

Electronic Supplementary Information

Redox-mediated photocatalysis towards separate hydrogen production and sulfide oxidation

Rui Li, Fei Lv, Xiaodan Jin, Pengfei Wang and Yubin Chen*

International Research Center for Renewable Energy, State Key Laboratory of Multiphase Flow in Power Engineering, Xi'an Jiaotong University, Shaanxi 710049, P. R. China

* E-mail: ybchen@mail.xjtu.edu.cn

Experimental section

Materials

Cd(OAc)₂·2H₂O, (Zn(OAc)₂·2H₂O, NaOH, thioacetamide, H₂PtCl₆·6H₂O, KOH, K₄[Fe(CN)₆]·3H₂O, K₃[Fe(CN)₆], KI, boric acid, sulfuric acid, KCl and ethanol were purchased from Sinopharm Chemical Reagent Co., Ltd without further purification. The water used in the experiments was deionized with a resistivity of 18.2 MΩ cm.

Synthesis of Cd_{0.1}Zn_{0.9}S photocatalysts

Cd_{0.1}Zn_{0.9}S was prepared by a hydrothermal method. Briefly, 2 mmol of Cd(OAc)₂·2H₂O and 18 mmol of Zn(OAc)₂·2H₂O were mixed in 40 mL of water and stirred for 5 min. Subsequently, 10 mL of NaOH solution (4 M) was added dropwise into the solution and stirred for 20 min. Then 25 mmol of thioacetamide was added and stirred for another 30 min. The suspension was then transferred into an 80 mL Teflon-lined autoclave and heated at 180 °C for 12 h. The products were washed thrice with deionized water and ethanol. Subsequently, the samples were dried in a vacuum oven at 70 °C for 7 h. Cd_{0.1}Zn_{0.9}S powders were obtained after grinding the dried samples.

Synthesis of Pt/Cd_{0.1}Zn_{0.9}S photocatalysts

Pt was photodeposited onto the Cd_{0.1}Zn_{0.9}S samples as a HER cocatalyst. Typically, 200 mg of Cd_{0.1}Zn_{0.9}S was dispersed into an aqueous KOH solution (80 mL, 1.0 M). H₂PtCl₆·6H₂O was then added into the solution as the Pt precursor with a Pt feed ratio of 1 wt.%. After ultrasonically dispersing for 1 min, the suspension was bubbled with Ar for 10 min to remove the air. The suspension was irradiated under full arc irradiation with a 300 W Xe lamp for 2 h. A circulating water system was used to maintain the temperature of the suspension at 25 °C. After washing with deionized water and centrifuging, dried in a vacuum at 70 °C for 7 h to obtain the Pt/Cd_{0.1}Zn_{0.9}S powders.

Synthesis of metal cyanoferrates

$K_2Zn_3[Fe(CN)_6]_2$ was prepared referencing a reported co-precipitation method.¹ 30 mL aqueous solution of $Zn(OAc)_2 \cdot 2H_2O$ (30 mmol) was added to 60 mL of aqueous solution of $K_4[Fe(CN)_6] \cdot 3H_2O$ (30 mmol). The reaction mixture was then stirred vigorously for 10 minutes using a magnetic stirrer. The preparation of $K_2Cd[Fe(CN)_6]$ was carried out using the same procedure, but with $Cd(OAc)_2 \cdot 2H_2O$ replacing $Zn(OAc)_2 \cdot 2H_2O$.

Characterization

The morphology and elemental distribution of the photocatalysts were characterized by a JEOL JSM7800F field emission scanning electron microscope (SEM) and FEI Tecnai G2 F30 S-Twin transmission electron microscope (TEM) equipped with an OXFORD MAX-80 energy-dispersive X-ray (EDX) detector. The crystal structure was analyzed by X-ray diffraction (XRD) using a PANalytical X'Pert MPD Pro X-ray diffractometer. Elemental analysis was carried out by X-ray photoelectron spectroscopy (XPS) using an Axis-Ultra DLD X-ray photoelectron spectrometer. The optical properties were determined by ultraviolet-visible (UV-Vis) absorption spectroscopy using a HITACHI U4100 spectrophotometer. Fourier transform infrared (FTIR) spectra were acquired on a Bruker Vertex 70 spectrophotometer. Raman measurement was conducted using a DXR Raman microscope with an excitation length of 532 nm. The element content was determined by inductively coupled plasma mass spectrometry (ICP-MS) using a PerkinElmer NxeION 5000G mass spectrometer and the S4 PIONEER X-ray fluorescence (XRF) spectrometer from Bruker, Germany.

