

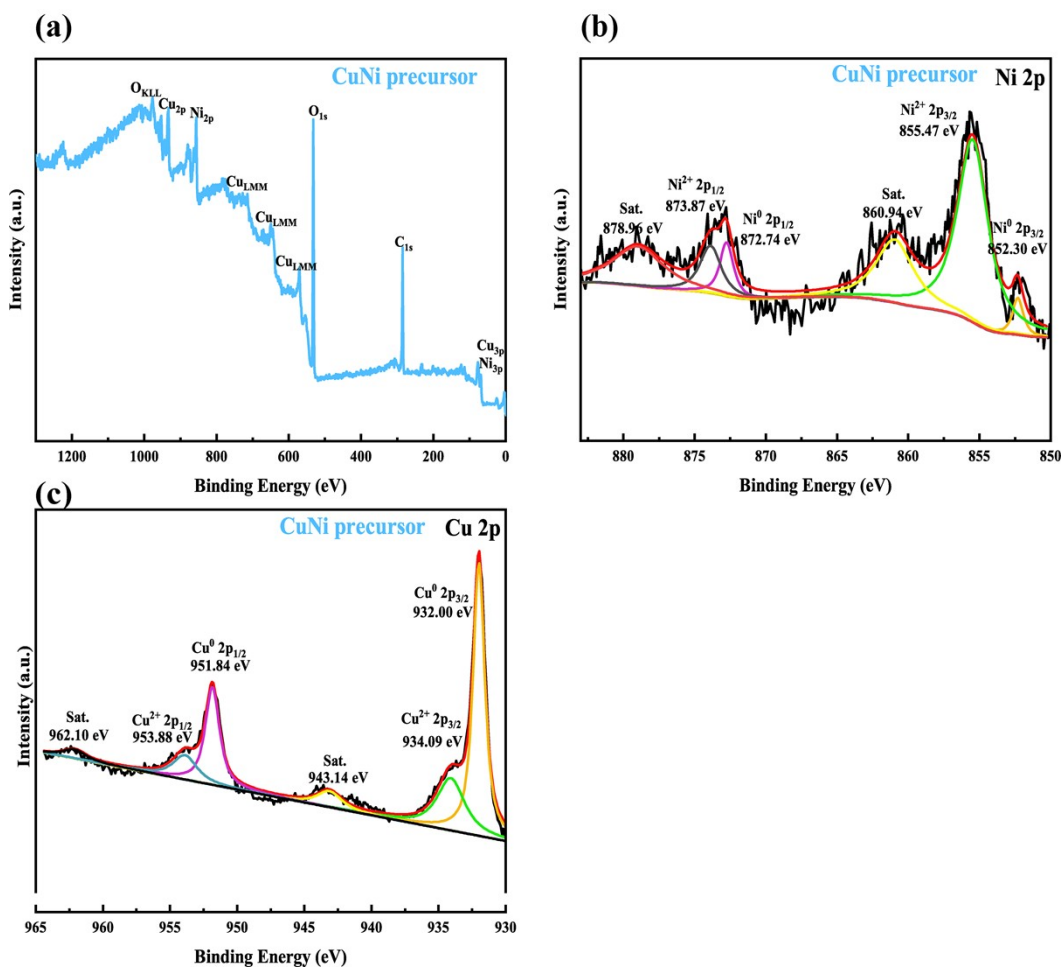
## Support information

### Electrochemical tuning of Cu<sub>3</sub>P/Ni<sub>2</sub>P hybrid towards promoted hydrogen evolution reaction

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