Supporting information

Cu_5FeS_4 quantum dots as single-component photo-assisted electrocatalyst for efficient hydrogen evolution

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Electrochemical Measurements

All the electrochemical measurements were performed with a CHI 760E electrochemical analyzer (CH Instruments, Inc., Shanghai) in a standard three-electrode system with a rate of 5 mV s^{-1}. Typically, the catalysts grown on Nickel foam (NF) were employed as working electrode, Hg/HgO as reference electrode, and graphite rod as the counter electrode for HER tests in 1.0 M KOH electrolyte, in which the NF was ultrasonically treated in acetone and ethanol solution and followed by washing with distilled water. Notedly, Ag/AgCl and Hg/HgO are used as reference electrodes when electrolyte pH=3 and 7, respectively. The potentials vs. reversible hydrogen electrode (RHE) were converted from the reference scale by using the following equations: $E_{(RHE)} = E_{(Hg/HgO)} + 0.098\ V + 0.059 \times pH$ and $E_{(RHE)} = E_{(Ag/AgCl)} + 0.1976\ V + 0.059 \times pH$.

The double-layer capacitance (C_{dl}) was measured in 1.0 M KOH solution by cyclic voltammetry (CV) with scanning rates of 10-100 mV/s in the potential range from 0.72 to 0.82 V versus RHE. Electrochemical impedance spectra (EIS) and Mott-Schottky plots of the samples were measured in three different electrolytes, including 0.5 M H_2SO_4, 1.0 M PBS and 1.0 M KOH.

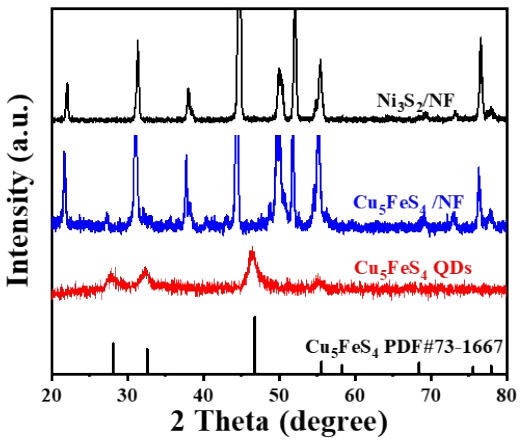

Fig. S1 The XRD patterns of Cu_5FeS_4 QDs (JCPDS no. 73-1667), Cu_5FeS_4/NF and Ni_3S_2/NF.

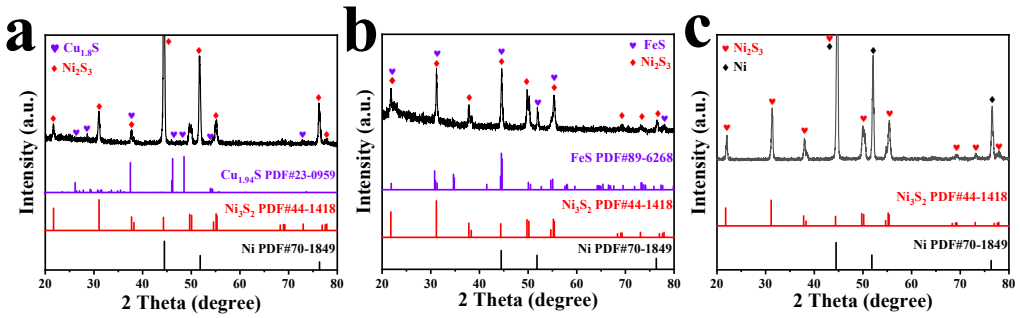

Fig. S2 The XRD patterns of (a) $Cu_{2-x}S$ (JCPDS no. 23-0959), (b) FeS (JCPDS no. 89-6268) and (c) Ni_3S_2 (JCPDS no. 44-1418) samples.

