wavelength as follows:

$$S(t) = e^{-\left(\frac{t-t_0}{t_p}\right)^2} \times \sum_i A_i e^{-t-t_0/t_i}$$

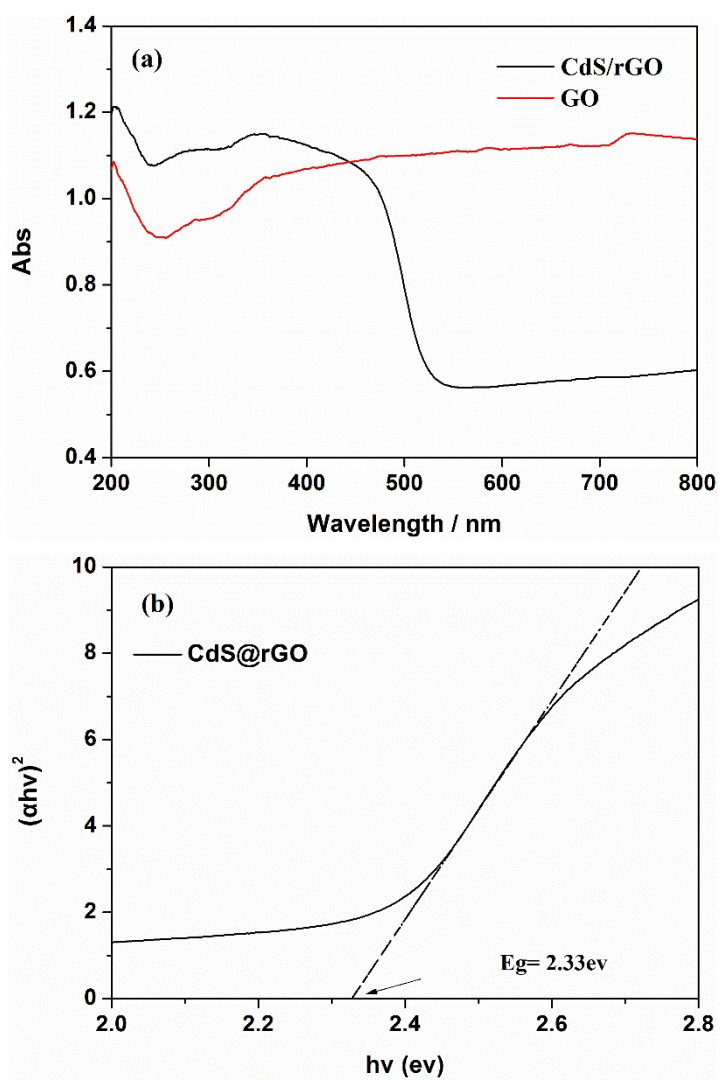
where  $t_p$  is the instrument response time;  $t_0$  is time zero; and  $A_i$  and  $t_i$  are amplitudes and decay times, respectively.

