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Supporting information

Cu_3P/PAN derived N-Doped Carbon Catalyst with Non-toxic Synthesis for Alkaline Hydrogen Evolution Reaction

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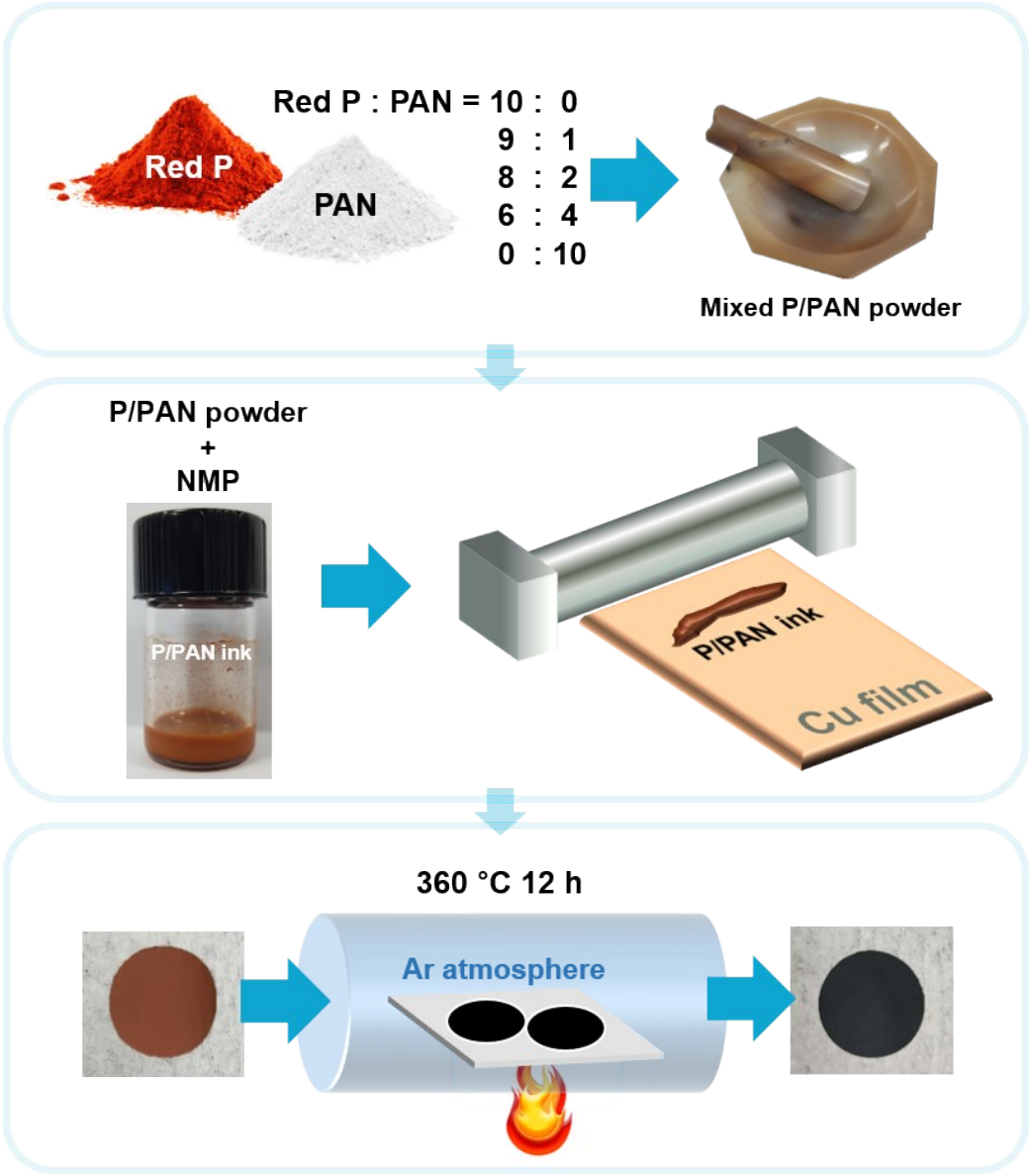

Figure S1. Schematic to the synthesis method of Cu_3P, Cu_3P/N-C and N-C.

