Supplementary Information

Interface, vacancy and morphology engineering synergistically improve In_2S_3@Cu_2S electrocatalytic performance for pH-universal HER

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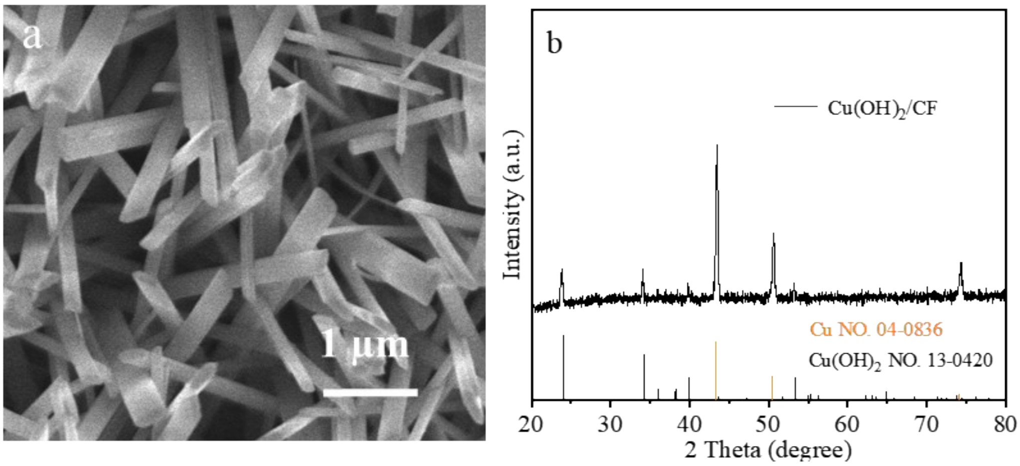

Fig. S1. The SEM (a) image and XRD pattern (b) of $Cu(OH)_2$/CF

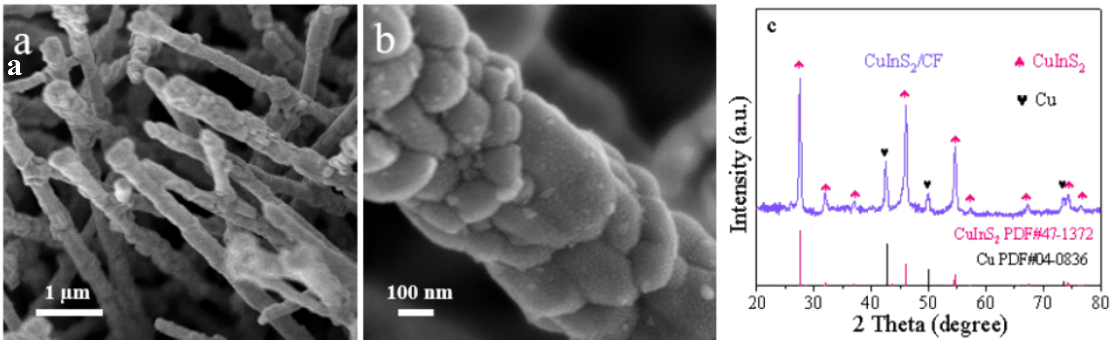

Fig. S2. The SEM (a, b) image and XRD pattern (c) of $CuInS_2$/CF.

Fig. S3. The SEM image of (a) In_2S_3@Cu_2S NAs/CF-1 and (b) In_2S_3@Cu_2S NAs/CF-3.

Table S1 the atomic percentage of each element in In_2S_3@Cu_2S NAs/CF-2 from XPS and EDS.

	XPS Atomic conc. [%]	EDS Atomic conc. [%]
Cu	31.53	29.55
In	22.87	26.82
S	45.6	43.63

Fig. S4. Voltammograms of the (a) In_2S_3@Cu_2S/CF-1, (b) In_2S_3@Cu_2S/CF-2, (c) In_2S_3@Cu_2S/CF-3 and (d) Cu_2S/CF at various scan rates (10-50 mV s^{-1}) in 0.5 M H_2SO_4.

Table S2 The charge transfer resistances obtained from Nyquist plots in 0.5 M H_2SO_4 solution.

Samples	R_{ct} (Ω)	R_s (Ω)
$In_2S_3@Cu_2S$/CF-1	8.48	1.093
$In_2S_3@Cu_2S$/CF-2	2.32	0.8122
$In_2S_3@Cu_2S$/CF-3	5.09	0.9236
Cu_2S/CF	14.72	1.16

Fig. S5. Voltammograms of the (a) $In_2S_3@Cu_2S$/CF-1, (b) $In_2S_3@Cu_2S$/CF-2, (c) $In_2S_3@Cu_2S$/CF-3 and (d) Cu_2S/CF at various scan rates (10-50 mV s^{-1}), (e) C_{dl} and (f) EIS of $In_2S_3@Cu_2S$/CF -1, $In_2S_3@Cu_2S$/CF -2, $In_2S_3@Cu_2S$/CF -3, and Cu_2S/CF in 1M KOH.

Table S3 The charge transfer resistances obtained from Nyquist plots in 1 M KOH solution.