### 3. TEM images

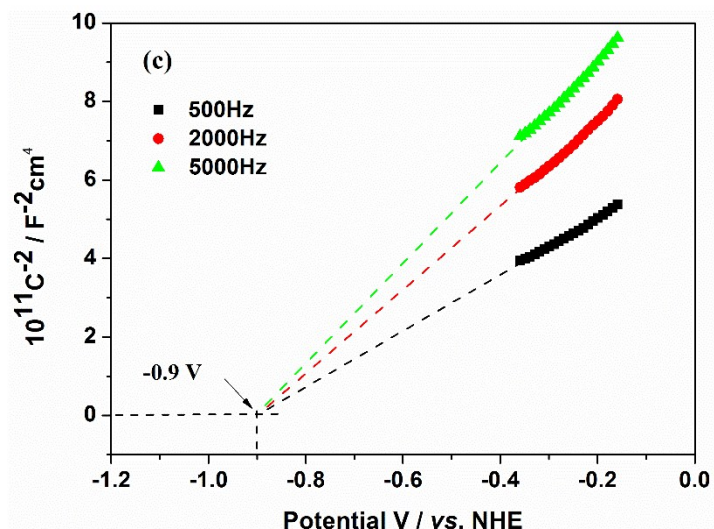


**Figure S1.** TEM image of CdS/rGO composite

#### 4. Diffuse reflectance spectra of CdS/rGO and GO

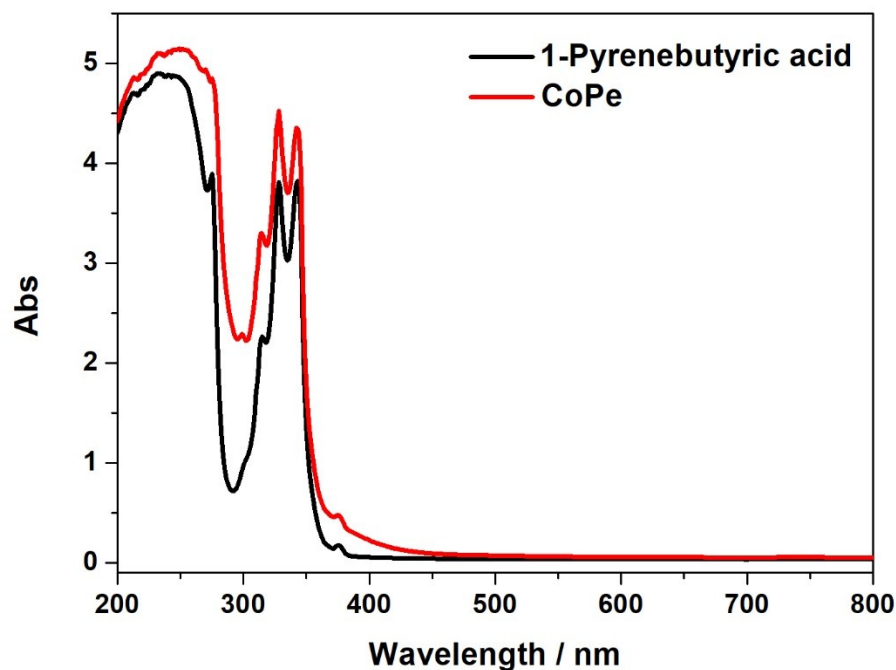






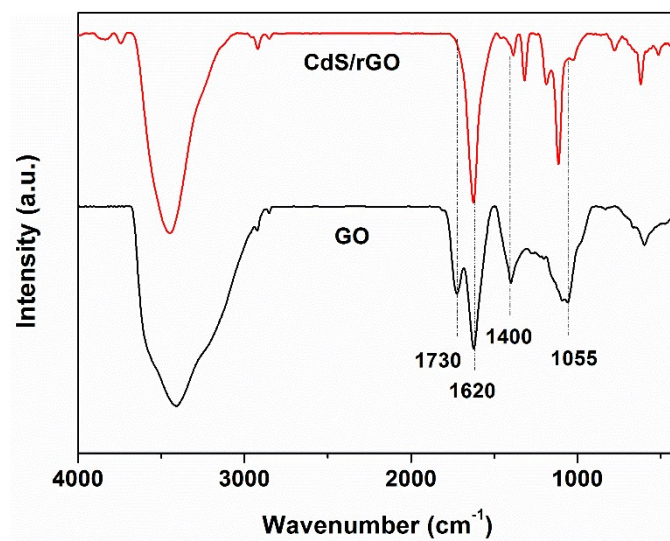
**Figure S2.** (a) Diffuse reflectance spectra of GO and CdS/rGO, (b) the corresponding Tauc plots  $((\alpha h\nu)^2)$  vs photon energy  $(h\nu)$  and (c) Mott-Schottky plots of CdS/rGO

