Supporting Information

Surface Assistant Charge Separation in PEC Cu$_2$S-Ni/Cu$_2$O Cathode

Wan Zhang[1], Ruotian Chen[2], Zhiguang Yin[1], Xinyu Wang[1], Zenglin Wang[1], Fengtao Fan[2], Yi Ma[1*]

[1] Key Laboratory of Applied Surface and Colloid Chemistry, Ministry of Education, School of Chemistry and Chemical Engineering, Shaanxi Normal University, Xi'an 710119, Shaanxi, China

2 State Key Laboratory of Catalysis, Dalian National Laboratory for Clean Energy, The Collaborative Innovation Centre of Chemistry for Energy Materials (iChEM), Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Zhongshan Road 457, Dalian 116023, China

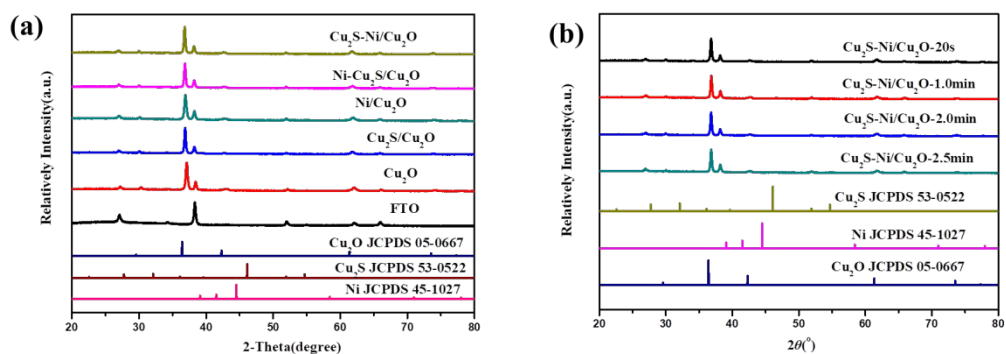[*]Corresponding author: mayi@snnu.edu.cn

Fig. S1 - XRD patterns of (a) Cu_2O, Cu_2S/Cu_2O, Ni/Cu_2O, $Ni-Cu_2S/Cu_2O$ and Cu_2S-Ni/Cu_2O and (b) Cu_2S-Ni/Cu_2O photoelectrodes with various Ni content.
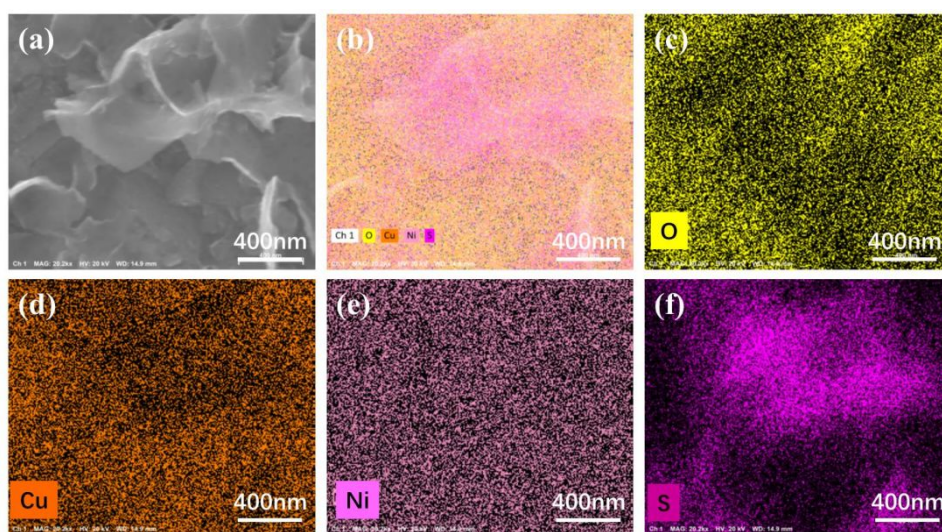
Fig. S2 Enlarged top-view SEM image of Cu$_2$S-Ni/Cu$_2$O (a) and corresponding EDX mapping for all elements (b), O (c), Cu (d), Ni (e) and S (f).