Samples	R_{ct} (Ω)	R_s (Ω)
$In_2S_3@Cu_2S$/CF-1	7.83	0.8851
$In_2S_3@Cu_2S$ /CF-2	3.29	1.081
$In_2S_3@Cu_2S$ /CF-3	6.24	0.6742
Cu_2S/CF	15.36	1.154

Fig. S6. Voltammograms of the (a) $In_2S_3@Cu_2S$/CF-1, (b) $In_2S_3@Cu_2S$/CF-2, (c) $In_2S_3@Cu_2S$/CF-3 and (d) Cu_2S/CF at various scan rates (10–50 mV s^{-1}), (e) C_{dl} and (f) EIS of $In_2S_3@Cu_2S$/CF-1, $In_2S_3@Cu_2S$/CF-2, $In_2S_3@Cu_2S$/CF-3, and Cu_2S/CF in 1M PBS.

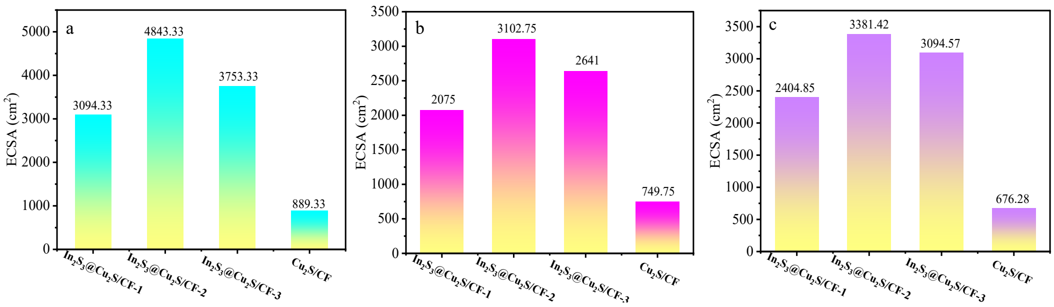

Fig. S7. The ECSA of $In_2S_3@Cu_2S$/CF-1, $In_2S_3@Cu_2S$/CF-2, $In_2S_3@Cu_2S$/CF-3 and Cu_2S/CF in (a) 0.5 M H2SO4, (b) 1 M KOH and (c) 1 M PBS.

Table S4 The charge transfer resistances obtained from Nyquist plots in 1 M PBS solution.

Samples	R_{ct} (Ω)	R_s (Ω)
In_2S_3@Cu_2S/CF-1	6.28	1.105
In_2S_3@Cu_2S /CF-2	3.55	1.074
In_2S_3@Cu_2S /CF-3	7.66	0.8565
Cu_2S/CF	19.29	1.744

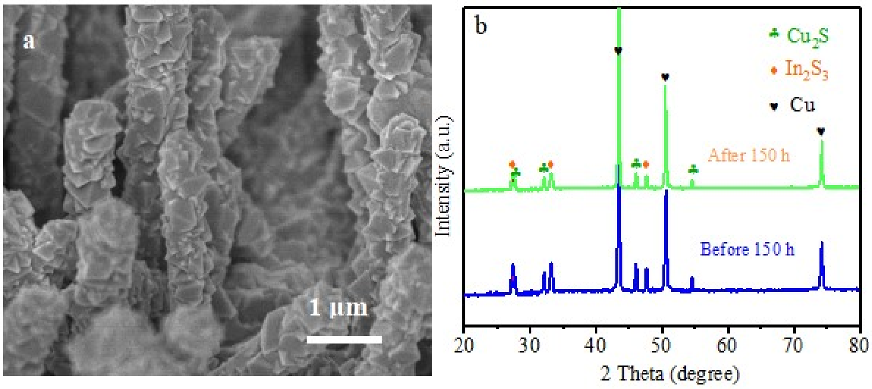

Fig. S8. The SEM image (a) and XRD pattern (b) of In_2S_3@Cu_2S/CF-2 after performing a 150 h test.

Table S5 HER activity comparison between In_2S_3@Cu_2S/CF-2 with the recently reported pH-universal non-noble-metal catalysts in different solutions. (η_{10}: Overpotentials at a current density of 10 mA cm^{-2})

Catalysts	0.5 M H_2SO_4	1 M PBS	1M KOH	Ref.
	η_{10} (mV)	η_{10} (mV)	η_{10} (mV)	
NiCoP/NF	105	97	98	1
W_2C/WP@NC-2	196.2	/	116.37	2
Fe-Mo_2C@NCF	129	130	65	3
W-MoP	63	71	82	4
Co-P@PC	72	91	/	5

S-MoP NPL	86	142	104	6
CoMoNiS-NF-31	103	117	113	7
MoS_2/NLG-3	110	142	145	8
MoP/Mo_2N	89	91	89	9
$Co_{0.5}W_{0.5}S_x$	200	198	189	10
MoPS	92	/	158	11
Cu@WC	92	173	119	12
Fe-(NiS_2/MoS_2)/CNT	98	127	87	13
MoS_2/NLG-3/CFP	110	142	145	14
$Co_{0.97}Ti_{0.03}SP$	44	/	132	15
In_2S_3@Cu_2S/CF-2	42	78	61	This work

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