

Cu-Doped CdZnS Nanocrystals: Leap Forward in Selective Photocatalytic CO₂ Reduction to Methane

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1. Experimental

1.1 Materials

Cadmium acetate ($\text{Cd}(\text{Ac})_2 \cdot 2\text{H}_2\text{O}$), zinc acetate ($\text{Zn}(\text{Ac})_2 \cdot 2\text{H}_2\text{O}$), copper acetate ($\text{Cu}(\text{Ac})_2 \cdot \text{H}_2\text{O}$), and sodium sulfide ($\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$) were of analytical reagent grade and used as received. Reaction and stock solutions were prepared by using deionized ultrapure water.

1.2 Preparation of CZS-x ($x = 0/1/2/3/5/10$) nanocrystals

The CZS-x ($x=0/1/2/3/5/10$) materials were synthesized via a simple hydrothermal method using deionized water as the solvent. In a typical synthesis for CZS-2, 2.5 mmol $\text{Cd}(\text{Ac})_2 \cdot 2\text{H}_2\text{O}$, 2.4 mmol $\text{Zn}(\text{Ac})_2 \cdot 2\text{H}_2\text{O}$, 0.1 mmol $\text{Cu}(\text{Ac})_2 \cdot \text{H}_2\text{O}$ and 5.0 mmol $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ were mixed in 20 mL distilled water under magnetic stirring for 1 h. The resultant brown mixture was then transferred into a 50 mL Teflon-lined autoclave and maintained at 160 °C for 12 h in oven. Finally, the precipitates were obtained by centrifugation and washed three times with deionized water and ethanol, respectively, dried at 70 °C for 6 h and named as CZS-2. For the synthesis of CZS-x, various ratio of $\text{Cu}(\text{Ac})_2 \cdot \text{H}_2\text{O}$ were used in the above described procedure.

2. Evaluation of photocatalytic CO_2 reduction activity

In a typical process, 5.0 mg of powder photocatalyst dispersed in 1.0 mL of deionized water was immobilized onto a $\phi 34$ mm quartz filter membrane, and then the water solvent was evaporated with the irradiation of an infrared lamp. The photocatalyst-loaded membrane was moved into a 250 mL photoreactor with 3.0 mL of aqueous solution and suspended on the top of the reactor. Prior to illumination, the reactor was vacuumed and subsequently back-filled with ultra-pure CO_2 (99.99%) for about 1 h to reach the adsorption/desorption equilibrium of CO_2 at the surface of photocatalyst. The pressure of the reactor was maintained at 60 kPa and temperature was kept at 4 °C using circulating water. The visible-light irradiation was provided by a light-intensity-controlled xenon lamp (PLS-SXE300D, Beijing, PerfectLight) equipped with a UV-cut filter ($\lambda \geq 420$ nm). The lamp was about 7.5 cm away from the catalyst membrane and the irradiance intensity was measured by a light power meter (PL-MW2000, Beijing, PerfectLight). Photocatalytic reactions were performed for 10 h at 4 °C, and

the gaseous products were analyzed online every hour by using an Agilent GC7820 gas chromatograph equipped with two tandem chromatographic columns (Porapak Q and 5A Molecular sieve), an FID detector and a TCD detector. During the durability test, the reaction system was evacuated every 5 h and refilled with ultra-pure CO₂ and water.