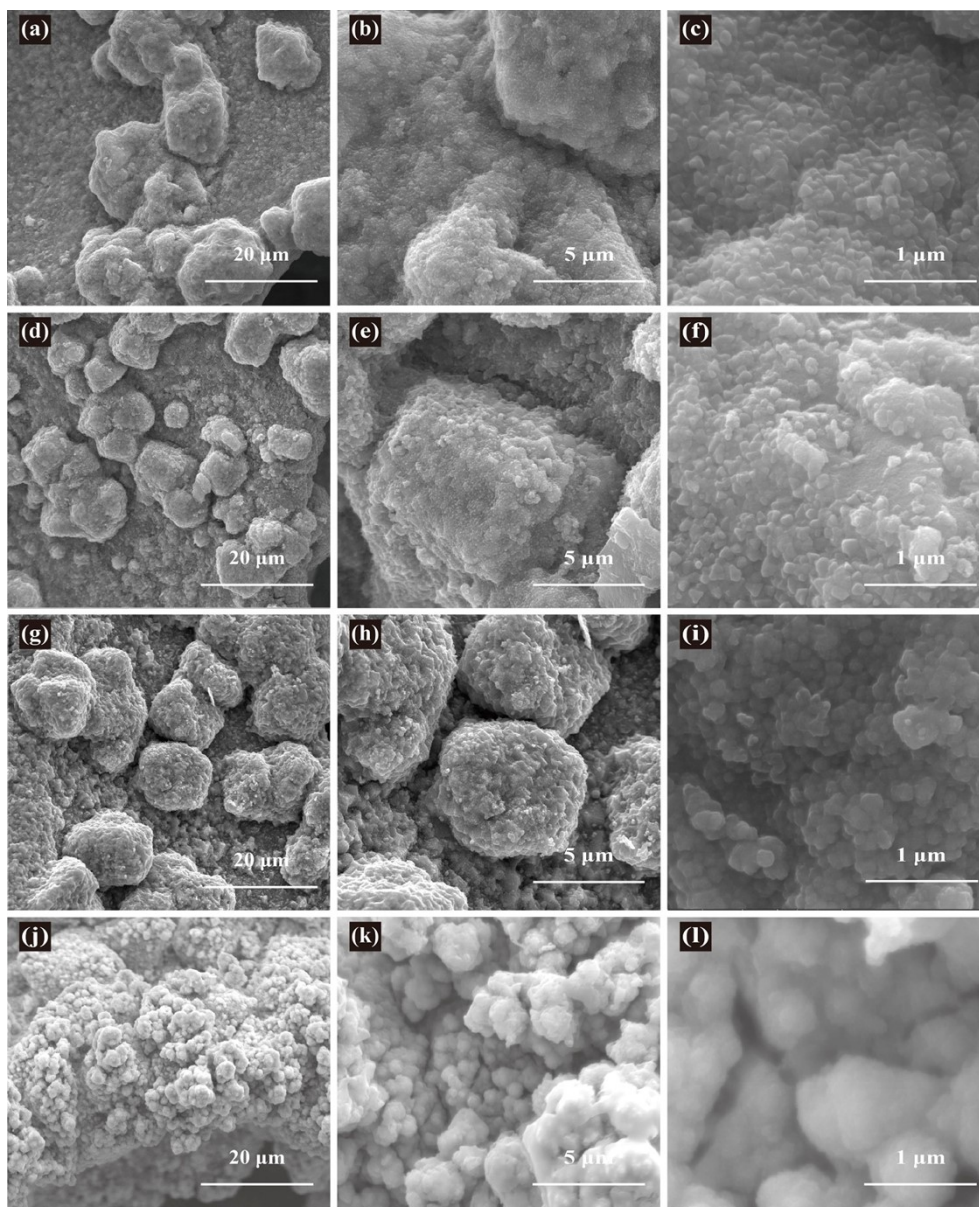
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**Figure S1.** XPS spectra of NiCu precursor: (a) Survey spectrum, (b) Ni 2p, (c) Cu 2p and (d) P 2p.