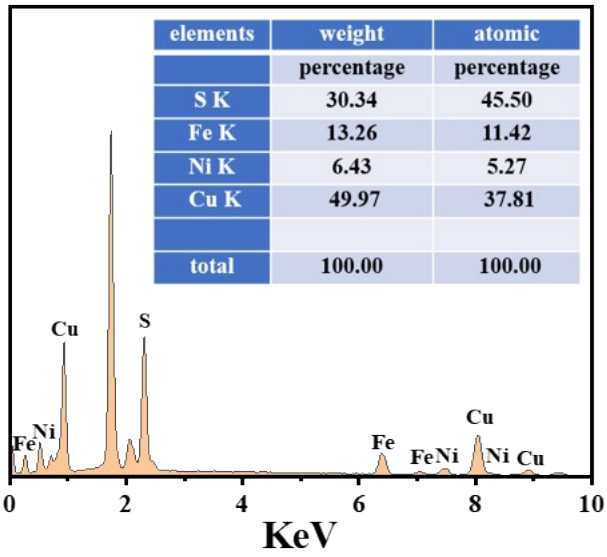

Fig. S3 EDX spectrum of the Cu_5FeS_4 QDs.

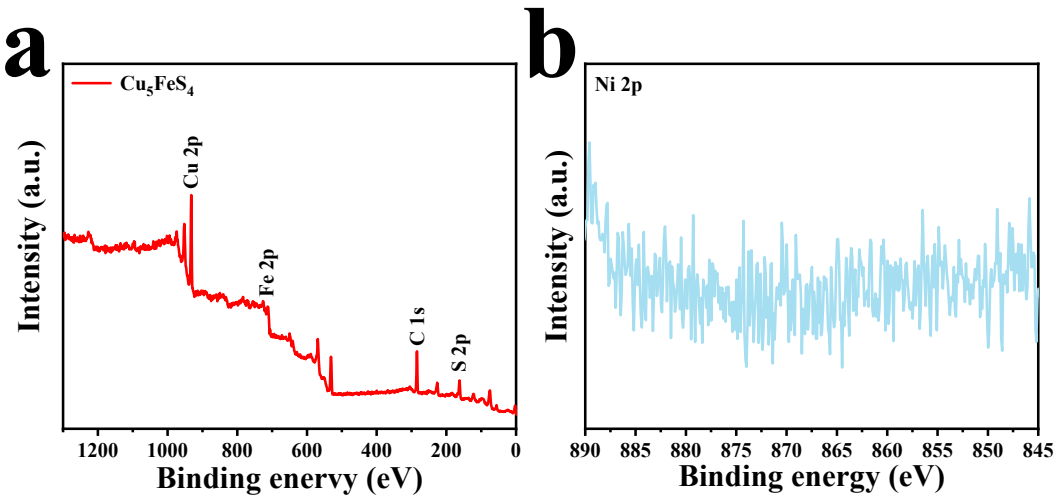

Fig. S4 XPS spectra of Cu_5FeS_4 QDs: (a) survey and (b) Ni 2p.

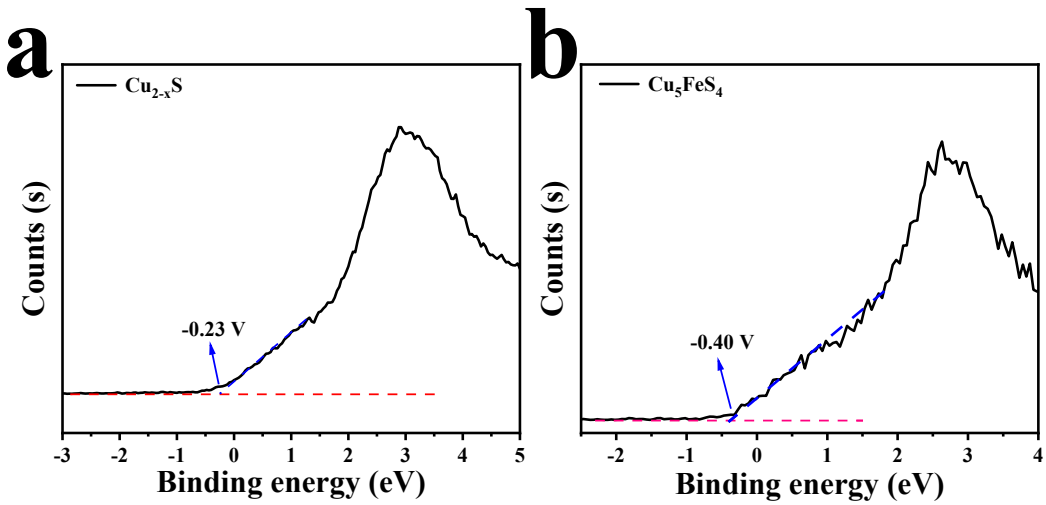

Fig. S5 The XPS valence band spectra of (a) $Cu_{2-x}S$ QDs and (b) Cu_5FeS_4.