Photocatalytic measurements

The photocatalytic H_2 production was measured in a 110 mL Pyrex glass bottle. Typically, 40 mg of the prepared photocatalyst was dispersed in 80 mL of an aqueous solution containing a certain

concentration of $\text{K}_4[\text{Fe}(\text{CN})_6] \cdot 3\text{H}_2\text{O}$. In some cases, a 0.1 M borate buffer (0.1 M boric acid, adjusted to a pH of 8.0 with KOH) was used to maintain the pH of the aqueous $\text{Fe}(\text{CN})_6^{4-}$ solution. In contrast trials, 10 mM of KI was used as the electron donor. The pH value of the aqueous solution containing I⁻ was adjusted to 4.0 to ensure the formation of its oxidation products I_3^- . After dispersing ultrasonically for 30 seconds, the solution was bubbled with Ar for 20 minutes to remove any air in the reaction cell. A 300 W Xe lamp served as the light source. A circulating water system was employed to maintain the suspension temperature at 25 °C. The gas generated was analyzed using gas chromatography with a thermal conductivity detector (TCD). The amounts of $\text{Fe}(\text{CN})_6^{3-}$ generated during photocatalysis were determined using a UV–visible spectrophotometer.

Electrochemical tests

Electrochemical measurements were conducted using a three-electrode system on an electrochemical workstation (CHI 760D, China).

Cyclic voltammetry (CV) measurements were performed at a scan rate of 50 mV s⁻¹. The working and counter electrodes were 3 × 3 cm² graphite sheets, and the reference electrode was an Hg/HgO electrode. The electrolyte was either 0.1 M borate buffer containing 10 mM $\text{K}_4[\text{Fe}(\text{CN})_6]$ or 0.2 M Na_2S aqueous solution.

Linear scanning voltammetry (LSV) tests for SOR were performed at 5 mV s⁻¹ with a voltage range from 0.2 to 1.38 V (vs. RHE). The counter and reference electrodes were a 1 cm² Pt electrode and an Hg/HgO electrode, respectively. The working electrodes comprised different electrode materials including graphite sheet, carbon cloth, and Pt. The electrolyte was 0.2 M Na_2S aqueous solution.

Mott–Schottky test was conducted at frequencies of 500 Hz and 1000 Hz with an amplitude of

10 mV. The counter and reference electrodes were a 1 cm² Pt electrode and a saturated Ag/AgCl electrode. The working electrode was fabricated as follows: 1 mg of the prepared photocatalyst was sonicated for 30 min in a mixture of 250 μL of deionized water and 250 μL of ethanol. Subsequently, 10 μL of Nafion solution (DuPont D1020, 10 wt.%) was added, and the mixture was sonicated for another 30 min. Next, 5 μL of the suspension was transferred to a rotating disc electrode and dried at room temperature for 2 h. The electrolyte was a nitrogen-saturated 0.5 M Na₂SO₄ solution.

Preparation of KCl salt bridge

97 mL of water was added to a 250 mL round-bottom flask and heated to 97 °C with stirring. 3 g of agar powder was then added and dissolved. Subsequently, 30 g of KCl was added. Once the KCl was completely dissolved, the solution was promptly transferred to a clean U-shaped glass tube and cooled to room temperature for further use.

Construction and test of the galvanic cell

The galvanic cell was constructed using two 100 mL spoutless beakers, two rubber stoppers with holes, a KCl salt bridge, two inert graphite sheet electrodes, and a wire. The beakers, sealed with rubber stoppers, served as chambers for the two half-reaction cells. The graphite electrodes were immersed in their respective electrolytes. The catholyte consisted of a specific concentration of Fe(CN)₆^{4-/3-} solution mixed with 0.1 M borate buffer, while the anolyte was 0.2 M Na₂S aqueous solution. A wire connected the two electrodes to complete the redox reactions: the reduction of Fe(CN)₆³⁻ and the oxidation of sulfide. A KCl salt bridge connected the two half-reaction cells to maintain charge balance. The open-circuit voltage and current-time curve of the galvanic cell were measured by connecting the electrodes to an electrochemical workstation.

Construction and test of the integrated photocatalytic-galvanic cell system

A 100 mL beaker with upper and lower spouts was used as the cathodic chamber of the galvanic cell. A peristaltic pump and pipes connected the cathodic chamber to the photocatalytic reactor. The system was purged with Ar for 20 minutes to expel internal air. A 180 mL photocatalytic reaction solution containing 90 mg of photocatalyst was prepared and purged with Ar. The first 90 mL was added to the photocatalytic reactor and then pumped through the pipes into the cathodic chamber. The remaining 90 mL of the reaction solution was subsequently added to the photocatalytic reactor. The system operated with the pump to achieve circulation of $\text{Fe}(\text{CN})_6^{4-/3-}$ between the photocatalytic reactor and the galvanic cell. The photocatalyst was homogeneously dispersed in the photocatalytic reactor and cathodic cell with the same mass concentration of 0.5 mg mL^{-1} . Refer to the above section for additional operations.

