Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.

Electronic Supplementary Information

Surface Defect Engineering of Mesoporous Cu/ZnS Nanocrystal-Linked Networks for Improved Visible-Light Photocatalytic Hydrogen Production

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Supporting Tables

Table S1. EDS results and chemical formulas of the mesoporous ZS, CZS and CZS′-5 NCAs.

Sample	Atomic ratio Zn:S:Cu	Cu doping[a] (mol%)	Chemical formula
ZS	51.2:48.8	0	ZnS
CZS-2	50.8:45.8:1.3	2.5	$Zn_{0.98}Cu_{0.02}S$
CZS-5	49.7:45.2:2.7	5.2	$Zn_{0.95}Cu_{0.05}S$
CZS-10	49.2:45.1:5.7	10.4	$Zn_{0.90}Cu_{0.10}S$
CZS′-5[b]	49.9:45.8:2.6	5.0	$Zn_{0.95}Cu_{0.05}S'$
CZS′-5_AC[c]	49.1:48.3:2.6	5.1	$Zn_{0.95}Cu_{0.05}S'$

[a]Based on EDS analysis. [b]Sulfurated CZS-5 sample. [c]CZS′-5 sample retrieved after photocatalytic reactions.

Table S2. EIS equivalent circuit fitted parameters for ZS, CZS and CZS′-5 NCAs catalysts.

Sample	R_s (Ω)	Q_f (F)	L_{ad} (H)	R_{ct} (Ω)	Q_s (F)	x^2
ZS	1.34	11.6×10^{-9}	75.0×10^{-6}	100.5	11.7×10^{-6}	3.2×10^{-4}
CZS-2	1.33	11.6×10^{-9}	77.6×10^{-6}	102.6	9.2×10^{-6}	4.5×10^{-4}
CZS-5	1.38	11.6×10^{-9}	78.3×10^{-6}	102.9	12.3×10^{-6}	2.6×10^{-3}
CZS-10	1.28	11.3×10^{-9}	78.3×10^{-6}	105.4	7.0×10^{-6}	5.6×10^{-4}
CZS′-5	1.36	11.4×10^{-9}	64.1×10^{-6}	95.6	13.37×10^{-6}	2.9×10^{-3}

Supporting Figures

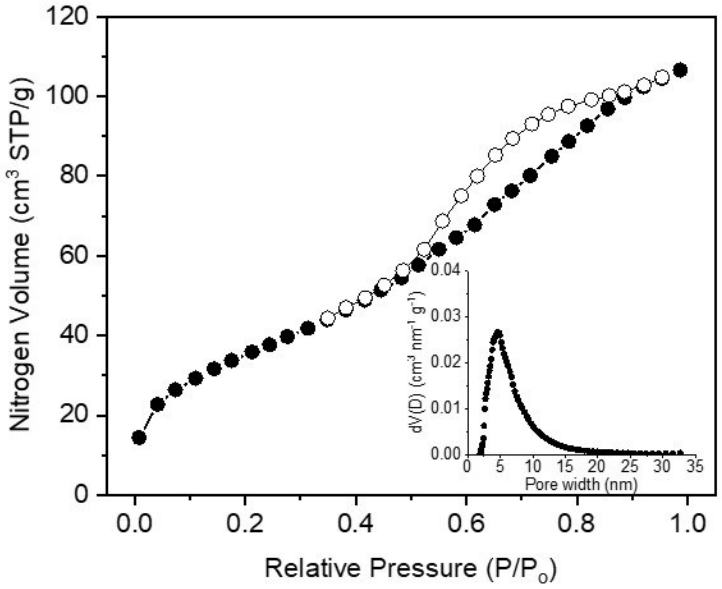

Fig. S1 N_2 adsorption and desorption isotherms at –196 °C and (inset) the corresponding pore-size distribution plot for the mesoporous CZS′-5 catalyst.

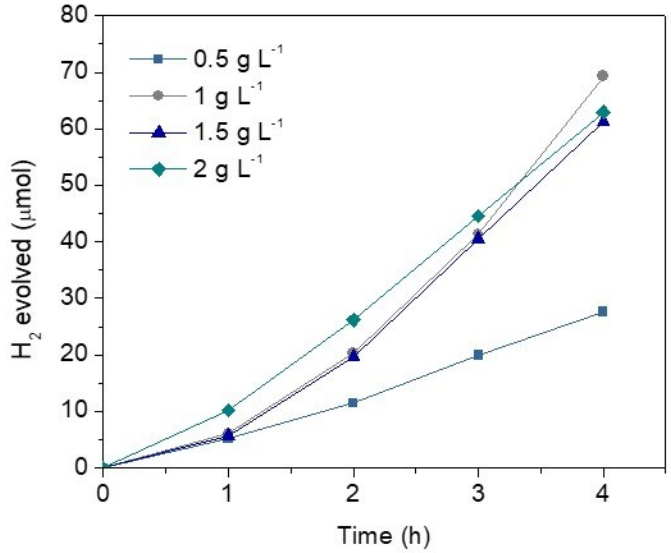

Fig. S2 Time courses for photocatalytic H_2 production for different loadings of the CZS-5 catalyst. The photocatalytic reactions were performed by suspending the catalyst in 20 mL of water containing 0.25 M Na_2SO_3 and 0.35 M Na_2S, under λ ≥ 420 nm light irradiation.