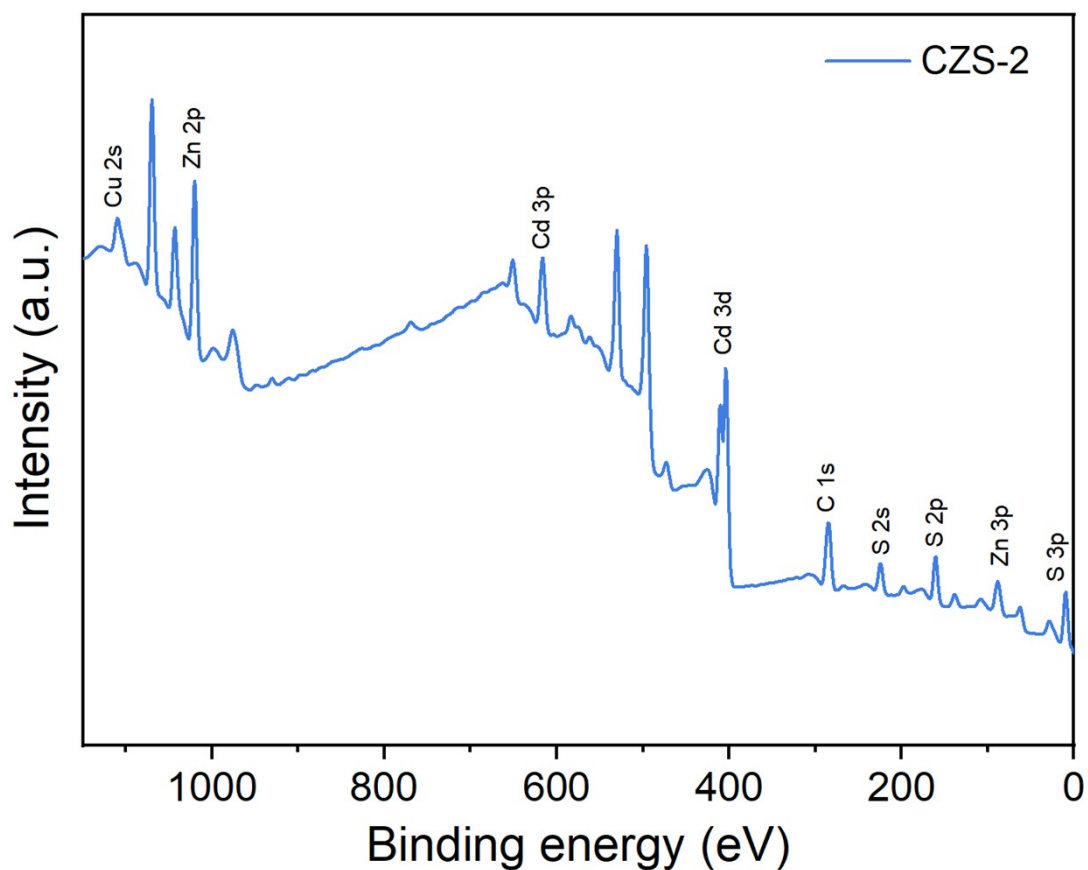


Fig. S1 XPS survey spectra of CZS-2.

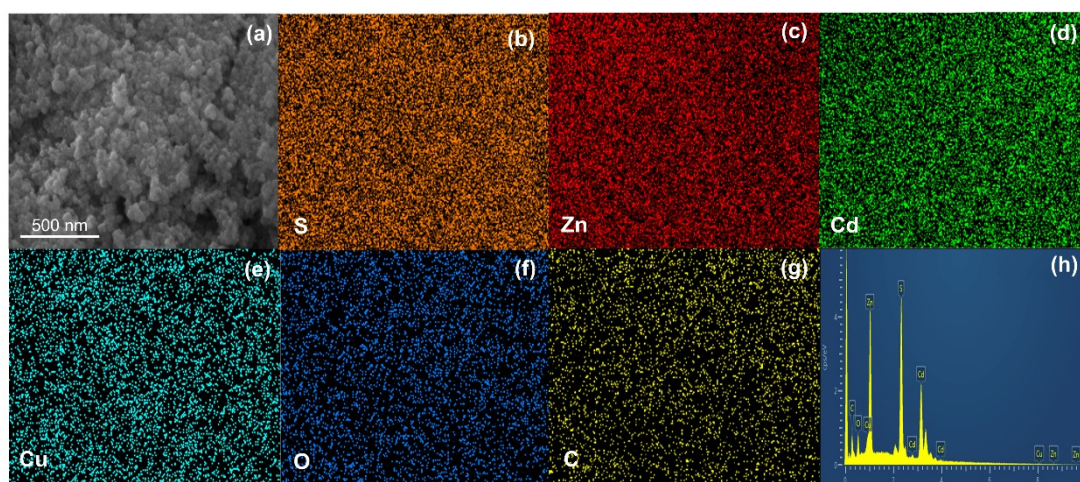


Fig. S2 (a) SEM image, (b-g) elemental mapping and Energy Dispersive X-Ray Spectrometer (EDX) of CZS-2.