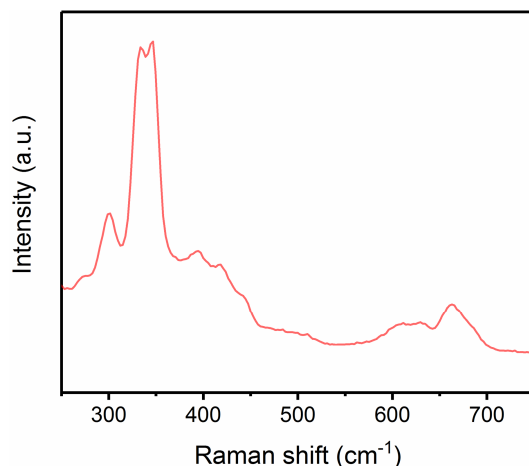


Figure S1 Raman spectrum of $\text{Cd}_{0.1}\text{Zn}_{0.9}\text{S}$ excited at 532 nm.

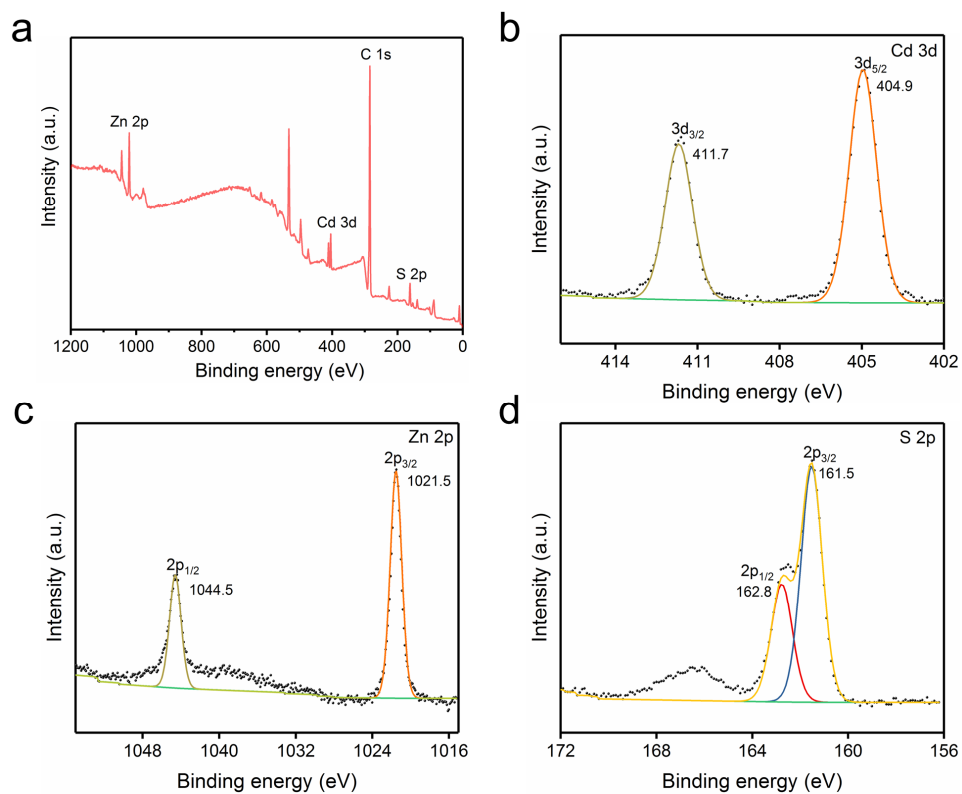


Figure S2 (a) XPS survey spectra of $\text{Cd}_{0.1}\text{Zn}_{0.9}\text{S}$. High-resolution XPS spectra of (b) Cd 3d, (c) Zn 2p, and (d) S 2p for $\text{Cd}_{0.1}\text{Zn}_{0.9}\text{S}$.