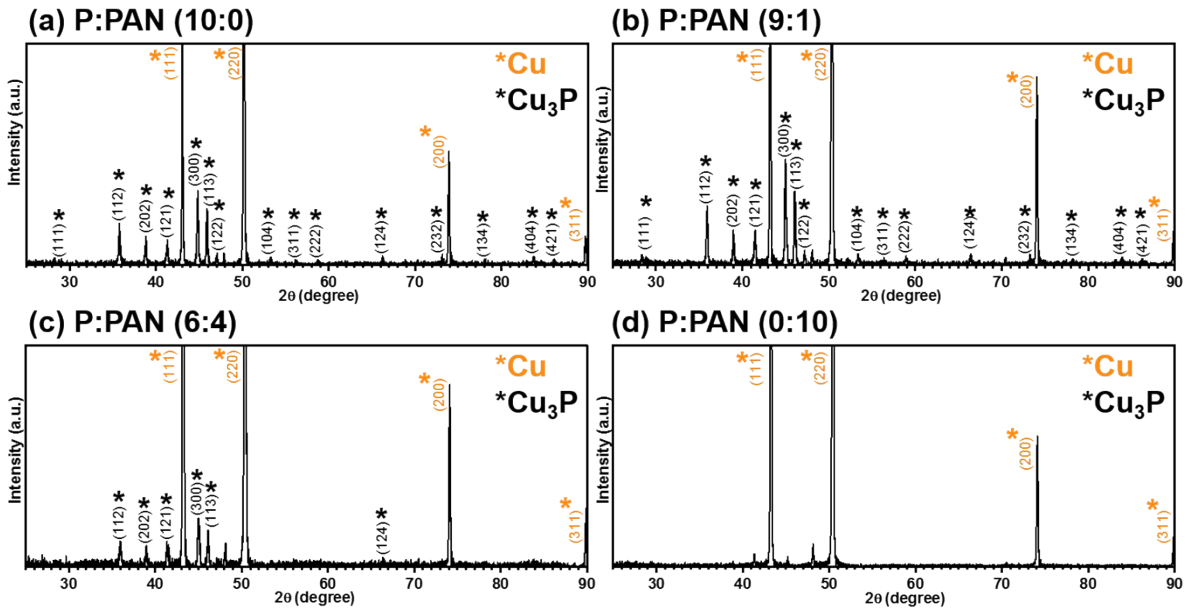

Figure S2. XRD patterns of (a) P:PAN (10:0), (b) P:PAN (9:1), (c) P:PAN (6:4) and (d) P:PAN (0:10). (Small peaks of 41, 45, and 48 observed in all specimens correspond to the Cuk_{β} peaks induced in the Cu source of XRD.)

