Supplementary Information

Constructing CuNi Dual Active Sites on $ZnIn_2S_4$ for Highly Photocatalytic Hydrogen Evolution

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EXPERIMENTAL SECTION

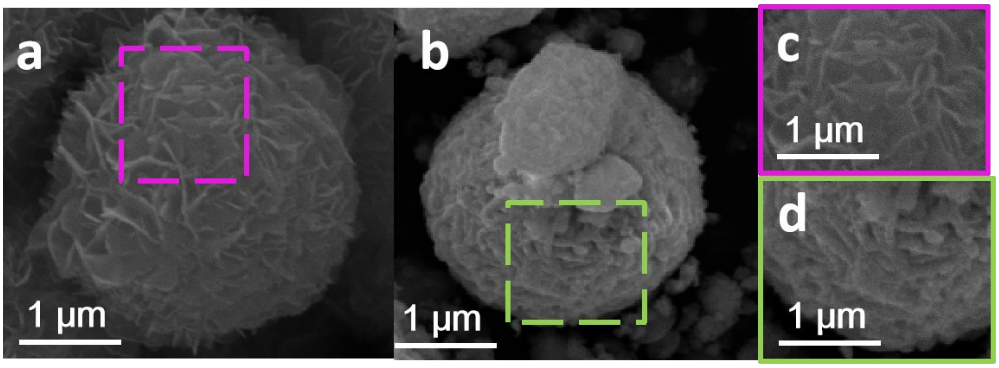

Fig. S1 SEM images of (a) pure $ZnIn_2S_4$ and (b) 12% Cu_2Ni_1-ZIS. The enlarged images of (c) pure $ZnIn_2S_4$ and (d) 12% Cu_2Ni_1-ZIS.

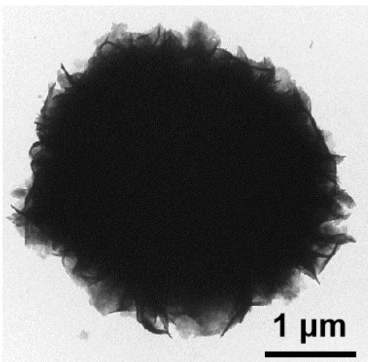

Fig. S2 TEM image of pure $ZnIn_2S_4$.

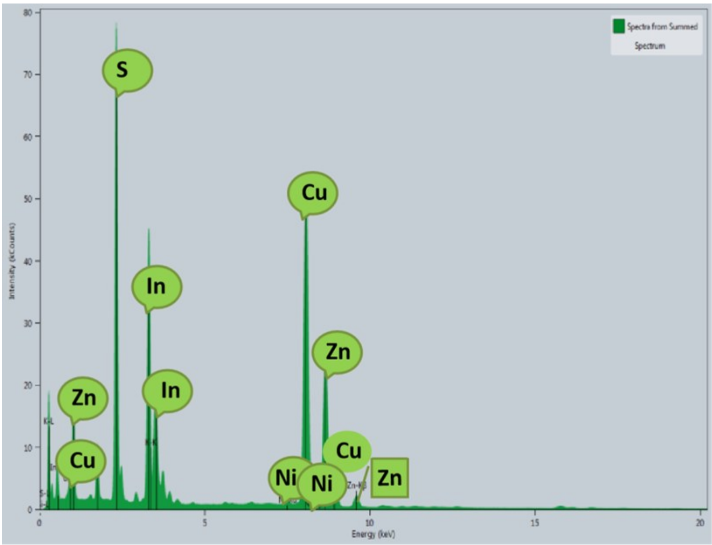

Fig. S3. The EDS spectrum of 12% Cu_2Ni_1-ZIS

Table S1. The surface element content from XPS characterization.

Element	Atomic %	Element	Atomic %
S	31.05	Cu	0.85
Zn	17.68	Ni	0.55
In	10.56	C	28.89
N	2.95	O	7.47
Exact mass ratio of Cu to $ZnIn_2S_4$ = 1.62%		Exact mass ratio of Ni to $ZnIn_2S_4$= 0.97%	

Table S2 Performance comparison of $ZnIn_2S_4$ modified by different types of cocatalyst