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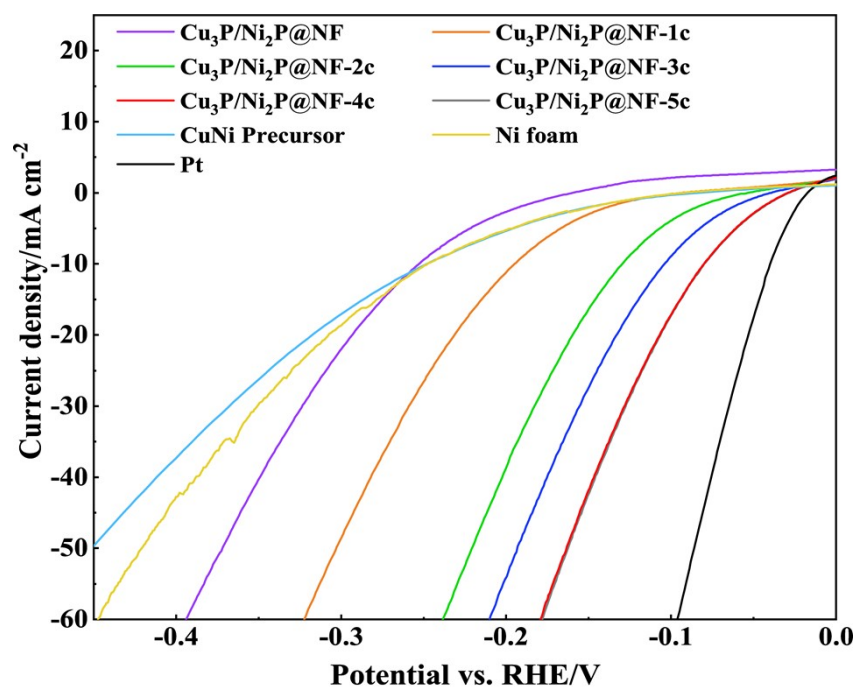
<sup>2</sup>Corresponding author, E-mail, [yinpingoral@163.com](mailto:yinpingoral@163.com) (P. Yin)



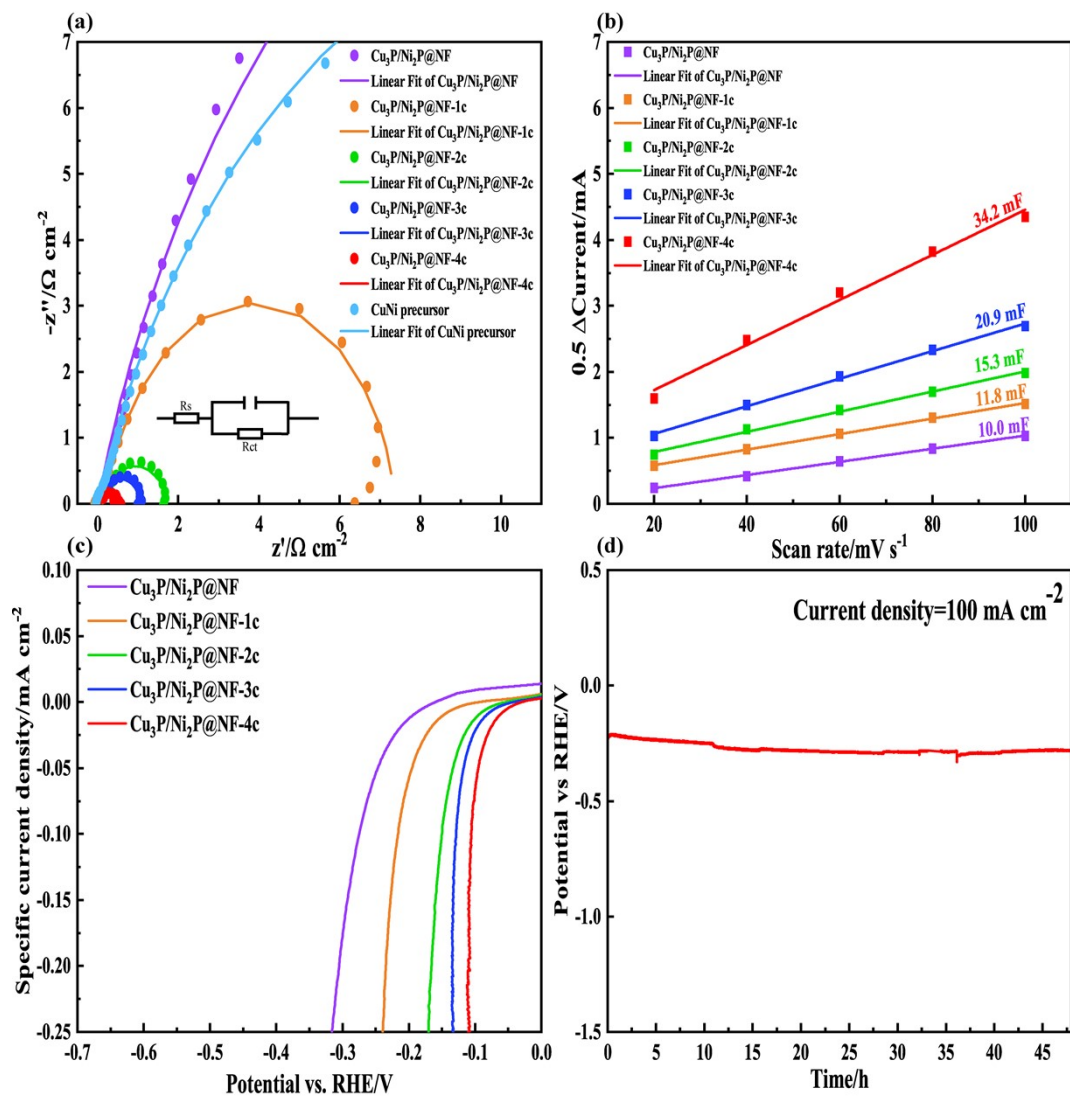
**Figure S2.** SEM images for Cu<sub>3</sub>P/Ni<sub>2</sub>P@NF modified by different CV scans in 0.5 M H<sub>2</sub>SO<sub>4</sub>:

(a-c) Cu<sub>3</sub>P/Ni<sub>2</sub>P@NF-1c, (d-f) Cu<sub>3</sub>P/Ni<sub>2</sub>P@NF-2c, (g-i) Cu<sub>3</sub>P/Ni<sub>2</sub>P@NF-3c and (j-l)

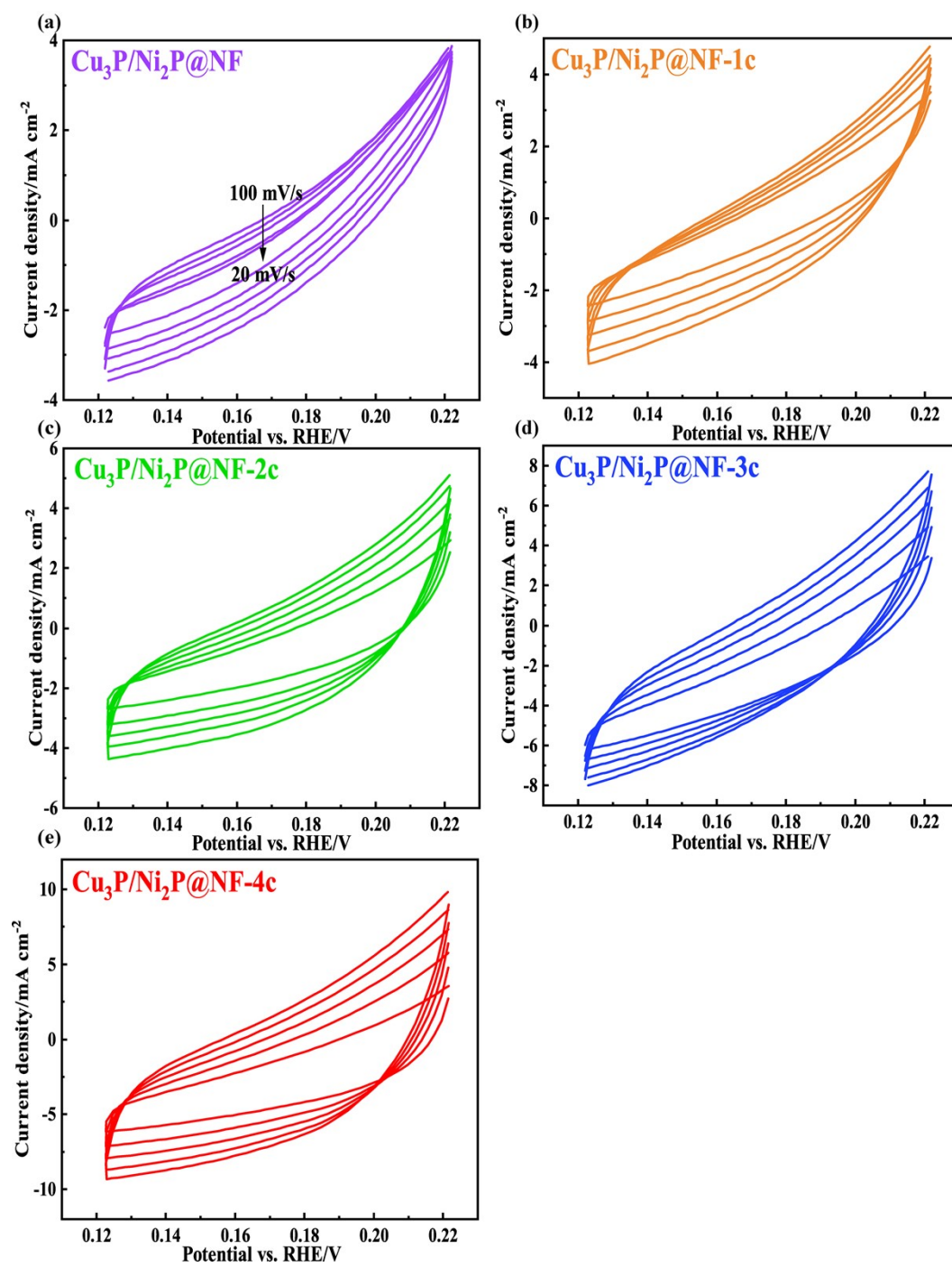
Cu<sub>3</sub>P/Ni<sub>2</sub>P@NF-5c.