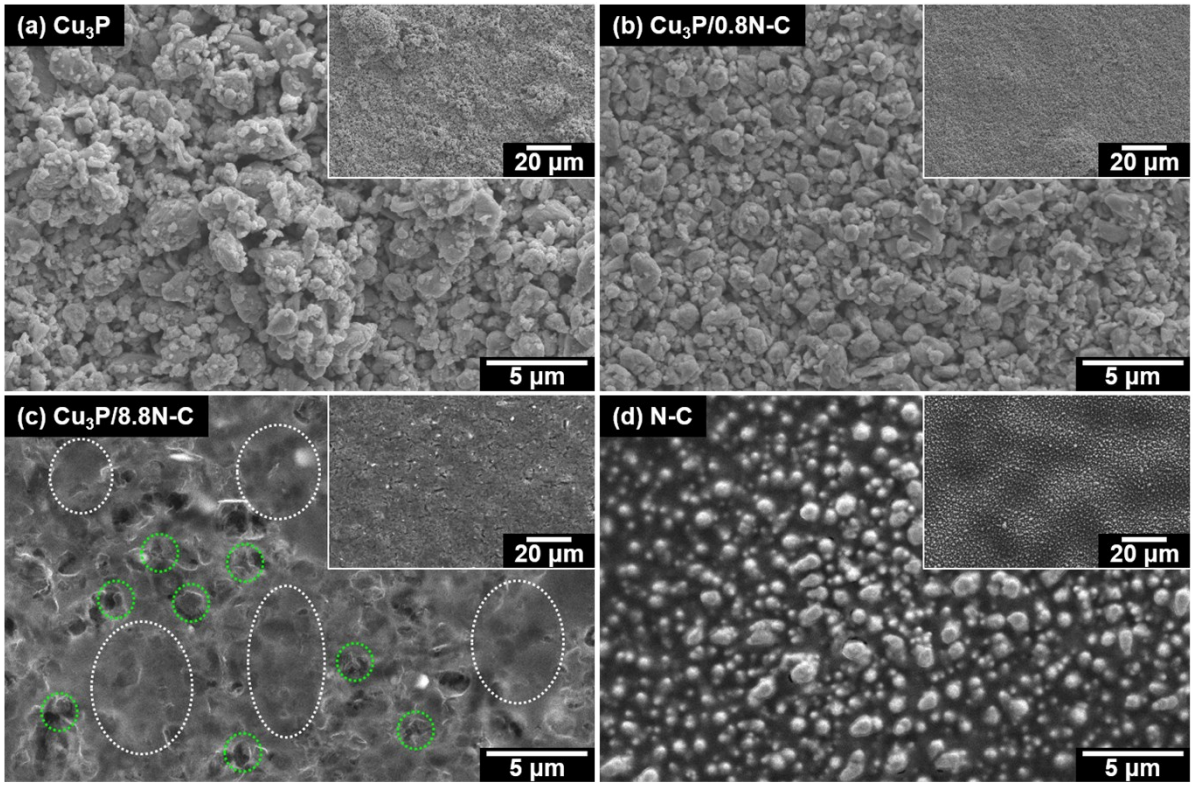

Figure S3. SEM images of (a) Cu_3P, (b) Cu_3P/0.8N-C, (c) Cu_3P/8.8N-C (white circle : N-doped carbon, green circle : Cu_3P) and (d) N-C.