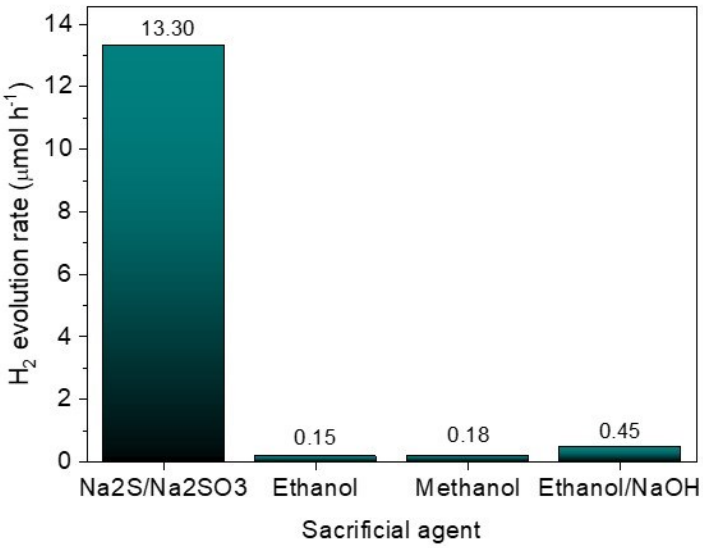

Fig. S3 Photocatalytic H_2 evolution rates for CZS-5 catalyst using different sacrificial electron donors. The photocatalytic reactions were performed by suspending 20 mg of catalyst in 20 mL of water containing the sacrificial agent, under λ ≥ 420 nm light irradiation. Sacrificial electron donors: 0.35M Na_2S/0.25M Na_2SO_3, 10% (v/v) ethanol, 10% (v/v) methanol, 10% (v/v) ethanol/5M NaOH.

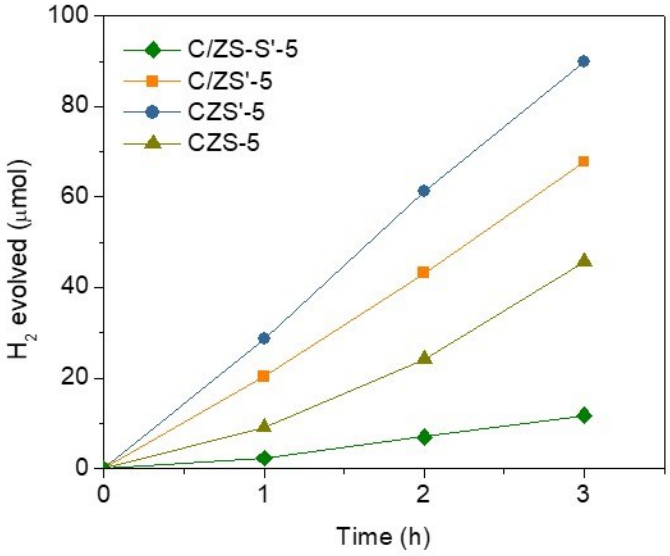

Fig. S4 Time courses for photocatalytic H_2 production for different sulfide-treated Cu/ZnS catalysts. The H_2-prodyction activity of the CZS-5 is also given for comparison. The photocatalytic reactions were performed by suspending 20 mg of catalyst in 20 mL of water containing 0.25 M Na_2SO_3 and 0.35 M Na_2S, under λ ≥ 420 nm light irradiation.