## 5. UV-vis absorption spectra

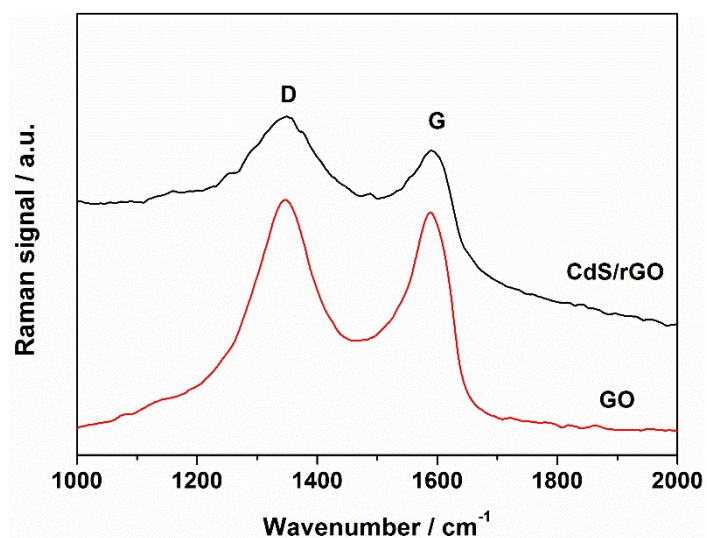


**Figure S3.** UV-vis absorption spectra of **CoPe** ( $5.00 \times 10^{-5}$  M) and 1-Pyrenebutyric acid ( $5.00 \times 10^{-5}$  M) in DMF

## 6. FT-IR and Raman spectra of CdS/rGO and GO

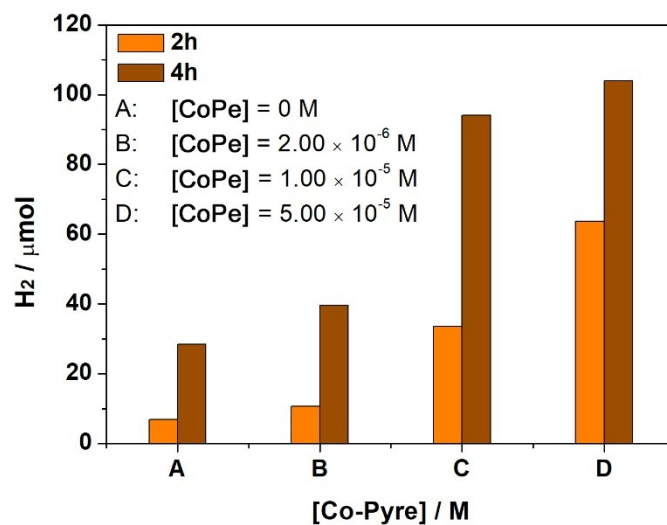


**Figure S4.** ATR FT-IR spectra for CdS/rGO and GO



**Figure S5.** Raman spectra of GO and CdS/rGO

## 7. Photocatalysis



**Figure S6.** Photocatalytic H<sub>2</sub> production with different **CoPe** concentration

**Table S1.** The TONs and rate of H<sub>2</sub> production of the photocatalytic systems in Figure 2c

System	[CoPe] / M	n(H <sub>2</sub> ) / μmol	TON <sub>total</sub>	TON <sub>CoPe</sub>	R <sub>CdS/rGO</sub> / μmol mg <sup>-1</sup> h <sup>-1</sup>
CoPe@CdS/rGO	1.00 × 10 <sup>-5</sup>	1736.2	21703	10467	27.1
CoPe@CdS/rGO	2.00 × 10 <sup>-6</sup>	1258.3	78642	22464	19.7
CdS/rGO	/	898.8	/	/	14.0

Irradiation time: 80 h

$$\text{TON}_{\text{total}} = \frac{n(\text{H}_2)}{n(\text{CoPe})}$$

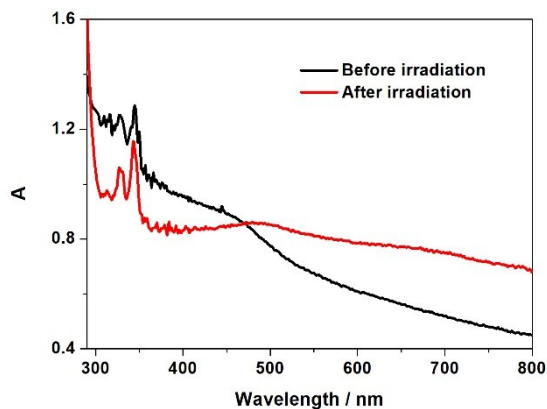
$$\text{TON}_{\text{CoPe}} = \frac{n(\text{H}_2) - n(\text{ref})}{n(\text{CoPe})}$$