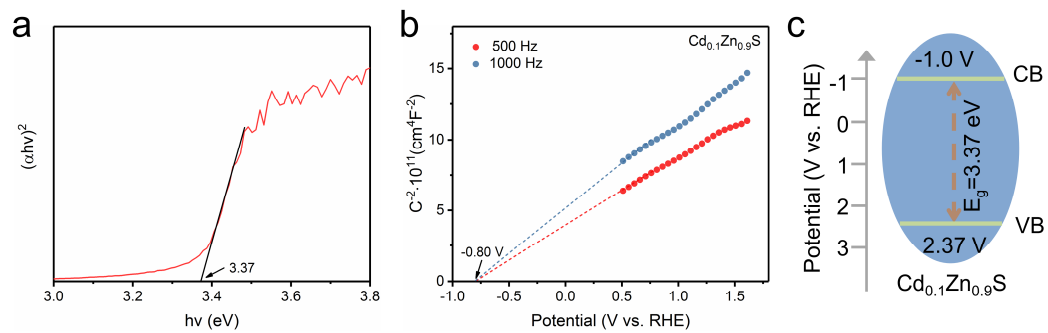


Figure S3 (a) Tauc plot of $\text{Cd}_{0.1}\text{Zn}_{0.9}\text{S}$. (b) Mott-Schottky plot of $\text{Cd}_{0.1}\text{Zn}_{0.9}\text{S}$. (c) Energy band structure of $\text{Cd}_{0.1}\text{Zn}_{0.9}\text{S}$.

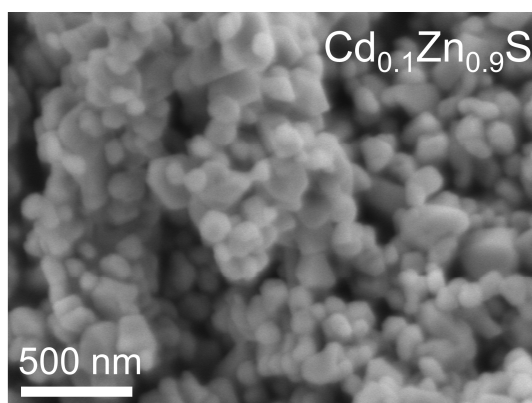


Figure S4 SEM image of $\text{Cd}_{0.1}\text{Zn}_{0.9}\text{S}$.

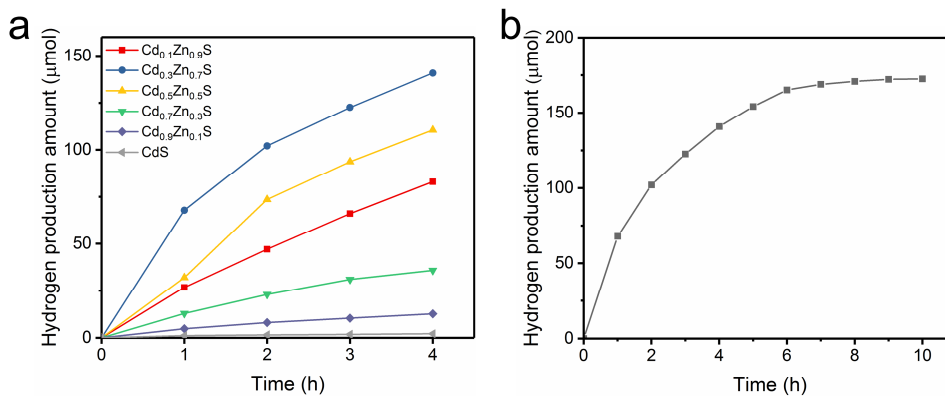


Figure S5 (a) Time courses of photocatalytic H₂ production over Cd_xZn_{1-x}S ($x = 0.1, 0.3, 0.5, 0.7, 0.9, 1.0$). (b) The long-term photocatalytic H₂ measurement over Cd_{0.3}Zn_{0.7}S. Reaction conditions: 40 mg of photocatalysts, 80 mL of reaction solution containing 10 mM Fe(CN)₆⁴⁻ with 0.1 M borate buffer, temperature maintained at 25 °C, simulated full-spectrum irradiation (300 mW cm⁻²).