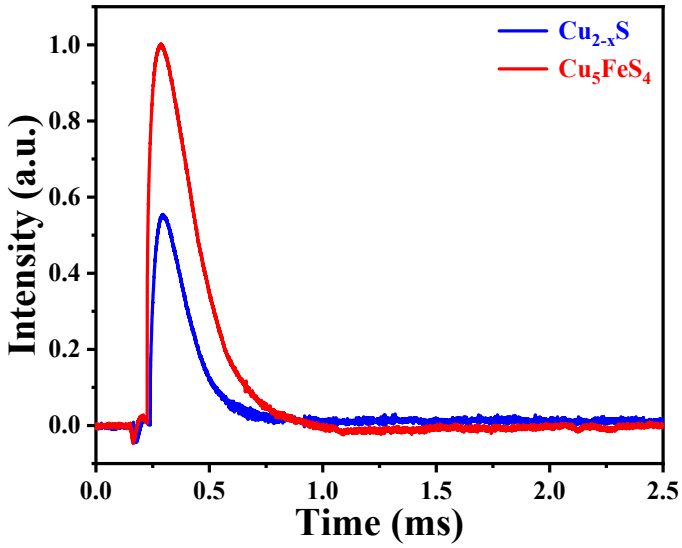

Fig. S6 TPV relaxation curves of $Cu_{2-x}S$ QDs and Cu_5FeS_4.

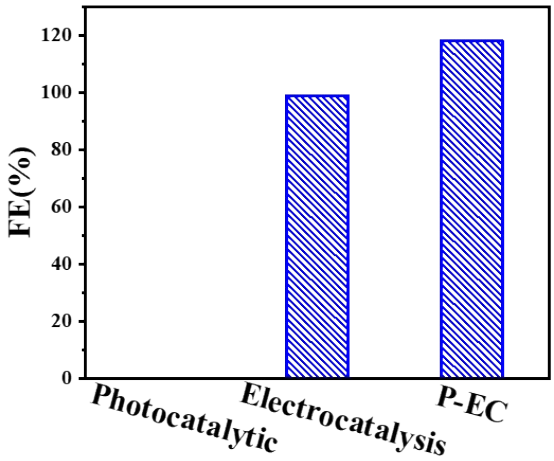

Fig. S7 The FE of electrocatalytic, photocatalytic and P-EC hydrogen production.

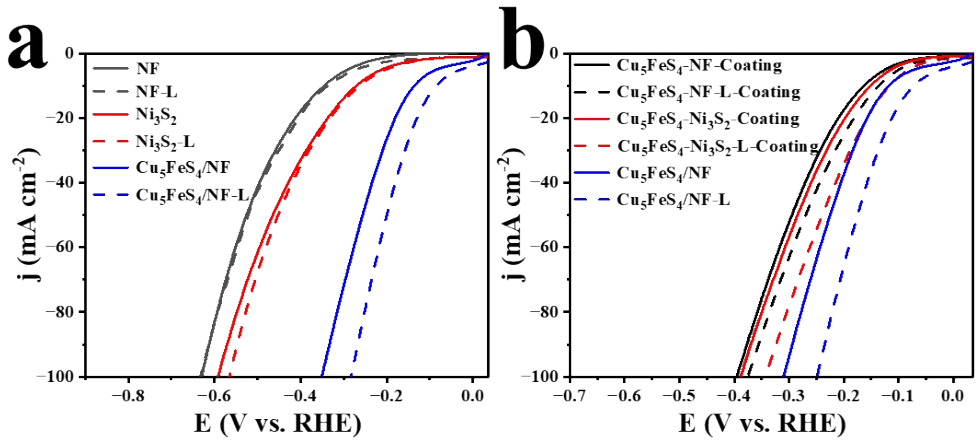

Fig. S8 The electrocatalytic and P-EC HER activity of (a) NF, NF-L, Ni_3S_2, Ni_3S_2-L, Cu_5FeS_4/NF and Cu_5FeS_4/NF-L and (b) Cu_5FeS_4-NF, Cu_5FeS_4-NF-L, Cu_5FeS_4-Ni_3S_2, Cu_5FeS_4-Ni_3S_2-L, Cu_5FeS_4/NF and Cu_5FeS_4/NF-L.