Category	Cocatalyst	Illumination conditions	Sacrifice agent	H_2 evolution Rate (μmol $g^{-1}\cdot h^{-1}$)	α*	Ref.
Bi-metals	**Cu-Ni**	**λ≥420 nm**	**0.35 M Na_2S 0.25 M Na_2SO_3**	**7825**	**29.5**	**This work**
	Co-Ni	λ>420 nm	Ascorbic acid	3336.6	4.3	[1]
	Co-P	λ>420 nm	Lactic acid	7840	44.0	[2]
Noble metal	Au	λ>420 nm	None	1633.4	4.41	[3]
	Pt	λ>420 nm	140 mmol Na_2S 100 mmol Na_2SO_3	1150	7.57	[4]
Metal oxides	Ag_2O	full spectrum	Triethanolamine	2334.19	3.39	[5]
	WO_3	λ>420 nm	0.25 M Na_2SO_3 0.35 M Na_2S	2202.9	5.22	[6]
Metal sulfides	MoS_2	λ>420 nm	Lactic acid	2512.5	8.73	[7]
		λ≥420 nm	0.43 M Na_2S 0.5 M Na_2SO_3	2060	10.85	[8]
	$MoSe_2$	λ>420 nm	Na_2S, Na_2SO_3	2228	2.18	[9]
Others	Ni_2P	λ≥400 nm	Lactic acid	2066	4.43	[10]
	CQD-Pt	λ>420 nm	Triethanolamine	1032.2	11.21	[11]
	rGO-Pt	λ>420 nm	0.25 M Na_2SO_3 0.35 M Na_2S	1210	26.3	[12]

* A parameter of α is adopted to describe the cocatalytic performance, which is defined by the quotient of the reaction rate of ZIS with cocatalysts and that of pure $ZnIn_2S_4$ without cocatalysts in each paper.

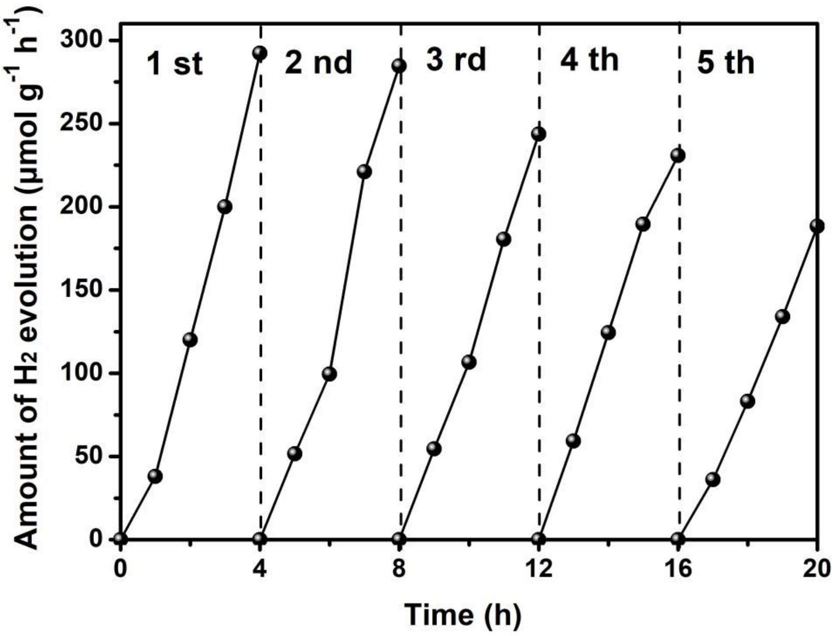

Figure S4. Stability test of pure $ZnIn_2S_4$ under the same condition as mentioned in this paper

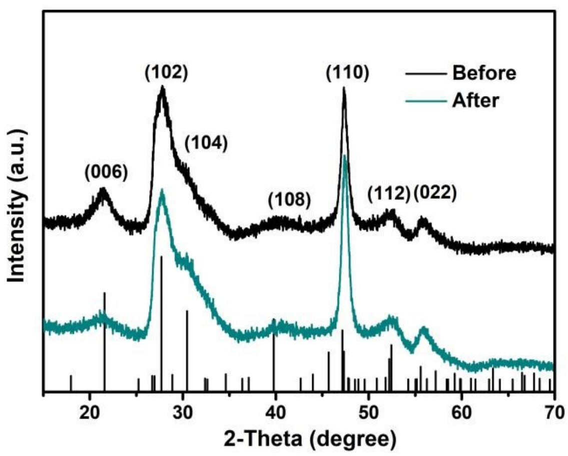

Figure S5. The XRD spectrum of 12% Cu_2Ni_1-ZIS before and after stability test

The XRD spectrum of 12% Cu_2Ni_1-ZIS after 20 h stability test didn't display evident characteristic peak migration compared with previous 12%Cu_2Ni_1-ZIS except the peak intensity of (006) lattice plane decreased a little.