**Figure S3.** (a) Polarization curves without  $iR$  correction of NiCu precursor,  $\text{Cu}_3\text{P}/\text{Ni}_2\text{P}@NF$ , electrochemically modified  $\text{Cu}_3\text{P}/\text{Ni}_2\text{P}@NF$ , Pt and Ni foam in 0.5 M  $\text{H}_2\text{SO}_4$  (scan rate:  $5 \text{ mV s}^{-1}$ );



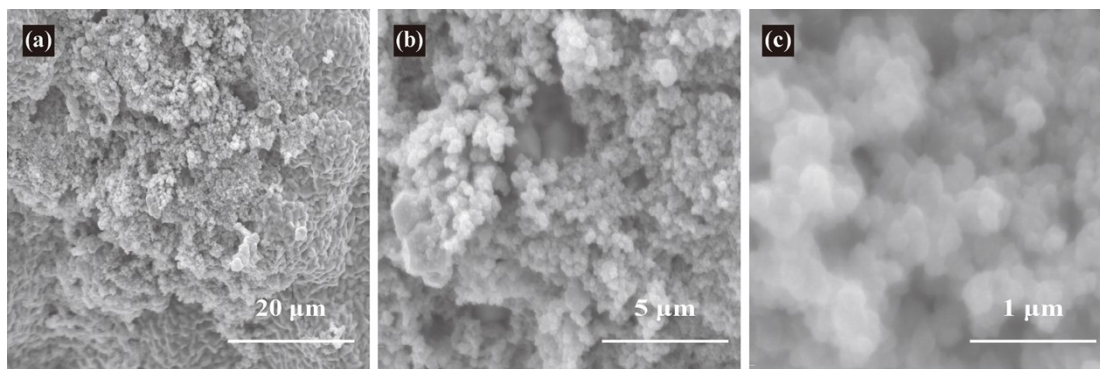
**Figure S4.** (a) Nyquist plots; (b)  $C_{dl}$ ; (c) Polarization curves related to specific current density of  $\text{Cu}_3\text{P}/\text{Ni}_2\text{P}@NF$  and  $\text{Cu}_3\text{P}/\text{Ni}_2\text{P}@NF$  modified by CV scans in  $0.5 \text{ M H}_2\text{SO}_4$ ; (d) chronopotentiometric curve for  $\text{Cu}_3\text{P}/\text{Ni}_2\text{P}@NF-4c$  at  $100 \text{ mA cm}^{-2}$  for 48 h in  $0.5 \text{ M H}_2\text{SO}_4$  without  $iR$  correction.