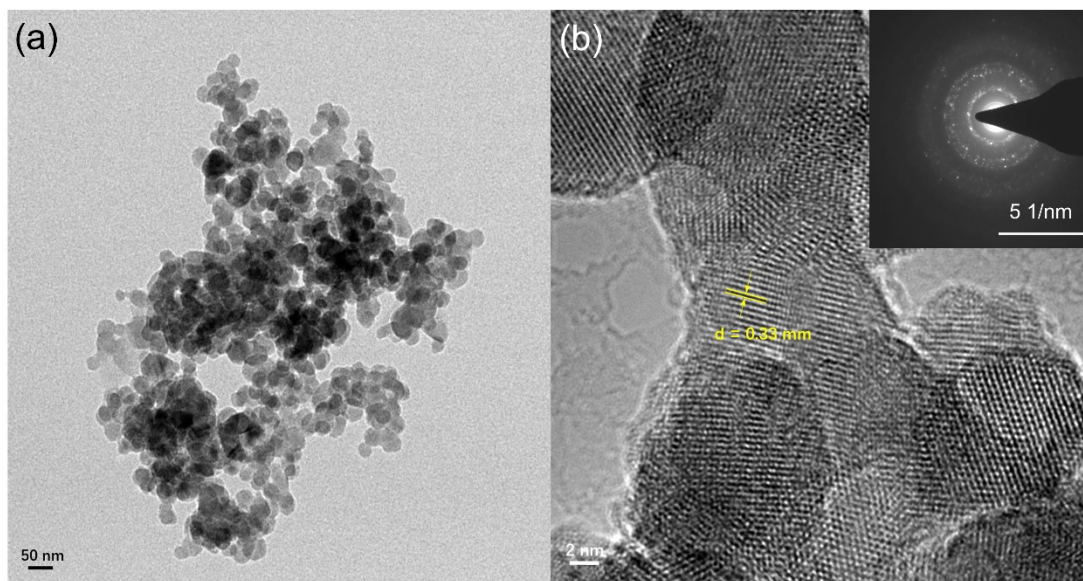


Fig. S3 (a) TEM, (b) HR-TEM image of CZS-2.