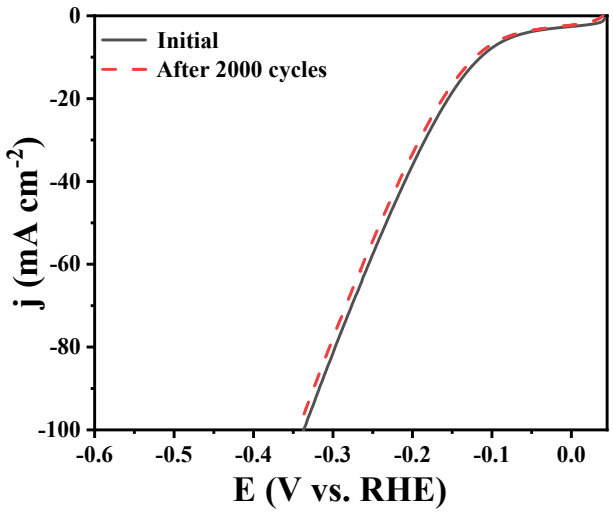

Fig. S9 Polarization curves of Cu_5FeS_4/NF before and after 2000 CV cycles under dark.

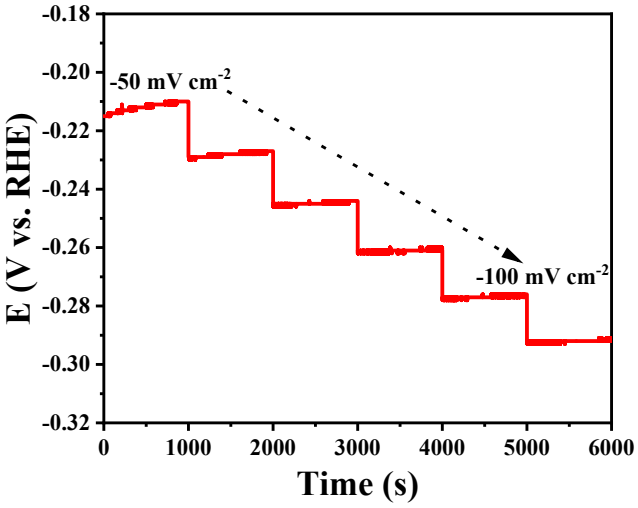

Fig. S10 The multi-current-process i-t curve of Cu_5FeS_4/NF under dark.

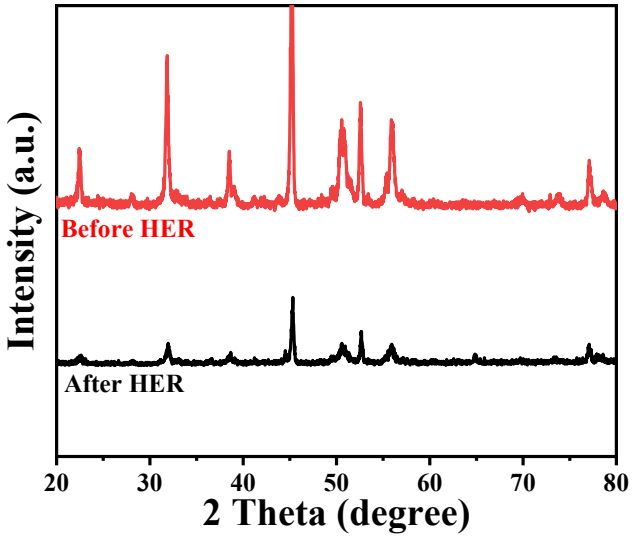

Fig. S11 XRD patterns of Cu_5FeS_4/NF before and after P-EC catalysis test of 20 h under continuous light irradiation.