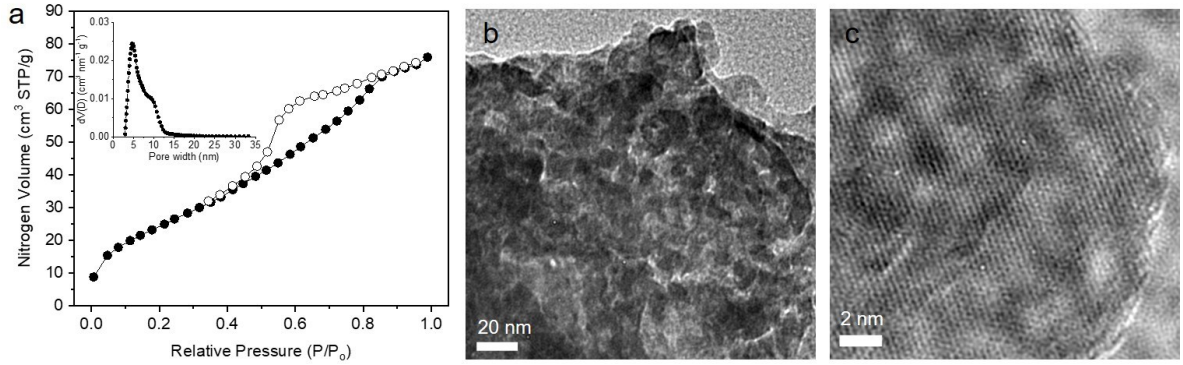

Fig. S5 (a) N_2 adsorption-desorption isotherm and (b, c) TEM images of mesoporous CZS′-5 NCAs retrieved after photocatalytic recycle tests. The TEM images reveal that the reused CZS′-5 catalyst preserves a porous network structure of interconnected, highly crystalline, nanoparticles.

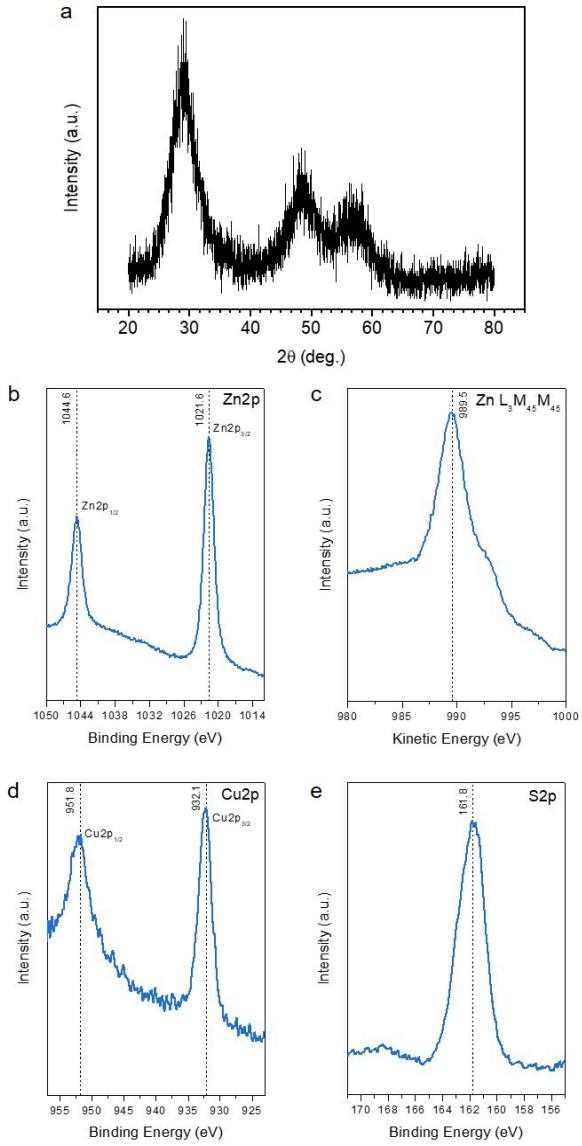

Fig. S6 (a) XRD pattern and (b-e) XPS spectra of the Zn 2p (b), Zn $L_3M_{45}M_{45}$ Auger (c), Cu 2p (d) and S 2p core-level (e) lines for the mesoporous CZS′-5 sample after photocatalytic recycle tests. The Auger parameter value at 2011.1 ±0.2 eV indicates that the dominant phase is ZnS. The absence of “shake-up” satellite peak in the Cu 2p spectrum suggests that the Cu species in the sample are Cu_2S.

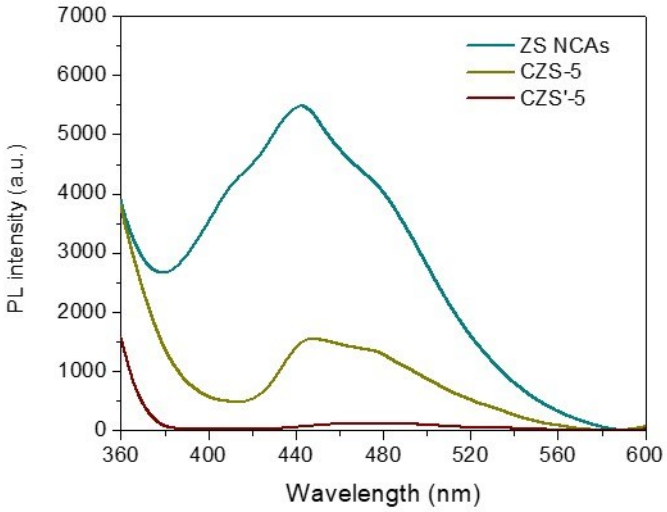

Fig. S7 Room-temperature PL emission spectra of the mesoporous ZS, CZS-5 and CZS′-5 catalysts. PL experiments were carried out in water (0.5 mg mL^{-1}) with 330 nm excitation wavelength.