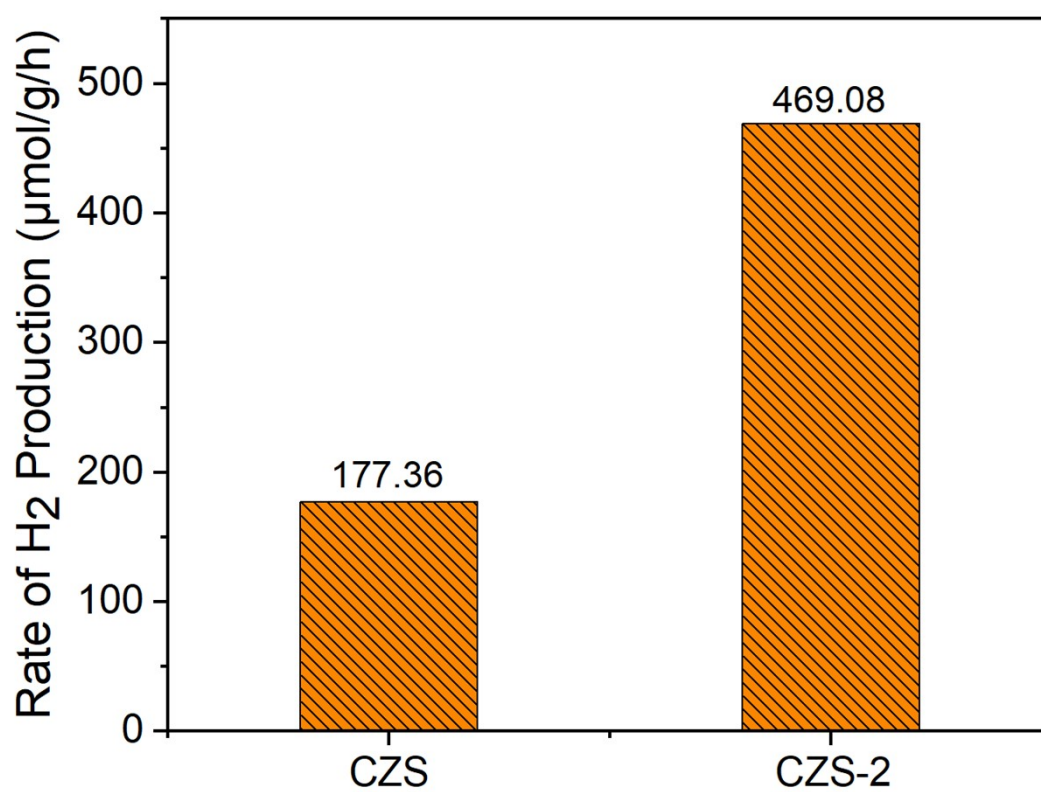


Fig. S4 H₂ evolution performance of CZS and CZS-2.

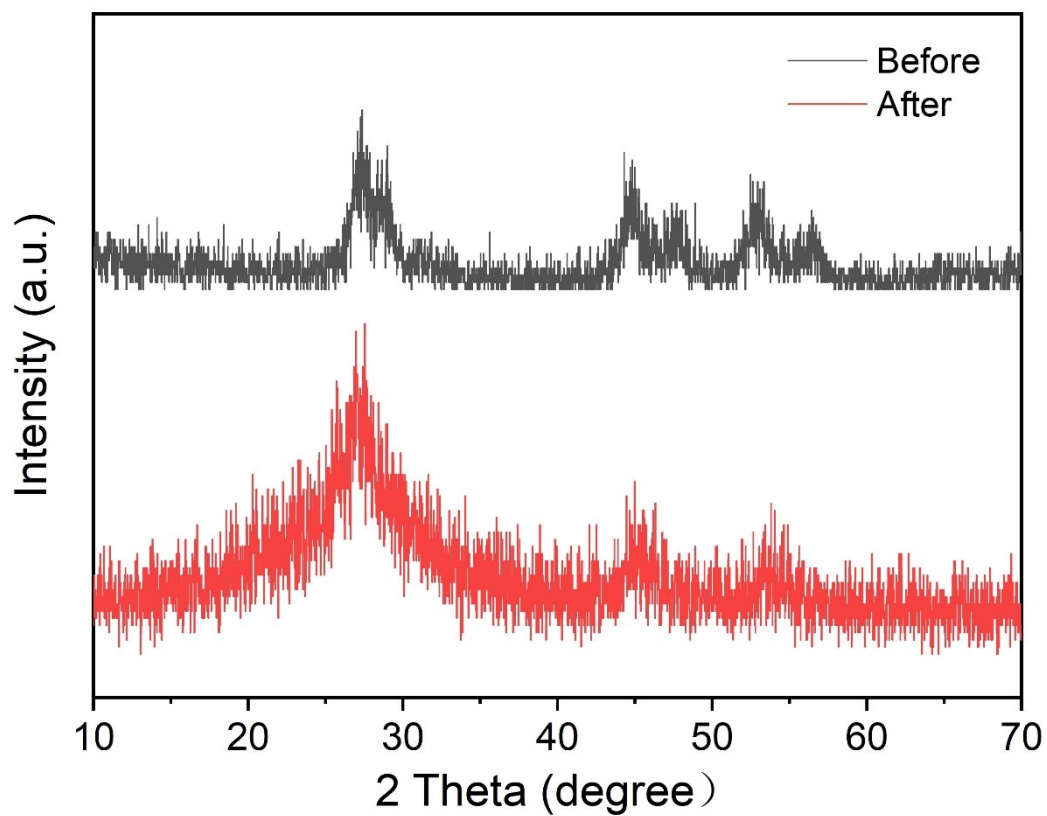


Fig. S5 The XRD pattern of CZS-2 after 15h reaction.