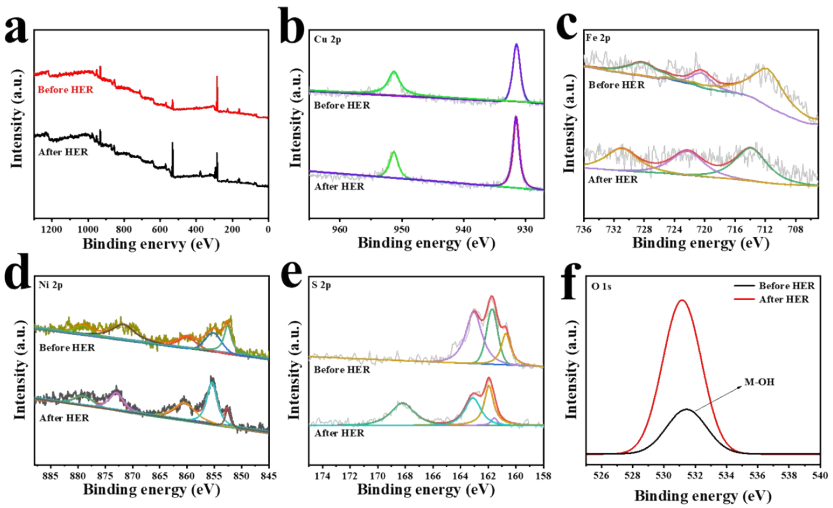

Fig. S12 XPS of Cu_5FeS_4/NF before and after P-EC test of 20 h under continuous light irradiation: (a) survey, (b) Cu 2p, (c) Fe 2p, (d) Ni 2p, (e) S 2p and (f) O 1s.

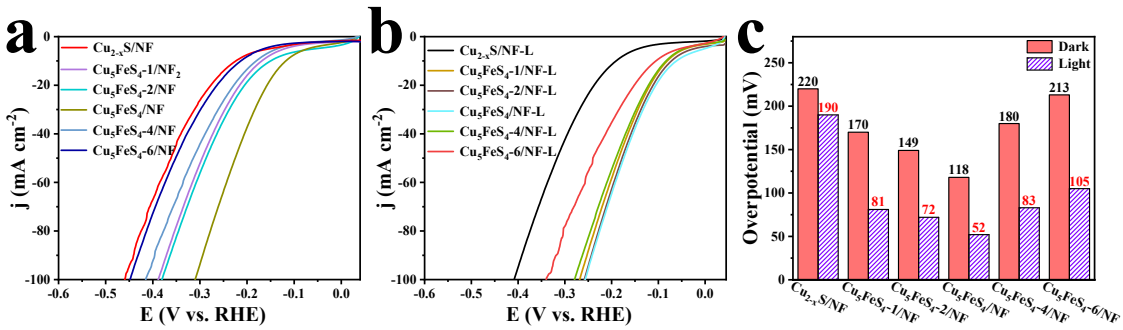

Fig. S13 Polarization curves of (a) electrocatalytic and (b) P-EC with different Cu/Fe ratios. (c) The corresponding overpotentials at current density of 10 mA cm^{-2} for different electrodes.

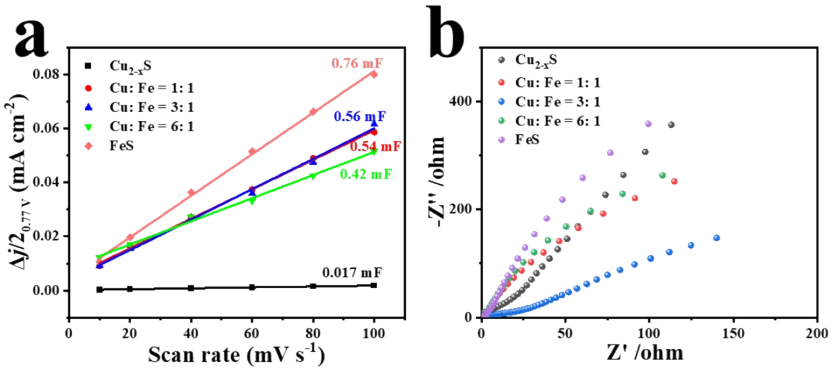

Fig. S14 (a) C_{dl} and (b) EIS patterns of the catalysts different Cu/Fe ratios.