(a)

Element	At. No.	Mass [%]	Mass Norm. [%]	Atom [%]	abs. error [%] (1 sigma)
Oxygen	8	7.32	8.52	27.01	0.89
Copper	29	78.54	91.48	72.99	2.12
		85.85	100.00	100.00	

(b)

Element	At. No.	Mass [%]	Mass Norm. [%]	Atom [%]	abs. error [%] (1 sigma)
Oxygen	8	6.27	6.85	22.12	1.01
Sulfur	16	2.42	2.64	4.26	0.12
Copper	29	82.92	90.51	73.62	2.27
		91.62	100.00	100.00	

(c)

Element	At. No.	Mass [%]	Mass Norm. [%]	Atom [%]	abs. error [%] (1 sigma)
Oxygen	8	7.53	7.97	25.58	1.17
Copper	29	86.44	91.51	73.96	2.37
Nickel	28	0.49	0.52	0.46	0.05
		94.46	100.00	100.00	

(d)

Element	At. No.	Mass [%]	Mass Norm. [%]	Atom [%]	abs. error [%] (1 sigma)
Sulfur	16	1.47	1.66	2.43	0.09
Nickel	28	0.46	0.53	0.42	0.05
Oxygen	8	10.15	11.50	33.63	1.48
Copper	29	76.17	86.31	63.53	2.09
		88.26	100.00	100.00	

(e)

Element	At. No.	Mass [%]	Mass Norm. [%]	Atom [%]	abs. error [%] (1 sigma)
Oxygen	8	3.04	3.49	11.52	0.60
Sulfur	16	8.83	10.15	16.71	0.35
Copper	29	75.01	86.23	71.65	2.06
Nickel	28	0.12	0.14	0.13	0.04
		87.00	100.00	100.00	

Fig. S3 Elements distributions of photoelectrodes analyzed by EDX spectra: (a) Cu_2O, (b) Cu_2S/Cu_2O,

(c) Ni/Cu_2O, (d) $Ni-Cu_2S/Cu_2O$, (e) Cu_2S-Ni/Cu_2O.

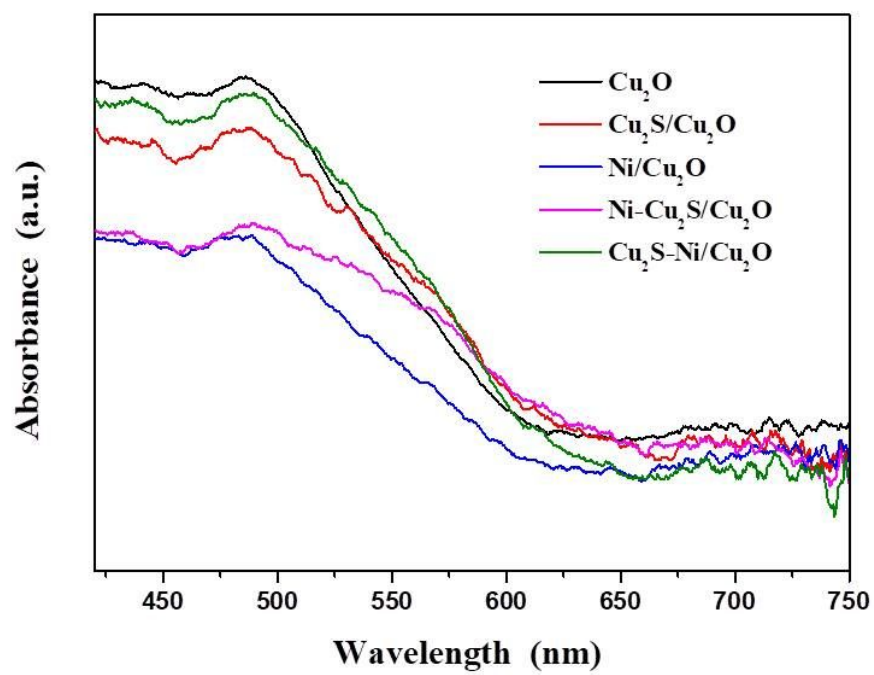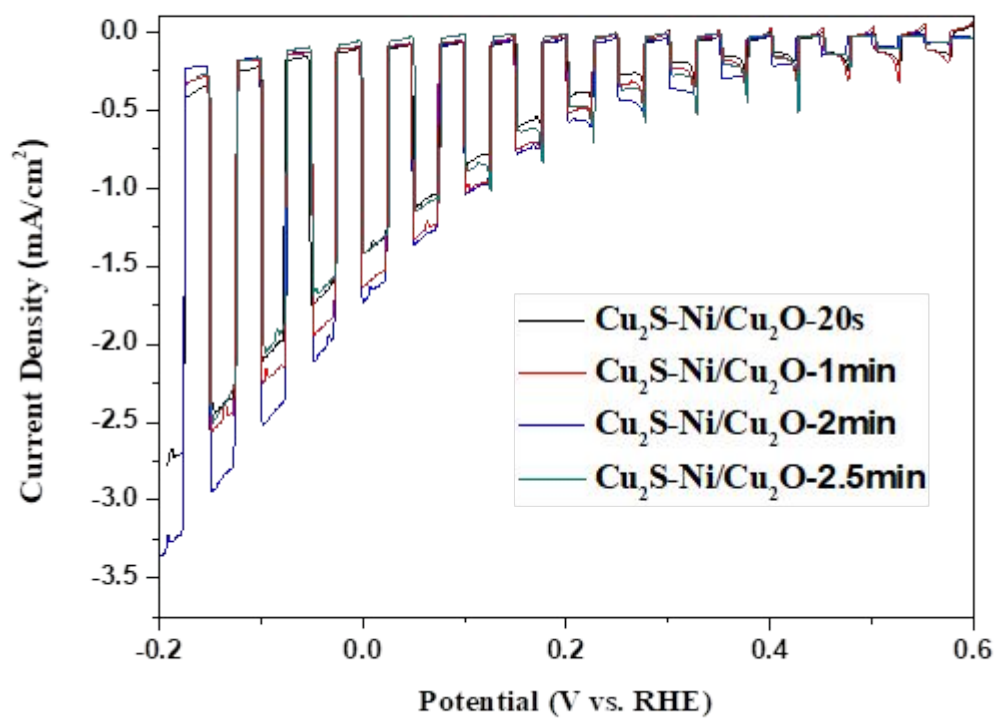**Figure S4.** UV-Vis diffuse reflectance spectra of the photoelectrodes.