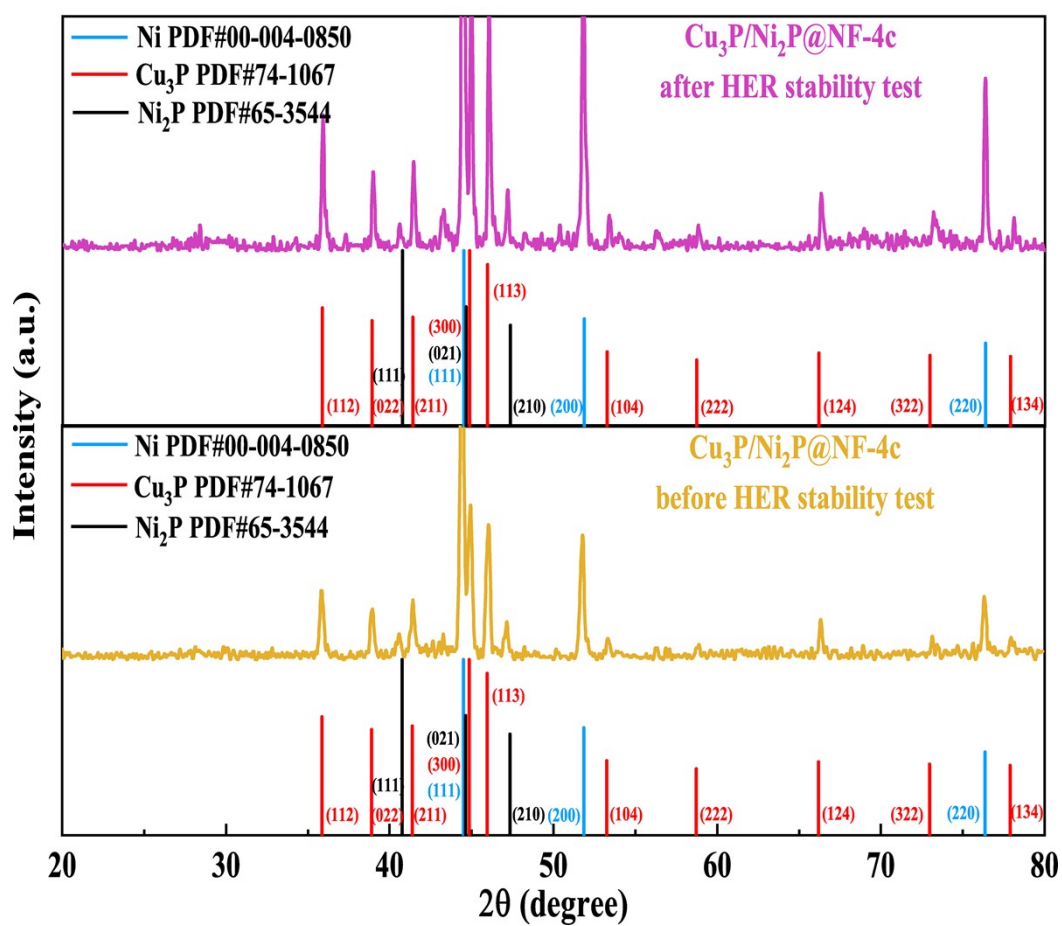
**Figure S5.** CV curves:  $\text{Cu}_3\text{P}/\text{Ni}_2\text{P}@NF$  (a),  $\text{Cu}_3\text{P}/\text{Ni}_2\text{P}@NF-1c$  (b),  $\text{Cu}_3\text{P}/\text{Ni}_2\text{P}@NF-2c$  (c),

$\text{Cu}_3\text{P}/\text{Ni}_2\text{P}@NF-3c$  (d) and  $\text{Cu}_3\text{P}/\text{Ni}_2\text{P}@NF-4c$  (e).





**Figure S6.** SEM images for post-HER  $\text{Cu}_3\text{P}/\text{Ni}_2\text{P}@/\text{NF-4c}$  with different magnifications.



**Figure S7.** XRD patterns for  $\text{Cu}_3\text{P}/\text{Ni}_2\text{P}@/\text{NF-4c}$  and post-HER  $\text{Cu}_3\text{P}/\text{Ni}_2\text{P}@/\text{NF-4c}$ .