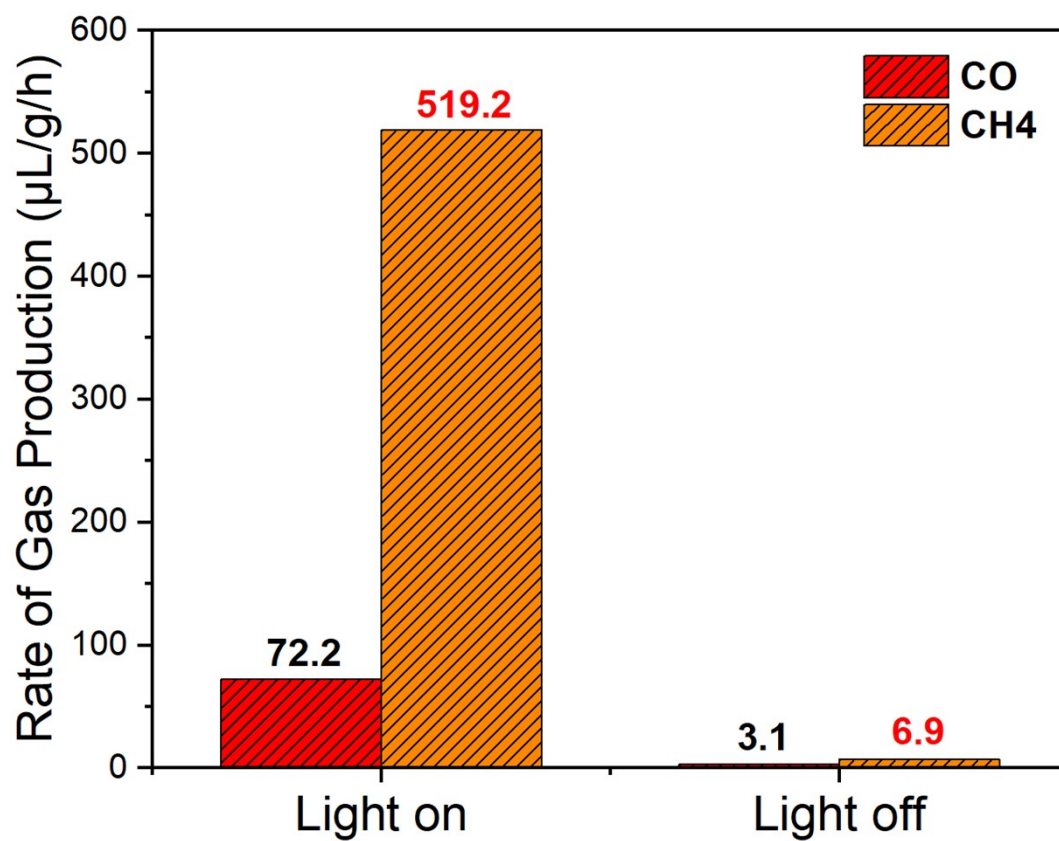


Fig. S6 CO₂ photoreduction performance under different condition of CZS-2.

