Electronic Supplementary Information

Zn_{0.5}Cd_{0.5}S photocatalysts with loaded Cu²⁺ and Ni²⁺ dual active sites for promoted syngas production

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Materials and methods

Chemicals and Materials

Zn(NO3)₂ (AR, Xilong Scientific CO., Ltd., China), Cd(NO3)₂ (AR, Sinopharm Chemical Reagent CO., Ltd), Na₂S·9H₂O (AR, Guangzhou Chemical Reagent Factory, China), , Nafion *D-521 dispersive solution (5% w/w in water and 1propanol aqueous solution, exchange capacity \geq 0.92 meq/g), K₂SO₄ (AR, Sinopharm Chemical Reagent Co., Ltd.) were used without further purification. Deionized (DI) water was used for the synthesis of all samples.

Characterizations

The crystal structure of the catalyst was characterized by Cu K α radiation (λ =0.15406 nm) on the Rigaku MiniFlex 600 X-ray diffractometer. The transmission electron microscope (TEM)and high-resolution TEM (HRTEM) images were recorded on FEI Tecnai G2 F20 field emission transmission electron microscope (200 kV). The scanning electron microscopy (SEM) images were acquired on a field emission-SEM (FE-SEM) (Jeol, JSM-7610Plus). For in situ diffuse-reflection FTIR (DRFTIR) measurements, a Thermo Nicolet 6700 FT-IR spectrometer was used. A praying mantis diffuse reflectance accessory and a reaction cell equipped with a heater (Harrick Scientific) formed the reaction system. The samples were housed in a sample cup inside the reaction cell. Then H₂O and CO₂ were introduced into the system by flowing CO₂ (20 ml·min-1) through water, and then sample was subjected to IR measurements irradiated by a 300W Xe-lamp. The diffuse reflectance spectra of the catalyst were measured on Shimadzu UV-2600 ultraviolet-visible spectrophotometer. X-ray photoelectron spectroscopy (XPS) measurements were performed over a Thermo Fisher ESCALAB 250Xi spectrophotometer. In the energy mode of the constant energy analyzer, the spectrum is excited by the Mg Ka (1253.6 eV) radiation (200 W working) of the double anode with energy of 30 eV. The binding energy is 284.8 eV from the C1s line of indeterminate carbon. The photoluminescence (PL) measurements were performed on a fluorescence spectrometer (JASCO FP-6500) with excitation wavelength of 360 nm.

Time-resolved fluorescence measurements were carried out with the Fluorolog using a 320 nm line of a Nano LED operating at room temperature.

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Experimental method

Preparation of Zn_{0.5}Cd_{0.5}S-Cu²⁺/Ni²⁺

All chemicals were reagent grade and used as received. Using Na₂S as S source, the photocatalysts were synthesized by a simple co-precipitation method. The colloidal $Zn_{0.5}Cd_{0.5}S$ with different doping molar ratios can be instantly obtained by injecting the freshly prepared Na₂S (20 ml, 2.052 mmol) solution into a solution containing Zn^{2+} (1.026 mmol), Cd²⁺ (1.026 mmol) at a rate of 4 ml/min using a micro-infusion pump

under vigorous stirring at room temperature. Then, $Cu(NO_3)_2$ (0.004 mmol, 0.2%) and $Ni(NO_3)_2$ (0.002 mmol, 0.1%) were added, and the mixture was stirred at room temperature for six hours to ensure the reaction proceeded thoroughly. The reaction was proceeded for 30 min under the ambient condition. The resulting yellow suspension was centrifuged, washed several times with DI water and then dried in freezer dryer for 24 h.

Photocatalytic Reduction of CO₂

In a typical experiment, 0.1 M K₂SO₃ and 0.5 M KHCO₃ were added to an aqueous suspension containing Zn_{0.5}Cd_{0.5}S (200 mg), and the volume of the reaction mixture was adjusted to 200 mL by adding fresh deionized water. The reaction system was then evacuated, and high-purity CO₂ (99.999%) was repeatedly introduced until the final pressure, as indicated by the barometer, reached atmospheric levels (101-102 kPa). The reactor was illuminated using a 300 W xenon lamp (Microsolar 300, Beijing Perfectlight Technology Co., Ltd) equipped with a 420 nm cut-off filter (L42, HOYA) at a constant temperature of 25°C. The CO generated in the reaction system was collected and quantified using a gas chromatograph (GC-2014, Shimadzu, N₂ as carrier gas) with a flame ionization detector (FID). Additionally, an online gas chromatograph (GC-2014C, Shimadzu, Ar as carrier gas) and a thermal conductivity detector (TCD) were employed to measure the H₂ content. The apparent quantum efficiency (AQE) was determined using a 300 W xenon lamp with a 420 nm band-pass filter (HOYA), and the number of incident photons was measured with a radiometer (Ushio Spectroradiometer, USR-40). The AQE was calculated using the following formula:

$$AQE(H_2) = \frac{N(H_2) \times 2}{N(Photons)} \times 100\%$$
$$AQE(CO) = \frac{N(CO) \times 2}{N(Photons)} \times 100\%$$

Among them, N (H₂), N (CO) and N (Photons) respectively represent the number of H_2 , CO and incident photons generated per unit time.

Isotope Tracing

In isotope tracing experiment, ¹³CO₂ was injected to reaction system and pre-absorbed by reaction solution where KHCO₃ was not added. Isotope tracing experiments for the identification of ¹³CO were performed by gas chromatography-mass spectrometry (GC-MS, JMS-K9, JEOL Co., Japan).

DFT Calculations

In this study, all the first principle calculations were carried out by the Vienna ab-initio Simulation Package (VASP) based on the density functional theory (DFT).¹ The generalized gradient approximation (GGA) in the form of Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional was used to describe the electron exchangecorrelation. The interaction between electron and ion was treated by the projector augmented wave (PAW) method.² The cut-off energy of 450 eV was set for all calculations. By using ZnGa₂S₄ unit cell as atomic model, the bulk model of Zn_{0.5}Cd_{0.5}S was established through a 2×2×1 supercell. The $Zn_{0.5}Cd_{0.5}S\text{-}Cu^{2+}\!/Ni^{2+}$ model was constructed by replacing a surface Zn atom with a Cu atom and Ni atom. The Zn_{0.5}Cd_{0.5}S (111) surface was built with a vacuum layer of 20 Å. The Zn_{0.5}Cd_{0.5}S:Cu Ni surface model was built on Zn_{0.5}Cd_{0.5}S surface model with two surface Zn atom replaced by a Cu atom and a Ni atom. All atoms were relaxed, and the final force on each atom was less than 0.02 eV/Å for each ionic step, and the convergence criterion for the self-consistent field energy was set to be 1.0×10^{-4} eV. The semi-empirical London dispersion corrections of Grimme et al were conducted to calculate the interactions between absorbers and samples.³

The characterizations, photocatalytic measurements, and DFT calculation methods are described in supporting information.

Photoelectrochemical Measurements

Photoelectrochemical experiments were performed at room temperature in the threeelectrode chamber of the Bio Logic VMP-3 (Bio Logic Science Instruments, Claix, France) electrochemical workstation. During the measurement, the reference electrode adopted Ag/AgCl (filled with 3.5 M KCl) electrode, the graphite electrode was used as counter electrode, and indium tin oxide (ITO) electrode grafted with catalyst acted as working electrode. To prepared photoelectrodes, about 20 mg of catalysts were scattered in 1 ml of ethanol and 1 ml of DI water to form an ethanol/water solution. Subsequently, 20 μ L Nafion solution (Nafion D-521 5% w/w in water and 1-propano, Alfa Aesar Co. Ltd.) was transferred to the ink as a proton conductive adhesive to insure good adhesion to the ITO electrode. The catalyst ink was ultrasonically treated for 30 minutes and stirred vigorously for 12 hours at room temperature to form a homogeneous solution. The catalyst ink with 100 μ L was coated on the surface with ITO electrode with 1 cm², which is dried in vacuum at 60 °C. All photoelectric electrochemical measurements were performed in 0.1 M K₂SO₄ electrolyte. The light source was a 300 W Xe-lamp with full arc and the photoelectrode was irradiated from the back of the prepared ITO/catalyst. Electrochemical impedance spectroscopy (EIS) was tested at an applied potential of 1.23 V, Ag/AgCl in the frequency range of 1 MHz to 0.1 Hz.