Fig. S5 The I-V curves of Cu_2S-Ni/Cu_2O photoelectrodes with different content of Ni under chopped light irradiation of a Xe-lamp with AM 1.5 G filter.
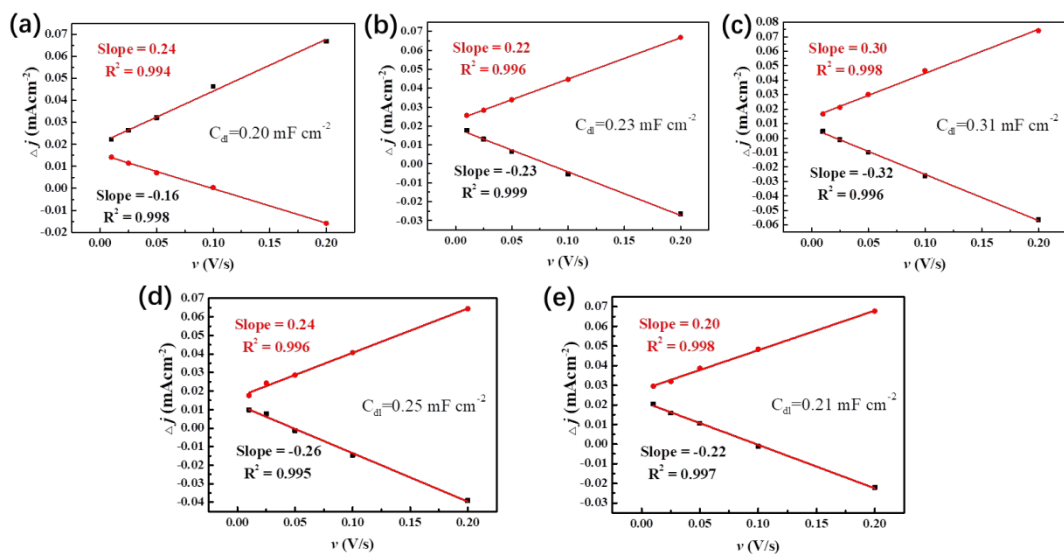
Fig. S6 Charging current density differences ploted against scan rate: (a) Cu_2O, (b) Cu_2S/Cu_2O, (c) Ni/Cu_2O, (d) $Ni-Cu_2S/Cu_2O$ and (e) Cu_2S-Ni/Cu_2O. The linear slope is equivalent to the double-layer capacitance C_{dl}, representing the electrochemical surface area.