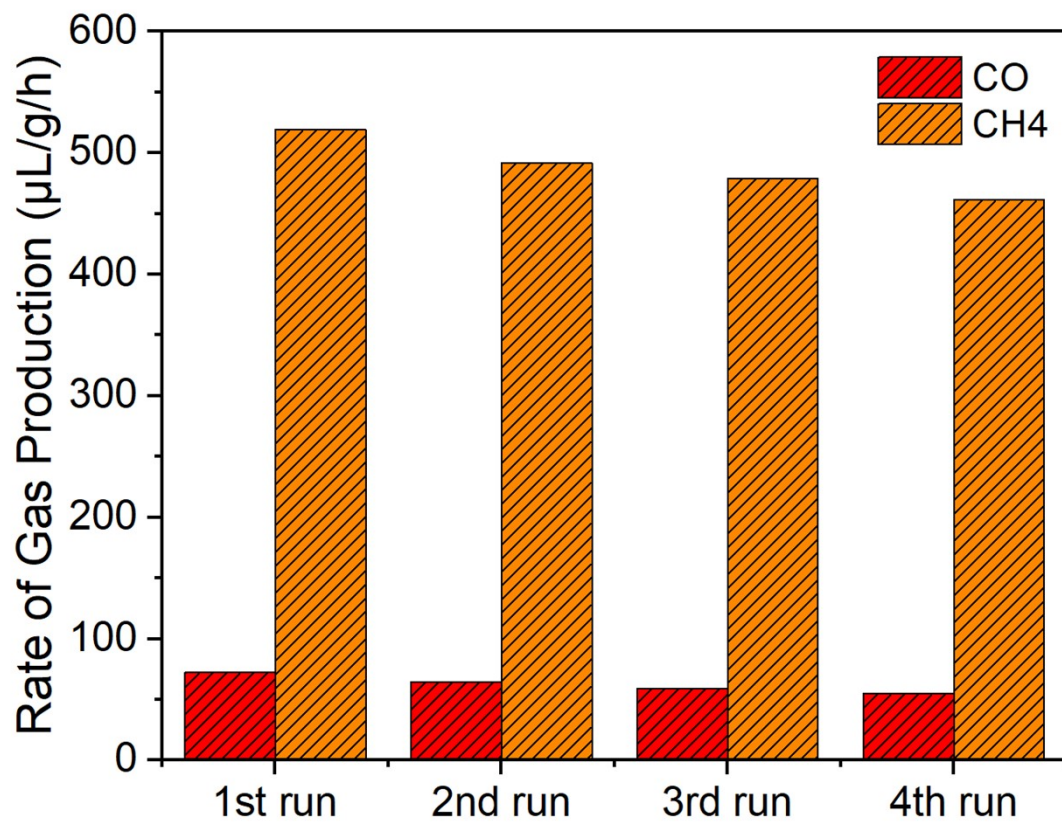


Fig. S7 Cyclic CO₂ photoreduction performance of CZS-2.

Table. S1 Comparison of CO₂ photoreduction capacity over various photocatalysts under different conditions.

Catalyst	Light source	Experimental condition	Production rate ($\mu\text{mol h}^{-1} \text{g}^{-1}$)	Reference
Bi/AgBiS ₂ /P25	300 W (Xe)	CO ₂ and H ₂ O	4.31	1
Br/g-C ₃ N ₄	300 W (Xe)	CO ₂ and H ₂ O	16.68	2
WO ₃ /In ₂ O ₃	300 W (Xe) ($\lambda \geq 420$ nm)	CO ₂ and H ₂ O	0.45	3
FeTPP/TiO ₂	300 W (Xe) ($\lambda \geq 420$ nm)	CO ₂ and H ₂ O vapor	20.48	4
Bi/Cs ₂ AgBiBr ₆	AM 1.5 G; 300 W (Xe)	CO ₂ and CH ₃ OH	1.49	5
SnS/SrTiO	300 W (Xe)	CO ₂ and H ₂ O vapor	12.5	6
PCN-250-Fe ₃	300 W (Xe) ($\lambda \geq 420$ nm)	CO ₂ and H ₂ O	4.08	7
CZS-2	300 W (Xe) $\lambda \geq 420$ nm	CO₂ and H₂O vapor	23.23	This work

Author contributions

Prof. H.T. and H.B.H. designed the project and wrote the manuscript; J.W.L. carried out most of the synthesis and characterization experiments in this work; Z.L. assisted the synthesis of materials; T.Q.Z. conducted the electron microscope studies.

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