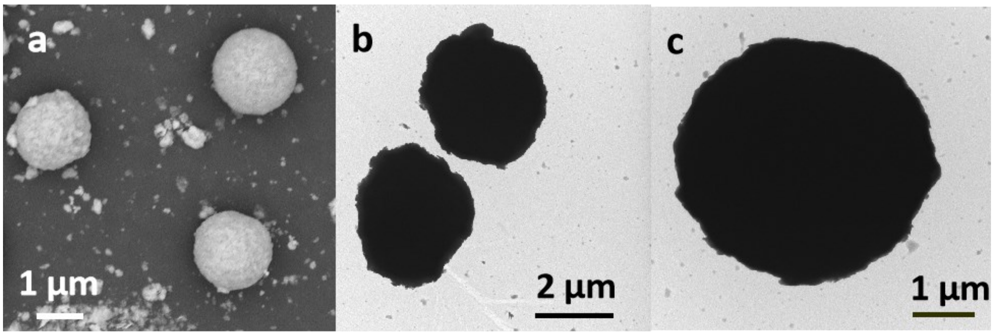

Fig. S6 (a) SEM (b-c) TEM images of 12% Cu_2Ni_1-ZIS after stability test.

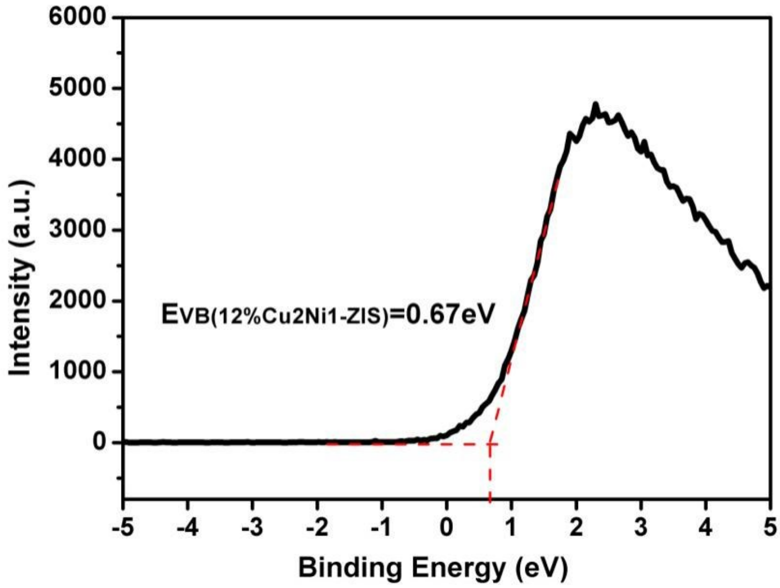

Figure S7 XPS valence band spectrum for 12%Cu_2Ni_1-ZIS showing the edge of valence band

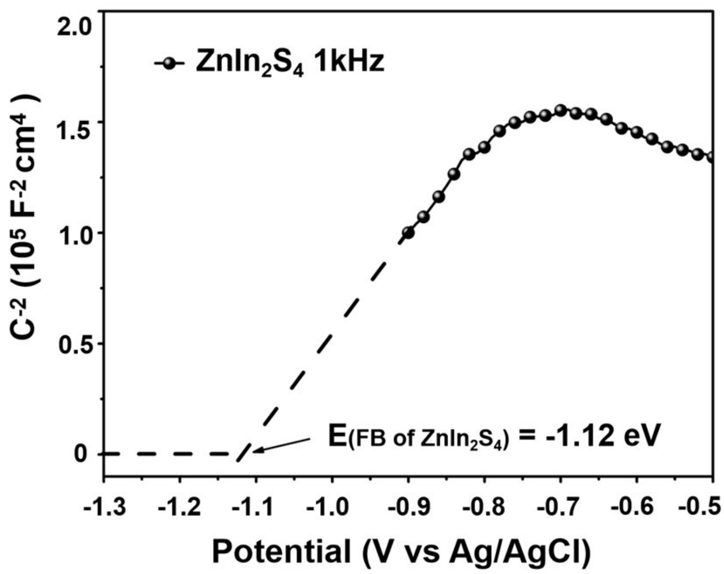

Figure S8 Mott-Schottky curve of pure $ZnIn_2S_4$

Mott-Schottky curves were taken at 1.0 kHz frequency. The potential ranged from -1.3 V to -0.5 V (vs. Ag/AgCl), and the modulation amplitude of 5 mV. The 0.5 M Na_2SO_4 was used as the electrolyte solution.