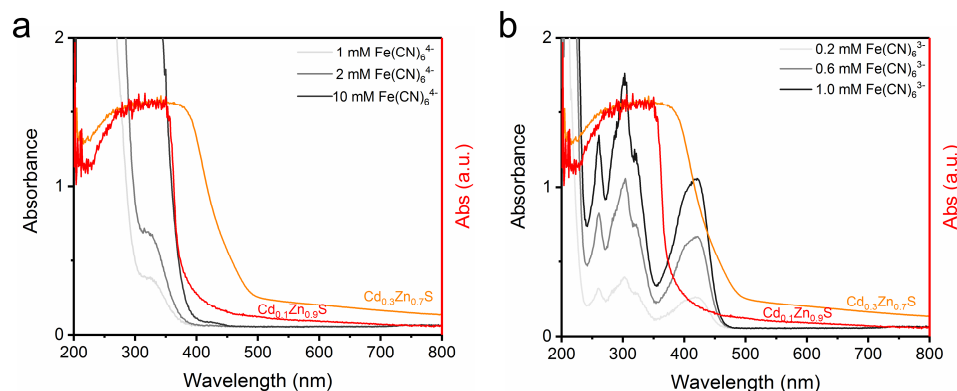


Figure S6 (a) UV-Vis absorption spectra of Fe(CN)₆⁴⁻ aqueous solution, Cd_{0.1}Zn_{0.9}S, and Cd_{0.3}Zn_{0.7}S. (b) UV-Vis absorption spectra of Fe(CN)₆³⁻ aqueous solution, Cd_{0.1}Zn_{0.9}S, and Cd_{0.3}Zn_{0.7}S. Fe(CN)₆³⁻ exhibited a distinct absorption peak at around 422 nm, while the absorption edge of Cd_{0.3}Zn_{0.7}S was at 430 nm. Consequently, Fe(CN)₆³⁻ significantly hindered the light absorption of Cd_{0.3}Zn_{0.7}S. As the photocatalytic reaction progressed, the concentration of Fe(CN)₆³⁻ increased rapidly, leading to a marked activity decrease of Cd_{0.3}Zn_{0.7}S. This also accounted for the good stability of Cd_{0.1}Zn_{0.9}S, which had an absorption edge at 370 nm and experienced only a minor light-shielding effect from Fe(CN)₆³⁻.

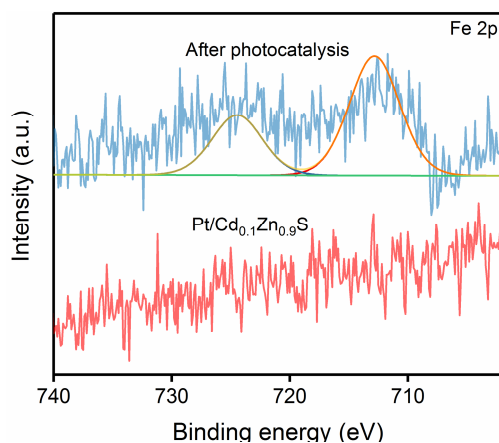


Figure S7 High-resolution XPS spectra of Fe 2p for Pt/Cd_{0.1}Zn_{0.9}S before and after the photocatalytic reaction in borate buffer solution containing 10 mM Fe(CN)₆⁴⁻.

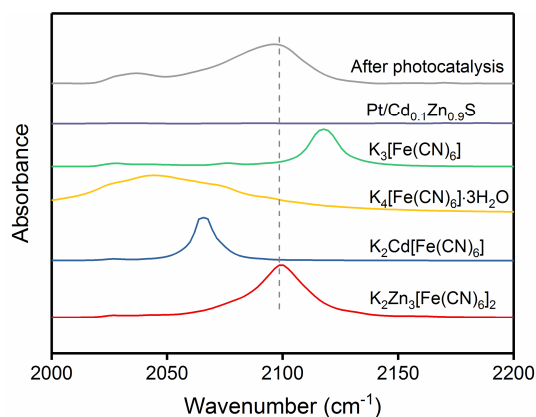


Figure S8 FTIR spectra of Pt/Cd_{0.1}Zn_{0.9}S before and after the photocatalytic reaction in borate buffer solution containing 10 mM Fe(CN)₆⁴⁻. For comparison, the spectra of K₃[Fe(CN)₆], K₄[Fe(CN)₆] \cdot 3H₂O, K₂Cd[Fe(CN)₆], and K₂Zn₃[Fe(CN)₆]₂ were also examined. K₄[Fe(CN)₆] \cdot 3H₂O and K₃[Fe(CN)₆] were purchased from Sinopharm Chemical Reagent Co., Ltd without further purification, while K₂Zn₃[Fe(CN)₆]₂ and K₂Cd[Fe(CN)₆] were synthesized using a previously reported co-precipitation method.¹ The new peak at 2098 cm⁻¹ observed in the Pt/Cd_{0.1}Zn_{0.9}S sample after photocatalysis was attributed to the formation of Zn metal cyanoferrates (K₂Zn₃[Fe(CN)₆]₂). No peak corresponding to Cd metal cyanoferrates (K₂Cd[Fe(CN)₆]) at 2068 cm⁻¹ was detected, likely due to the low Cd content in Cd_{0.1}Zn_{0.9}S.