*n(H<sub>2</sub>): the amount of H<sub>2</sub> produced from the system*

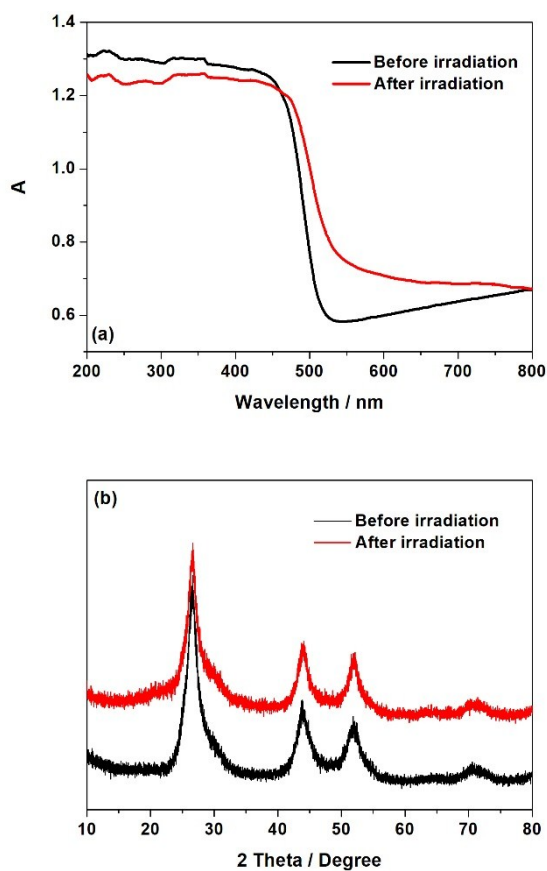
*n(ref): the amount of H<sub>2</sub> produced from the reference CdS/rGO system*

*n(CoPe): the amount of **CoPe** used in the system*

## 8. Inactivation analysis



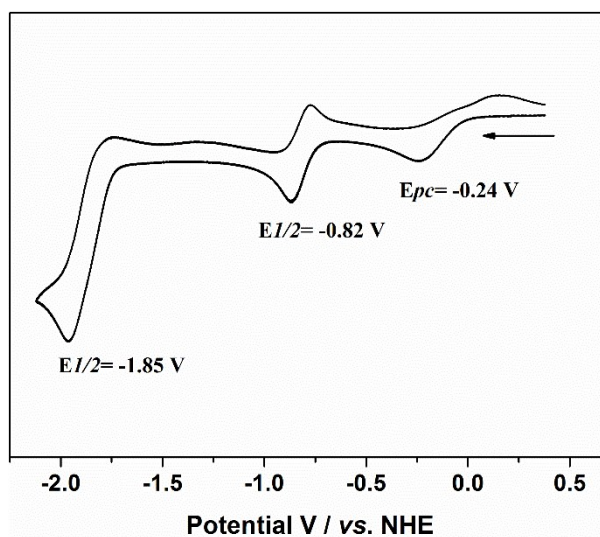
**Figure S7.** UV-vis absorption spectra of the **CoPe@CdS/rGO** photocatalytic  $H_2$  production system before and after photocatalysis



**Figure S8.** (a) Diffuse reflectance spectra and (b) XRD spectra of the solid sample isolated from **CoPe@CdS/rGO** photocatalytic  $H_2$  production system before and