According to Fig. S8, the flat band (FB) potential is -1.12 V (vs. Ag/AgCl). In general, the flat band potential of n-type semiconductors obtained from Mott-Schottky curves is about 0.2 V more positive than its conduction band potential [13]. Therefore, the conduction band potential of $ZnIn_2S_4$ is about -1.32 V vs. Ag/AgCl. According to the following equation:

$$E_{FB}(vs. NHE) = E_{FB}(vs. Ag/AgCl) + 0.197$$

The conduction band of $ZnIn_2S_4$ is -1.13 V vs. NHE. Combining its band gap (2.54 eV), the valence band potential of $ZnIn_2S_4$ is 1.41 V vs. NHE.

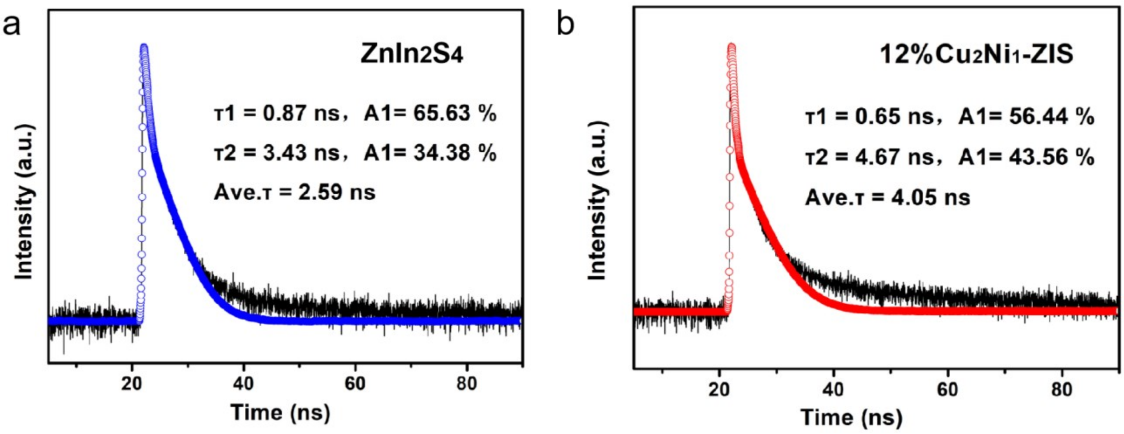

Figure S9 Transient-state photoluminescence spectra: (a) $ZnIn_2S_4$ (b) 12% Cu_2Ni_1-ZIS

Table S3 Fluorescence emission lifetime and relevant percentage data of $ZnIn_2S_4$ and 12%Cu_2Ni_1-ZIS

Samples	τ_1 (ns)	A_1 (%)	τ_2 (ns)	A_2 (%)	Average lifetime (τ_a) (ns)
$ZnIn_2S_4$	0.87	65.62	3.43	34.38	2.59
12%Cu_2Ni_1-ZIS	0.65	56.44	4.67	43.56	4.05

The fitted parameters of the above transient-state photoluminescence spectra are acquired via the following bi-exponential formulas:

$$I_{(t)} = I_0 + A_1\exp(-t/\tau_1) + A_2\exp(-t/\tau_2)$$

The above average lifetime value is obtained according to the following formulas:

$$\tau_a = (A_1\tau_1^2 + A_2\tau_2^2)/(A_1\tau_1 + A_2\tau_2)$$

where I_0 is the baseline correction value, A_1 and A_2 represent the bi-exponential factors. A_1, A_2 represent the double exponential factors. τ_1, τ_2 and τ_a corresponding the lifetime in different stages (radiation, non-radiation) and average lifetime respectively.

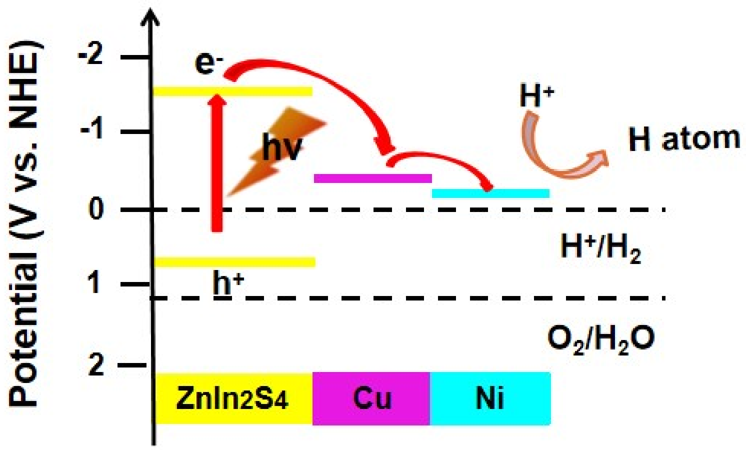

Figure S10 The energy level position and mechanism of electrons migration in 12%Cu_2Ni_1-ZIS

Reference

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