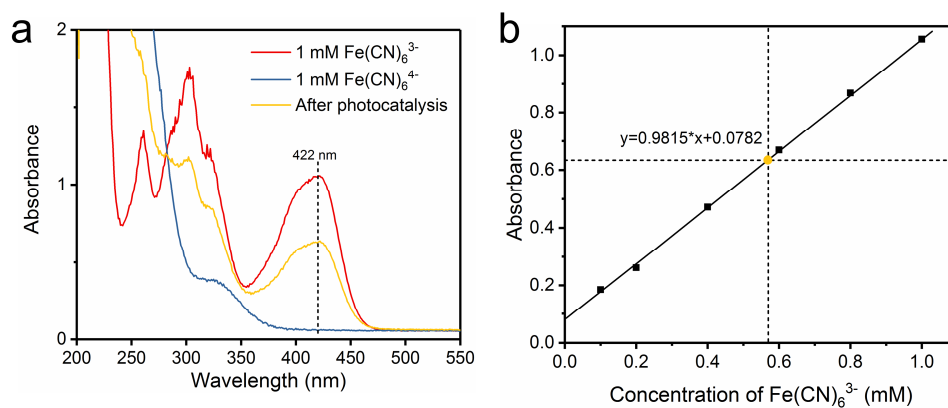


Figure S9 (a) UV-Vis absorption spectra of aqueous solution containing $\text{Fe}(\text{CN})_6^{3-}$ or $\text{Fe}(\text{CN})_6^{4-}$. (b)

The calculated linear relationship between absorbance and concentration of aqueous $\text{Fe}(\text{CN})_6^{3-}$ solution at 422 nm. The photocatalytic reaction solution was diluted 10 times for testing. The yellow dot represents the absorbance of $\text{Fe}(\text{CN})_6^{3-}$ aqueous solution after an 8-hour photocatalytic test. The concentration of the produced $\text{Fe}(\text{CN})_6^{3-}$ was calculated to be approximately 5.7 mM, corresponding to an amount of 456.0 μmol .

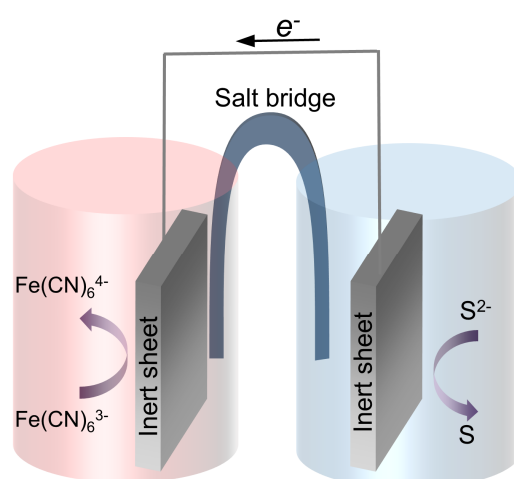


Figure S10 Schematic of the galvanic cell for $\text{Fe}(\text{CN})_6^{3-}$ reduction and sulfide oxidation with electricity generation.

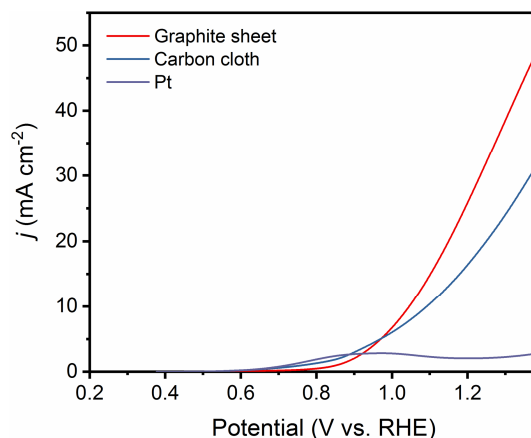


Figure S11 LSV curves of SOR over different electrode materials, including graphite sheet, carbon cloth, and Pt. 0.2 M Na_2S aqueous solution was used as the electrolyte.

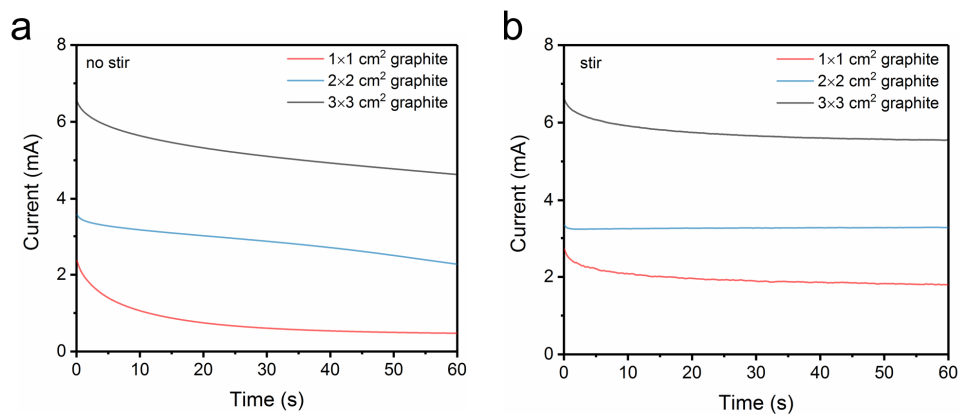


Figure S12 Current-time curves of the galvanic cell were obtained using graphite sheet electrodes of different areas, either (a) without catholyte stirring or (b) with catholyte stirring. The catholyte consisted of 10 mM $\text{K}_3[\text{Fe}(\text{CN})_6]$ in 0.1 M borate buffer, while the anolyte was 0.2 M Na_2S aqueous solution.