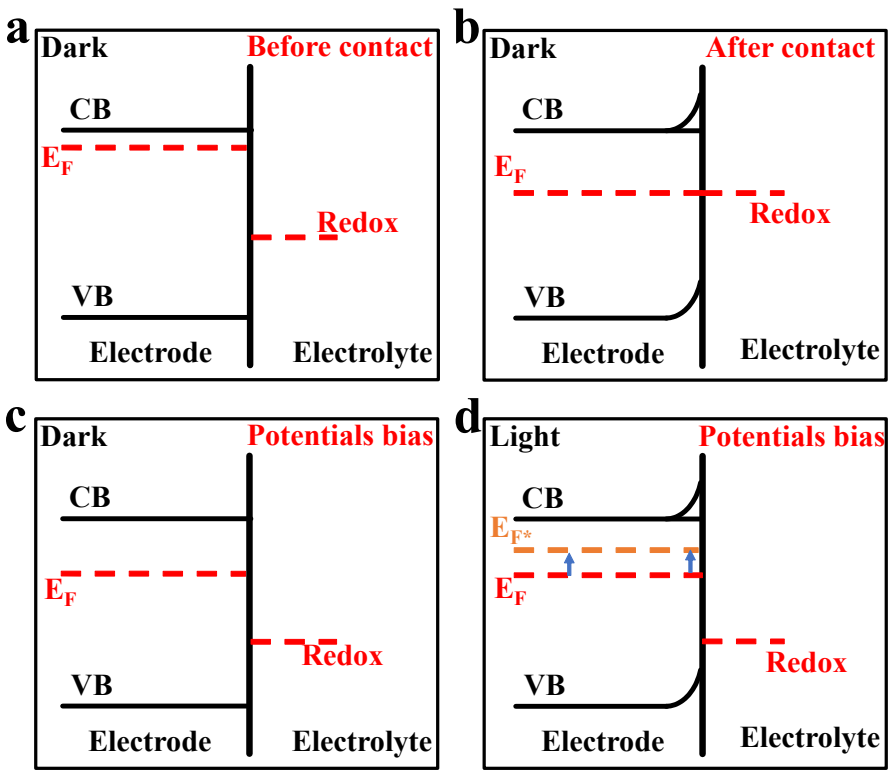

Fig. S15 Conduction and Valence band behaviour in electrode and electrolyte interface: (a) before contact, (b) after contact, (c) and (d) under potential bias without and with light, respectively.

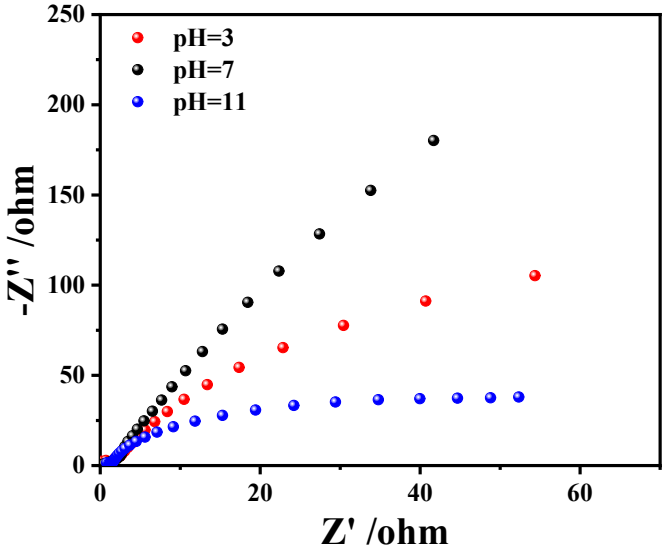

Fig. S16 EIS patterns of Cu_5FeS_4/NF in three different electrolytes (pH = 3, 7 and 11).