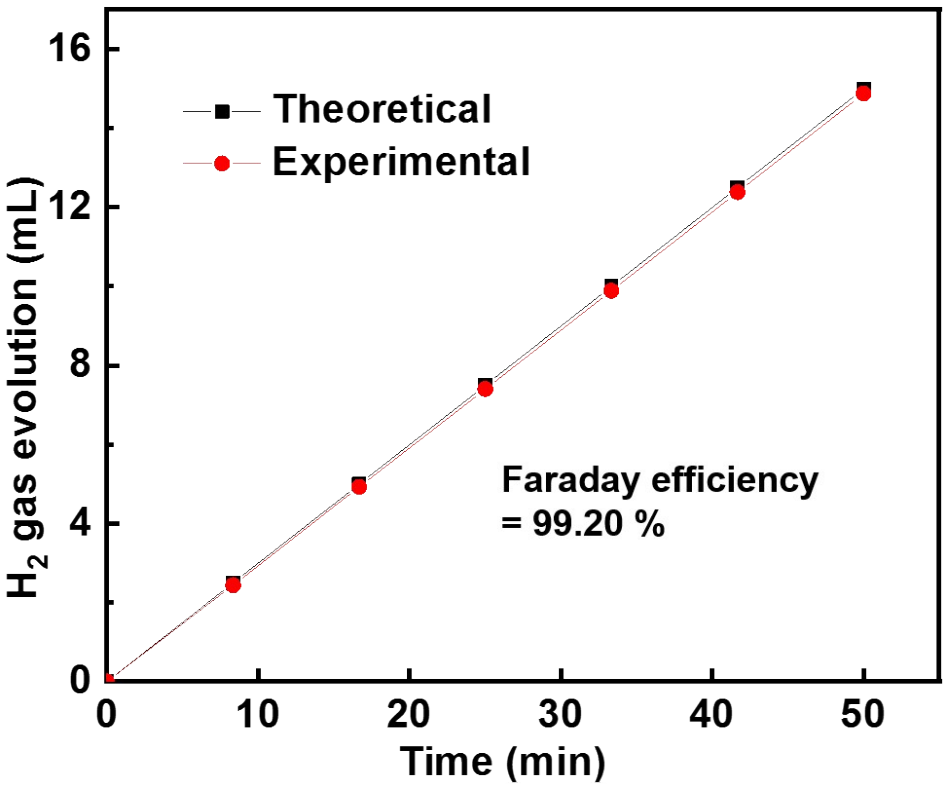

Figure S4. The theoretically-calculated and experimentally-measured amounts of H_2 gas. (applied current: 50 mA/cm^2, temperature: 26.5 ^{o}C, electrode rea: 0.785 cm^2)