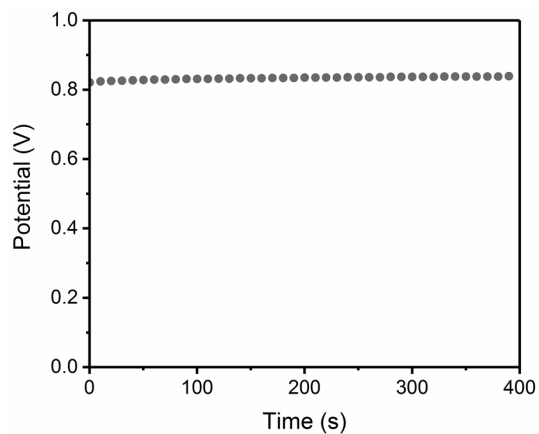


Figure S13 Open-circuit voltage plot for the galvanic cell.

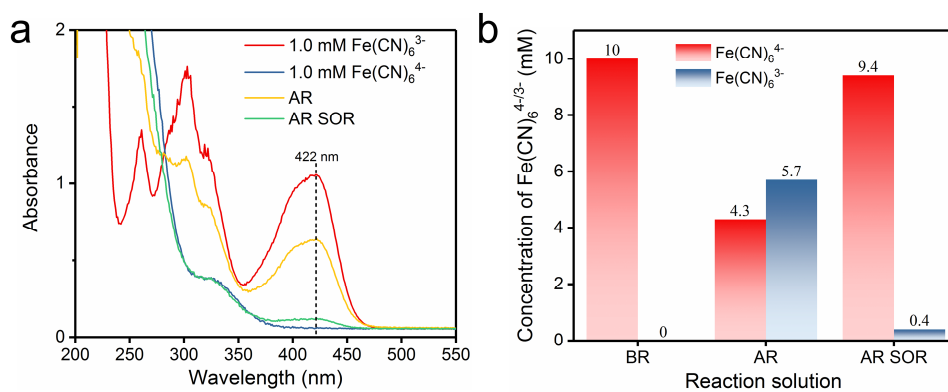


Figure S14 (a) UV-Vis absorption spectra of aqueous solution containing Fe(CN)_6^{3-} or Fe(CN)_6^{4-} .

(b) The calculated $\text{Fe(CN)}_6^{4/3-}$ concentration of reaction solution containing 10 mM Fe(CN)_6^{4-} and 0.1 M borate buffer in different periods. BR: before photocatalytic reaction; AR: after photocatalytic reaction; AR SOR: after galvanic cell reaction. The reaction solution of AR and AR SOR were diluted 10 times for testing.

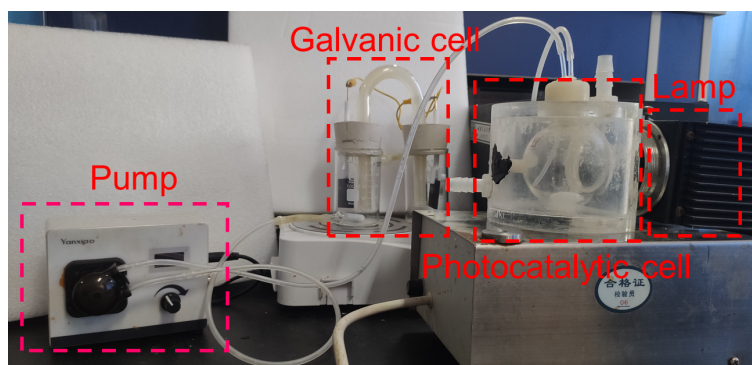


Figure S15 The image of the photocatalytic-galvanic cell system.

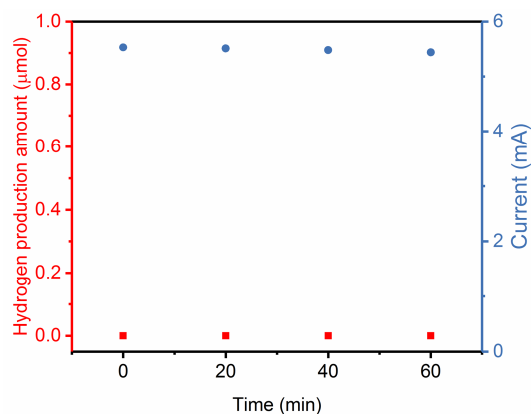


Figure S16 Time course of H₂ production and current generated in the galvanic cell. The catholyte consisted of 5 mM Fe(CN)₆³⁻ and 5 mM Fe(CN)₆⁴⁻ in 0.1 M borate buffer containing Pt/Cd_{0.1}Zn_{0.9}S at a mass concentration of 0.5 mg mL⁻¹, while the anolyte was 0.2 M Na₂S aqueous solution.