Analysis of Mott-Schottky Curves

Under different frequency (2000, 3000 Hz) DC potential polarization conditions, the Mott-Schottky curves were obtained. The potential range was -1.5-1.5 V (vs. Ag/AgCl). The intersection point is the $E_{fb} + k_bT/e$ (*V vs. Ag/AgCl*) (*V vs. Ag/AgCl*), where E_{fb} is the flatband potential, k_b is the Boltzmann constant, the value is 1.380649×10-23 J/K, T is the absolute temperature with a value of 298, and e is the electronic charge with a value of 1.6021892×10-19 C. The equation $E_{NHE} = E(Ag/AgCl) + E^0(Ag/AgCl)$ is used to convert the NHE (pH = 0) reference scale, where E⁰ (Ag/AgCl) is 0.197 V at 25 °C. ⁴



Fig. S1 (a, b and c) SEM images, (d) SEM EDS and elemental mapping of Zn, Cd and S in $Zn_{0.5}Cd_{0.5}S$; (e, f and g) SEM images, (h) SEM EDS and elemental mapping of Zn, Cd, Cu and S in $Zn_{0.5}Cd_{0.5}S-Cu^{2+}$; (i, j and k) SEM images, (l) SEM EDS and elemental mapping of Zn, Cd and Ni in $Zn_{0.5}Cd_{0.5}S-Ni^{2+}$; (m, n and o) SEM images, (p) SEM EDS and elemental mapping of Zn, Cd, Cu, Ni and S in $Zn_{0.5}Cd_{0.5}S-Cu^{2+}/Ni^{2+}$.



Fig. S2 (a and b) TEM images, (c) HRTEM image, and SAED pattern (insert of (c)) of $Zn_{0.5}Cd_{0.5}S$; (d and e) TEM images, (f) HRTEM image, and SAED pattern (insert of (f)) of $Zn_{0.5}Cd_{0.5}S$ -Cu²⁺ (g and h) TEM images, (i) HRTEM image and SAED pattern (insert of (i)) of $Zn_{0.5}Cd_{0.5}S$ -Cu²⁺ (g and h) TEM images, (i) HRTEM image and SAED pattern (insert of (i)) of $Zn_{0.5}Cd_{0.5}S$ -Ni²⁺ (j and k) TEM images, (l) HRTEM image and SAED pattern (insert of (l)), (m) TEM EDS and elemental mapping of Zn, Cd, Cu, Ni and S in $Zn_{0.5}Cd_{0.5}S$ -Cu²⁺/Ni²⁺.



Fig. S3 (a) Irradiation spectra of using a 420nm cut-off band pass filter (HOYA), (b) Irradiation spectrum of using a 420nm band-pass filter ($\lambda 1/2 = 19.1 \text{ nm}$,HOYA) (c) Irradiation spectrum of using a 460nm band-pass filter ($\lambda 1/2 = 19.1 \text{ nm}$,HOYA) (d) Irradiation spectrum of using a 500nm band-pass filter ($\lambda 1/2 = 19.1 \text{ nm}$,HOYA) (e) Irradiation spectrum of using a 560nm band-pass filter ($\lambda 1/2 = 19.1 \text{ nm}$,HOYA).



Fig. S4 Representative ¹H NMR spectrum after photocatalytic CO_2 reduction over $Zn_{0.5}Cd_{0.5}S-Cu^{2+}/Ni^{2+}$ and acid-etched nanocrystals to identify the liquid products. (formate, methanol, etc.). No peak signal was found at the position of 8.3 ppm and 3.2 ppm, indicating formate and methanol doesn't exist in the CO_2 reduction products.



Fig. S5 Cycling measurements for the evolution of CO and H_2 over ZnCdS-Cu²⁺/Ni²⁺.



Fig. S6 H_2 and CO evolution rates of $Zn_xCd_{1-x}S$ with different Zn/Cd ratios (reaction time: 8 hours).



Fig. S7 (a) H_2 and CO evolution rates of $Zn_{0.5}Cd_{0.5}S-Cu^{2+}/Ni^{2+}$ with different Ni doping concentrations, (b) H_2 and CO evolution rates of ZnCdS with different Cu doping concentrations, (c) H_2 and CO evolution rates of ZnCdS with a fixed Cu²⁺ concentration of 0.2% and varying Ni²⁺ doping concentrations. All reaction times are 8 hours.



Fig. S8 CO evolution rate over $Zn_{0.5}Cd_{0.5}S$ - Cu^{2+}/Ni^{2+} under control experiments using Ar instead of CO₂ and in the absence of KHCO₃.



Fig. S9 SEM image of $Zn_{0.5}Cd_{0.5}S$ - Cu^{2+}/Ni^{2+} (a) before CO_2 reduction and (b) after CO_2 reduction.