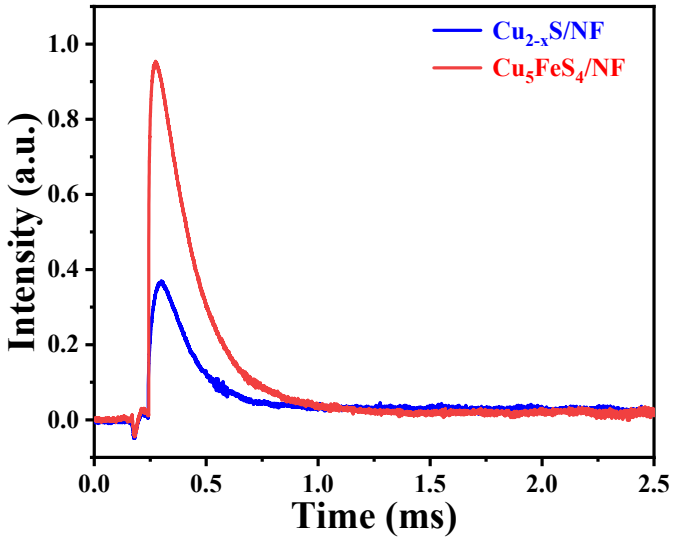

Fig. S17 TPV relaxation curves of $Cu_{2-x}S$/NF and Cu_5FeS_4/NF.

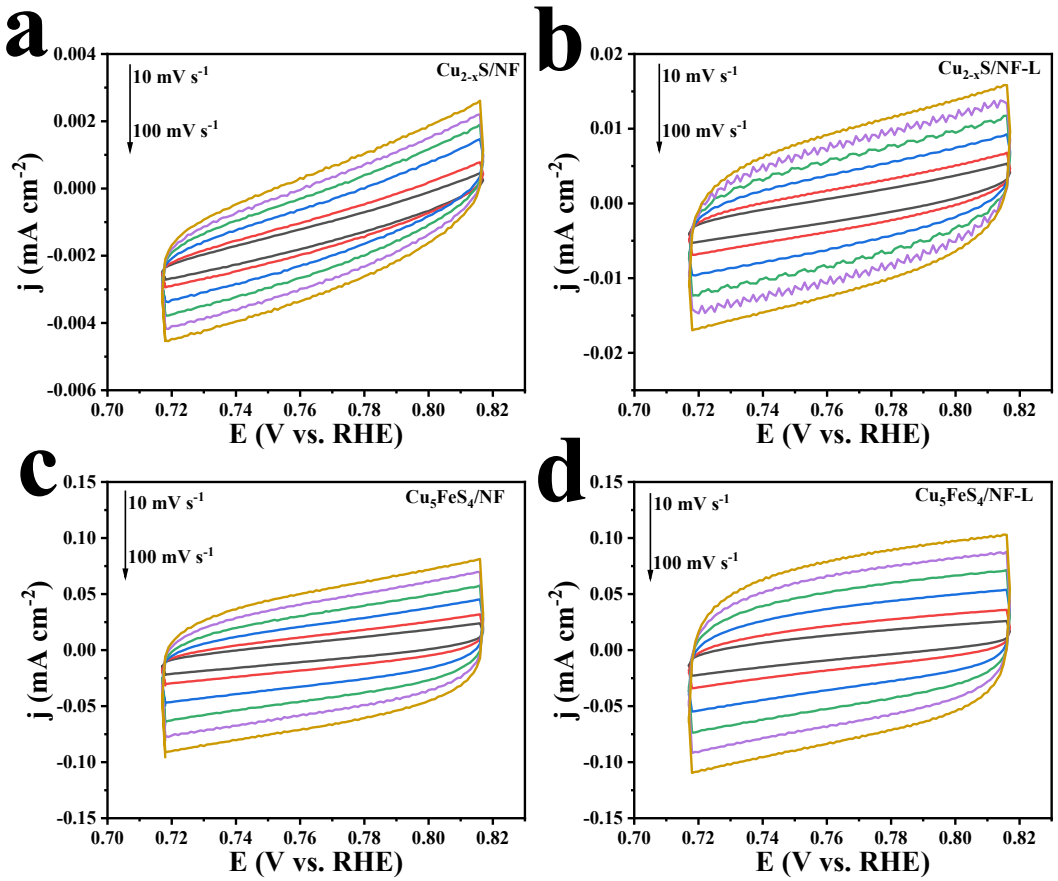

Fig. S18 CV curves at different scan rates of $Cu_{2-x}S$/NF without (a) and with light (b); CV curves at different scan rates of Cu_5FeS_4/NF without (c) and with light (d).