This setup outputs a current greater than 5 mA. However, no H₂ production was observed, indicating that electrons at the cathode reduced Fe(CN)₆³⁻ to Fe(CN)₆⁴⁻ instead of H⁺ to H₂. Consequently, the current generated by the galvanic cell did not affect H₂ production.

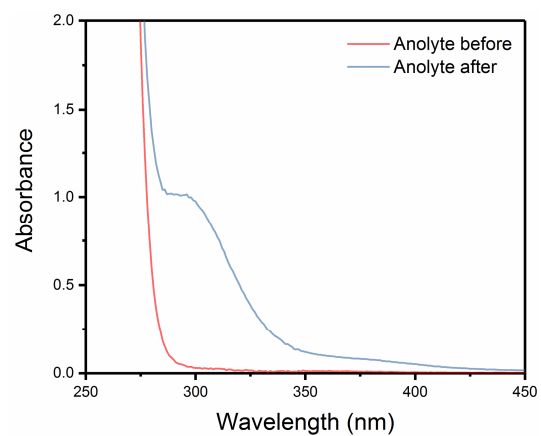


Figure S17 UV-Vis absorption spectra of the analyte before and after the 8-hour operation for the photocatalytic-galvanic cell system.

Table S1 Comparison of Cd/Zn feed ratio and actual ratio of Cd_{0.1}Zn_{0.9}S determined by XRF analysis.

	Feed ratio	Actual ratio
Cd	0.1	0.16
Zn	0.9	0.84

Table S2 Comparison of the current photocatalytic H₂ production with reported redox-mediated photocatalysis results.

Photocatalyst	Redox mediator	Light source	Dosage (mg)	Average activity ($\mu\text{mol g}^{-1} \text{h}^{-1}$)	Year/Ref.
Pt/Cd _{0.1} Zn _{0.9} S	Fe(CN) ₆ ^{4-/3-}	300 W Xe-lamp	40	928	This work
Pt/CdS	Fe(CN) ₆ ^{4-/3-}	300 W Xe-lamp ($\lambda > 400 \text{ nm}$)	50	327	2017 ³
Pt/Zn _{0.75} Cd _{0.25} Se	Fe(CN) ₆ ^{4-/3-}	300 W Xe-lamp ($420 < \lambda < 800 \text{ nm}$)	100	95	2021 ²
InHCF/Rh _x Cr _{2-x} O/TaON	Fe ³⁺ /Fe ²⁺	300 W Xe-lamp ($\lambda > 400 \text{ nm}$)	50	824	2023 ¹
NiS/CdS	Fe ³⁺ /Fe ²⁺	AM 1.5	50	557	2023 ⁴
NiS/CdS	I ₃ ⁻ /I ⁻	AM 1.5	50	31	2023 ⁴
MoSe ₂ /MAPbBr _{3-x} I _x	I ₃ ⁻ /I ⁻	300 W Xe-lamp ($\lambda > 420 \text{ nm}$)	150	1748	2023 ⁵
MoS ₂ /CdS	[Co(bpy) ₃] ^{3+/2+}	300 W Xe-lamp ($\lambda > 420 \text{ nm}$)	100 mg	145	2017 ⁶

References

1. H. Matsuoka, T. Inoue, H. Suzuki, O. Tomita, S. Nozawa, A. Nakada and R. Abe, *Sol. RRL*, 2023, **7**, 2300431.
2. Y. Kageshima, Y. Gomyo, H. Matsuoka, H. Inuzuka, H. Suzuki, R. Abe, K. Teshima, K. Domen and H. Nishikiori, *ACS Catal.*, 2021, **11**, 8004-8014.

3. T. Shirakawa, M. Higashi, O. Tomita and R. Abe, *Sustainable Energy Fuels*, 2017, **1**, 1065-1073.
4. X. Wang, Z. Zhuo, C. Shen, M. Cai, D. Li, K. Liu, S. Cao, Y. Wei, Z. Xue and S. Sun, *ChemPhotoChem*, 2023, **7**, e202200211.
5. X. Liu, Q. Zhang, S. Zhao, Z. Wang, Y. Liu, Z. Zheng, H. Cheng, Y. Dai, B. Huang and P. Wang, *Adv. Mater.*, 2023, **35**, 2208915.
6. Y.-J. Yuan, D. Chen, S. Yang, L.-X. Yang, J.-J. Wang, D. Cao, W. Tu, Z.-T. Yu and Z.-G. Zou, *J. Mater. Chem. A*, 2017, **5**, 21205-21213.