Fig. S10 Representative GC-MS spectrum after photocatalytic CO_2 reduction using isotope 13 CO_2 over confirm the carbon source in the gaseous products (¹³CO).



Fig. S11 The built atomic model of $Zn_{0.5}Cd_{0.5}S$ and $Zn_{0.5}Cd_{0.5}S$ - Cu^{2+}/Ni^{2+} at (111) face.



Fig. S12 The adsorption process of *CO2, *COOH, *CO, and *H intermediates on Zn and Cu sites in $Zn_{0.5}Cd_{0.5}S$.



Fig. S13 CO_2 conversion into CO over $Zn_{0.5}Cd_{0.5}Son Zn$ atom (red line) and Cd atom (blue line) based on DFT calculations



Fig. S14 the process of H_2O conversion into H_2 over $Zn_{0.5}Cd_{0.5}S$ on Zn atom (red line) and Cd atom (blue line) based on DFT calculations.



Fig. S15 The adsorption process of CO_2 , COOH, and CO, and intermediates on Zn, Cu and Ni sites in $Zn_{0.5}Cd_{0.5}S-Cu^{2+}/Ni^{2+}$.



Fig. S16 CO₂ conversion into CO over $Zn_{0.5}Cd_{0.5}S$ -Cu²⁺/Ni²⁺ on Cu atom (red line), Zn atom (yellow line) and Ni atom (blue line) based on DFT calculations



Fig. S17 The adsorption process of *H, and intermediates on Zn, Cu and Ni sites in $Zn_{0.5}Cd_{0.5}S$ -Cu²⁺/Ni²⁺.



Fig. S18 the process of H_2O conversion into H_2 over $Zn_{0.5}Cd_{0.5}S-Cu^{2+}/Ni^{2+}$ on Ni atom (red line), Cu atom (blue line) and Cd atom (yellow line) based on DFT calculations.

Table.	S1	Inductively	Coupled	Plasma	Optical	Emission	Spectrometer	(ICP-OES)
elemen	tal c	content analy	sis of ZnO	CdS and	ZnCdS:0	Cu Ni.		

Atomic content	ZnCdS	$Zn_{0.5}Cd_{0.5}S$ - Cu^{2+}/Ni^{2+}
Zn	27.50	27.30
Cd	29.50	29.49
S	43.00	42.89
Cu	0	0.21
Ni	0	0.11

Sample	τ_1 (ns)	τ_2 (ns)	I ₁ (%)	I ₂ (%)	$\tau_{avg}\left(ns ight)$
Zn _{0.5} Cd _{0.5} S	0.9119	4.5339	47.21	32.79	2.0995
$Zn_{0.5}Cd_{0.5}S$ - Cu^{2+}	0.5274	2.5864	13.88	86.12	2.3007
$Zn_{0.5}Cd_{0.5}S$ - Ni ²⁺	0.2040	6.3148	40.28	59.72	3.8534
$Zn_{0.5}Cd_{0.5}SCu^{2+}/Ni^{2+}$	0.1997	0.0048	31.94	68.06	4.8805

Table. S2 The TRPL decay data of cubic ZnS and hexagonal ZnS.

Samples	$R_{s}(\Omega)$	$R_{ct}(\Omega)$
$Zn_{0.5}Cd_{0.5}S$	27.8	8639
$Zn_{0.5}Cd_{0.5}S\text{-}Cu^{2+}$	25.6	5633
$Zn_{0.5}Cd_{0.5}S$ - Ni ²⁺	23.7	4733
$Zn_{0.5}Cd_{0.5}S\text{-}Cu^{2+}\!/Ni^{2+}$	23.3	4532

Table. S3 Fitting parameters of the electronic components in the equivalent circuit as shown in the inset of Fig. 6d.