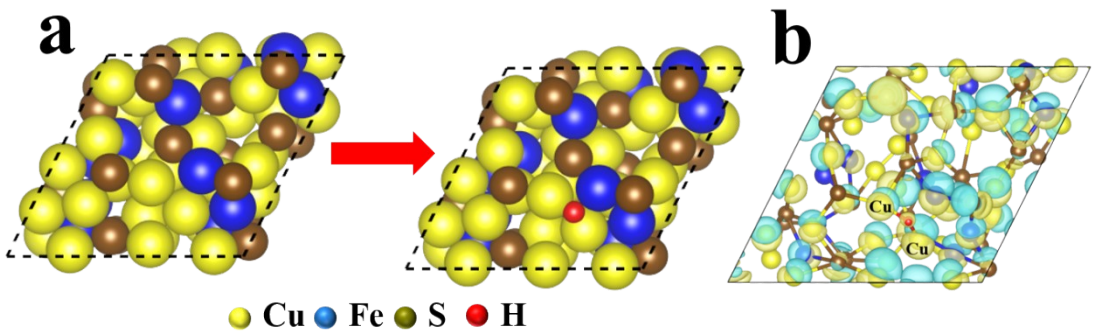

Fig. S19 (a) Top view of H^* adsorption and (b) charge density difference of Cu_5FeS_4 QDs without light.

Table S1 HER performance comparison between Cu_5FeS_4/NF-L in our work and other cheap transition metal catalysts reported previously.

Catalysts	Electrolyte	Overpotential at 10 mA cm^{-2} (mV)	Refs.
Cu_5FeS_4/NF-L	**1M KOH**	**52**	**This work**
TiS_{2-x}/NiS	1M KOH	63	1
Ni-Fe-P-Ni_3S_2/NF	1M KOH	65	2
MoS_2-RGO	0.5 M H_2SO_4	66	3
N-NiMoS	0.1 M KOH	68	4
CdS@Co_8S_9/Ni_3S_2	1M KOH	69.6	5
$Fe_xNi_{3-x}S_2$@NF	1M KOH	72	6
N-NiS_2/CoS_2	1M KOH	73	7
NiFeCoSx@$FeNi_3$	1M KOH	88	8
N-$NiMoO_4$/NiS_2	1M KOH	99	9
NiSe-$Ni_{0.85}Se$	1M KOH	101	10
Fe-Ni_3S_2@$FeNi_3$	1M KOH	105	11
B-Fe_7S_8/FeS_2	1M KOH	113	12
W-NiO/NiS_2	1M KOH	116	13
$NiCo_2S_4$/Ni_3S_2	1M KOH	127	14
Fe-CoMoS	1M KOH	137	15
$Co_{0.9}S_{0.58}P_{0.42}$	1M KOH	141	16
FeS	1M KOH	142	17
Ni_3S_2	1M KOH	147	18
Co_9S_8-MoS_2/N-CNAs@CNFs	1M KOH	163	19
$Fe_{0.95-x}Ni_xS_{1.05}$	1M KOH	263	[0

Table S2 The R_{ct} values of Cu_5FeS_4/NF in different electrolytes with/without light.

Samples	Dark (Ω cm^2)	Light (Ω cm^2)
pH=3	320.5	155.6
pH=7	478.9	424.2
pH=11	270.7	73.8

Table S3 Fitting parameters of the EIS data of different samples using the equivalent circuit in the inset of Fig. 5f.

Samples	R_s (Ω cm^2)	R_{ct} (Ω cm^2)
$Cu_{2-x}S$/NF	112.3	1165.3
$Cu_{2-x}S$/NF-L	28.8	283.9
Cu_5FeS_4/NF	19.4	268.8
Cu_5FeS_4/NF-L	1.3	24.9

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