after photocatalysis

## 9. Cyclic voltammetry of CoPe



**Figure S9.** Cyclic voltammetry of CoPe

## 10. Lifetime

**Table S2.** The lifetimes of kinetic decays at 497 nm of CdS/rGO and **CoPe@CdS/rGO** systems

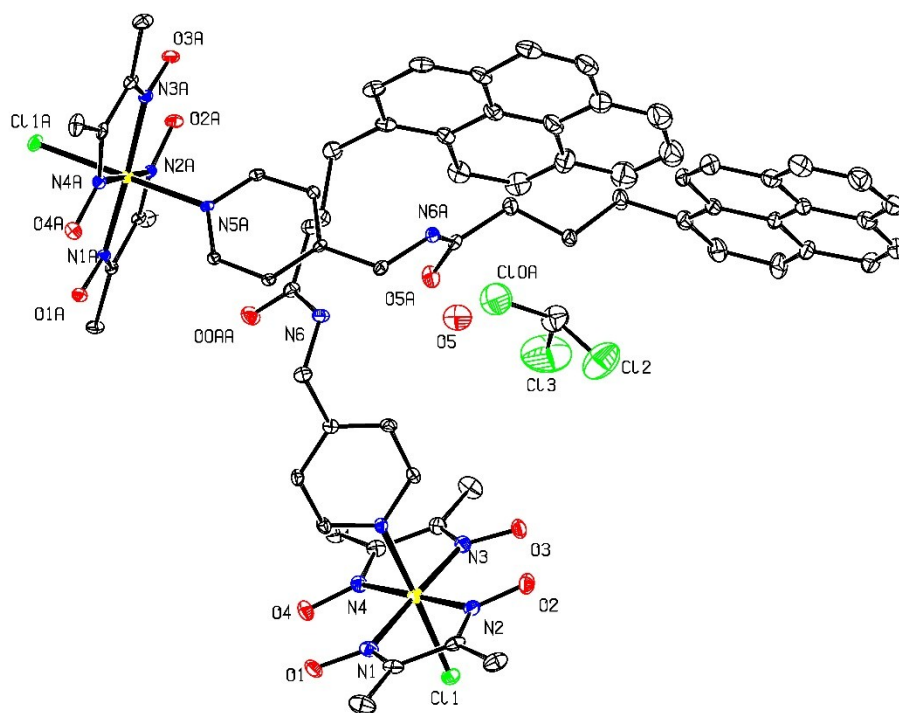
system	Lifetime 1		Lifetime 2		Lifetime 3	
	$\tau_1$ (ps)	Rel.%	$\tau_2$ (ps)	Rel.%	$\tau_3$ (ns)	Rel.%
CdS/rGO	2.94	33.1	50.4	37.7	0.67	22.3
<b>CoPe@CdS/rGO</b>	3.70	21.8	113	51.6	1.38	21.0

## 11. Single-Crystal structure analysis information

**Table S3.** Crystal data and structure refinement for mo\_191030b\_0m.

Identification code	mo_191030b_0m
Empirical formula	C <sub>34</sub> H <sub>36</sub> ClCoN <sub>6</sub> O <sub>5</sub> , 0.5(CHCl <sub>3</sub> ), 0.5(H <sub>2</sub> O)
Formula weight	771.76
Temperature/K	296(2)
Crystal system	triclinic
Space group	P-1
a/Å	8.8077(6)
b/Å	14.2501(11)
c/Å	28.349(2)
α/°	95.311(2)
β/°	91.077(2)
γ/°	95.834(2)
Volume/Å <sup>3</sup>	3523.0(4)
Z	4
ρ <sub>calc</sub> /cm <sup>3</sup>	1.455
μ/mm <sup>-1</sup>	0.729
F(000)	1600.0
Crystal size/mm <sup>3</sup>	0.06 × 0.05 × 0.04
Radiation	MoKα (λ = 0.71073)
2θ range for data collection/°	2.886 to 47.99
Index ranges	-9 ≤ h ≤ 10, -15 ≤ k ≤ 16, -31 ≤ l ≤ 32
Reflections collected	25133
Independent reflections	10443 [R <sub>int</sub> = 0.0630, R <sub>sigma</sub> = 0.1200]
Data/restraints/parameters	10443/161/904
Goodness-of-fit on F <sup>2</sup>	1.011
Final R indexes [I ≥ 2σ (I)]	R <sub>1</sub> = 0.0694, wR <sub>2</sub> = 0.1557
Final R indexes [all data]	R <sub>1</sub> = 0.1506, wR <sub>2</sub> = 0.1942
Largest diff. peak/hole / e Å <sup>-3</sup>	0.82/-0.76





**Figure S10.** The asymmetric unit of **CoPe** with displacement ellipsoids drawn at the 10% probability level. Hydrogen atoms are omitted for clarity.

## 12. References

- [1] P. Du, K. Knowles and R. Eisenberg. *J. Am. Chem. Soc.*, **2008**, *130*, 12576-12577.
- [2] Q. Li, B. Guo, J. Yu, J. Ran, B. Zhang, H. Yan and J. R. Gong. *J. Am. Chem. Soc.*, **2011**, *133*, 10878-10884.