**Table S1.** Comparison of the HER performance of  $\text{Cu}_3\text{P}/\text{Ni}_2\text{P}@/\text{NF}$  and electrochemically

modified Cu<sub>3</sub>P/Ni<sub>2</sub>P@NF in 0.5 M H<sub>2</sub>SO<sub>4</sub>.

Materials	Media	$\eta_{10}$ (mV)	Tafel slopes (mV·dec <sup>-1</sup> )	Exchange current density (mA·cm <sup>-2</sup> )	$R_{ct}$ ( $\Omega$ )	$C_{dl}$ (mF)	ECSA (cm <sup>2</sup> )	$RF$
Cu <sub>3</sub> P/Ni <sub>2</sub> P@NF	0.5 M H <sub>2</sub> SO <sub>4</sub>	240	86.7	0.02	33.54	10.0	250	250
Cu <sub>3</sub> P/Ni <sub>2</sub> P@NF-1c	0.5 M H <sub>2</sub> SO <sub>4</sub>	182	74.9	0.04	7.54	11.8	295	295
Cu <sub>3</sub> P/Ni <sub>2</sub> P@NF-2c	0.5 M H <sub>2</sub> SO <sub>4</sub>	117	54.8	0.07	1.76	15.3	383	383
Cu <sub>3</sub> P/Ni <sub>2</sub> P@NF-3c	0.5 M H <sub>2</sub> SO <sub>4</sub>	91	50.9	0.16	1.10	20.9	523	523
Cu <sub>3</sub> P/Ni <sub>2</sub> P@NF-4c	0.5 M H <sub>2</sub> SO <sub>4</sub>	67	43.9	0.28	0.49	34.2	855	855

**Table S2.** Comparison of the HER performance of Cu<sub>3</sub>P/Ni<sub>2</sub>P@NF-4c and other HER electrocatalysts.

Materials	Media	$\eta_{10}$ / mV	Tafel slopes (mV·dec <sup>-1</sup> )	Reference
Ni <sub>2</sub> P-WO <sub>3</sub>	0.5 M H <sub>2</sub> SO <sub>4</sub>	107	55.9	1
Cu <sub>3</sub> P@NPC-CF	0.5 M H <sub>2</sub> SO <sub>4</sub>	81.94	81.25	2
Cu <sub>2</sub> S-Cu <sub>3</sub> P@C	0.5 M H <sub>2</sub> SO <sub>4</sub>	85	34	3
Ni <sub>2</sub> P/Ni <sub>3</sub> P <sub>4</sub> @3DNG	0.5 M H <sub>2</sub> SO <sub>4</sub>	139	59	4
Ni <sub>12</sub> P <sub>5</sub> -Ni <sub>2</sub> P	0.5 M H <sub>2</sub> SO <sub>4</sub>	166	60	5
Ni <sub>2</sub> P/NF	0.5 M H <sub>2</sub> SO <sub>4</sub>	78	33	6
N-C@CoP/Ni <sub>2</sub> P	0.5 M H <sub>2</sub> SO <sub>4</sub>	153	53.01	7
Co <sub>2</sub> P/Ni <sub>2</sub> P/CNT-3	0.5 M H <sub>2</sub> SO <sub>4</sub>	151	41.64	8
Ni <sub>2</sub> P/CC	0.5 M H <sub>2</sub> SO <sub>4</sub>	119	50	9
Ni <sub>2</sub> P/NF-PECVD	0.5 M H <sub>2</sub> SO <sub>4</sub>	97	79	10
Ni <sub>2</sub> P/CoP@ NPC	0.5 M H <sub>2</sub> SO <sub>4</sub>	160	57	11

Cu <sub>x</sub> Ni <sub>1-x</sub> P@PC	0.5 M H <sub>2</sub> SO <sub>4</sub>	102	85.8	<sup>12</sup>
Cu <sub>3</sub> P/Ni <sub>2</sub> P@NF 4000c	0.5 M H <sub>2</sub> SO <sub>4</sub>	67	43.9	This work

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