	СО	H_2	НСООН		
Catalyst	evolution	evolution	evolution	Solution	Ref.
	rate	rate	rate		
CuGaS ₂	0.19	110.0	Trace	K ₂ SO ₃	5
CuGa ₂ In ₃ S ₈	n. d	112.0	Trace	Na_2S	6
CuGa ₅ S ₈	n. d	25.0	n. d	K ₂ SO ₃	6
MnGaInS ₄	n. d	0.5	n. d	Na_2S	6
$Cu_{0.12}Zn_{0.88}Ga_2S_{3.94}$	n. d	4.0	n. d	Na_2S	6
Cu _{0.15} Zn _{0.85} Ga ₂ S _{3.925}	n. d	10.0	n. d	Na_2S	6
ZnGa _{0.5} In _{1.5} S ₄	0.1	140.0	n. d	Na_2S	6
Ag ₂ ZnGeS ₄	n. d	380.0	1.40	K ₂ SO ₃	6
AgGaS ₂	n. d	180.0	n. d	K ₂ SO ₃	6
(CuGa) _{0.3} Zn _{1.4} S ₂	0.52	0.6	0.12	$[Co(tpy)_2]^{2+}$	7
Cd ²⁺ /(CuGa) _{0.3} Zn _{0.4} Ga ₂ S ₄	0.81	587.8	n. d	K ₂ SO ₃	8
ZnS	3.92	1371	0.75	K_2SO_3	9
ZnCdS	1.89	2129.46	n.d.	K ₂ SO ₃	10
Zn _{0.5} Cd _{0.5} S-Cu ²⁺ /Ni ²⁺	18.12	5562.91	n.d.	K ₂ SO ₃	This work

Table S4. Comparison of CO_2 photoreduction performance catalyzed by variousmetal sulfide photocatalyst.

	ZnCdS		$Zn_{0.5}Cd_{0.5}S$ - Cu^{2+}/Ni^{2+}			
Atoms	Charge	Transfer	Atoms	Charge	Transfer	
Zn-1	11.152151	-0.84722	Cd-1	11.12813	-0.87187	
Zn-2	11.112182	-0.83751	Zn-1	11.16103	-0.83897	
Cd-4	1.92154	-1.07846	Zn-2	1.91147	-0.8387	
Cd-9	1.92826	-1.07174	Cd-1	1.93542	-0.8458	
Cd-14	1.97139	-1.02861	Cd-2	1.97090	-0.8455	
Cd-4	1.94064	-1.05936	Ga-4	1.94607	-1.05393	
S-1	6.75441	0.72468	Cu-1	6.75441	-0.83241	
S-3	6.73799	0.75575	Ni-1	6.73799	-0.84799	
S-11	6.78798	0.78798	S-11	6.75403	0.75403	
S-16	6.72468	0.72468	S-16	6.71040	0.71040	
S-21	6.75575	0.75575	S-21	6.73844	0.73844	
S-26	6.76390	0.76390	S-26	6.76384	0.76384	
S-31	6.77078	0.77078	S-31	6.77542	0.77542	
S-36	6.67082	0.67082	S-36	6.69027	0.69027	

Table. S5 The charge distribution of Zn, Cd, Cu, Ni and S surface atoms

References

- 1. P. Li, S. Hussain, L. Li, L. Guo and T. He, Chinese J. Catal., 2020, 41, 1663-1673.
- 2. Y. Su, Z. Zhang, H. Liu and Y. Wang, Appl. Catal. B, 2017, 200, 448-457.
- Y.-C. Chen, Y.-S. Huang, H. Huang, P.-J. Su, T.-P. Perng and L.-J. Chen, Nano Energy, 2020, 67, 104225.
- J. Song, H. Zhao, R. Sun, X. Li and D. Sun, *Energy Environ. Sci.*, 2017, 10, 225-235.
- S. Wu, H. Pang, W. Zhou, B. Yang, X. Meng, X. Qiu, G. Chen, L. Zhang, S. Wang, X. Liu, R. Ma, J. Ye and N. Zhang, *Nanoscale*, 2020, 12, 8693-8700.
- T. Takayama, H. Nakanishi, M. Matsui, A. Iwase and A. Kudo, J. Photochem. Photobiol. A: Chem., 2018, 358, 416-421.
- T. M. Suzuki, S. Yoshino, T. Takayama, A. Iwase, A. Kudo and T. Morikawa, Chem. Commun., 2018, 54, 10199-10202.
- P. Liu, B. Yang, Z. Xiao, S. Wang, S. Wu, M. Liu, G. Chen, X. Liu, R. Ma and N. Zhang, J. Energy Chem., 2023, 79, 365-372.
- W. Luo, A. Li, B. Yang, H. Pang, J. Fu, G. Chen, M. Liu, X. Liu, R. Ma, J. Ye and N. Zhang, ACS Appl. Mater. Interfaces, 2023, 15, 15387-15395.
- A. Li, H. Pang, P. Li, N. Zhang, G. Chen, X. Meng, M. Liu, X. Liu, R. Ma and J. Ye, *Appl. Catal. B Environ.*, 2021, 288, 119976.