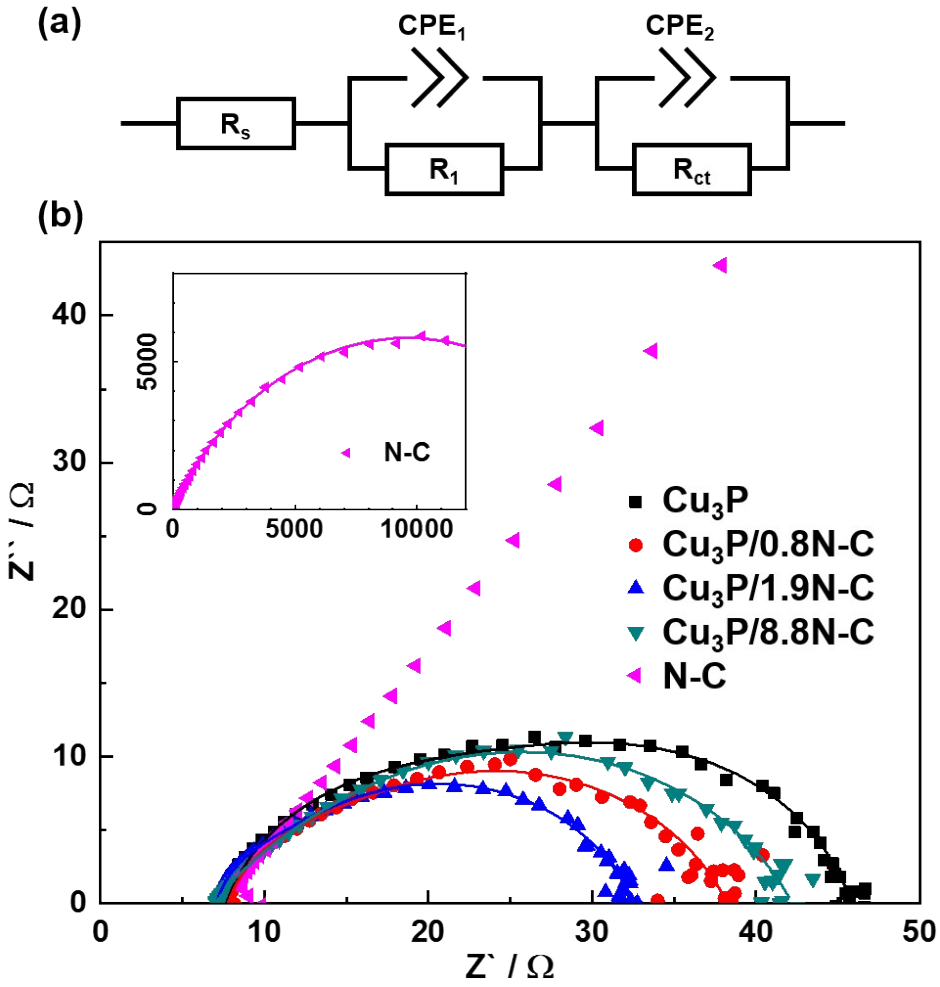

Figure S5. (a) Equivalent circuit models (two-time constant serial model, 2TS) and (b) Nyquist plots for Cu_3P, Cu_3P/0.8N-C, Cu_3P/1.9N-C, Cu_3P/8.8N-C and N-C measured at a potential of -0.29 V_{RHE} in the frequency range from sweep 10^{-2} to 10^5 Hz in 1 M KOH solution. (solid lines: theoretical fitted curves based on the 2TS model, symbols: experimental data)

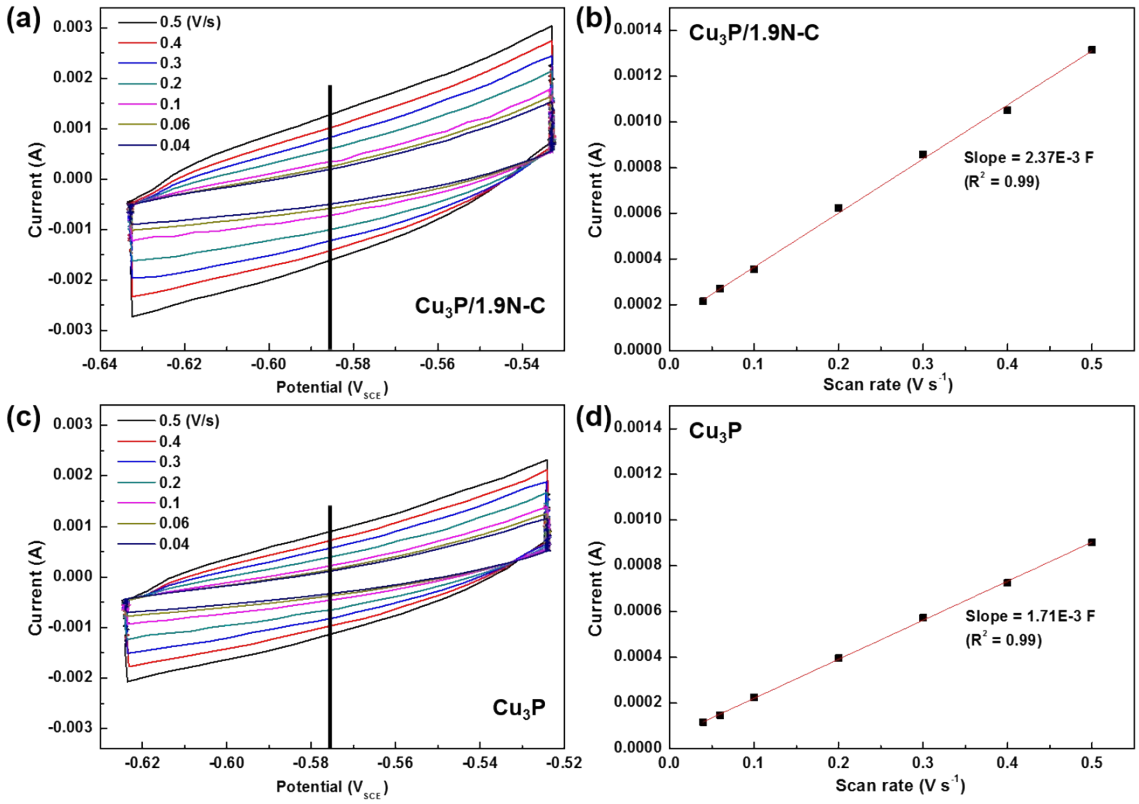

Figure S6. Cyclic voltammograms measured at scan rates from 0.04 to 0.5 V/s (a, c) and corresponding j vs. scan rates plots (b, d) for Cu_3P/1.9N-C (a, b) and Cu_3P (c, d).

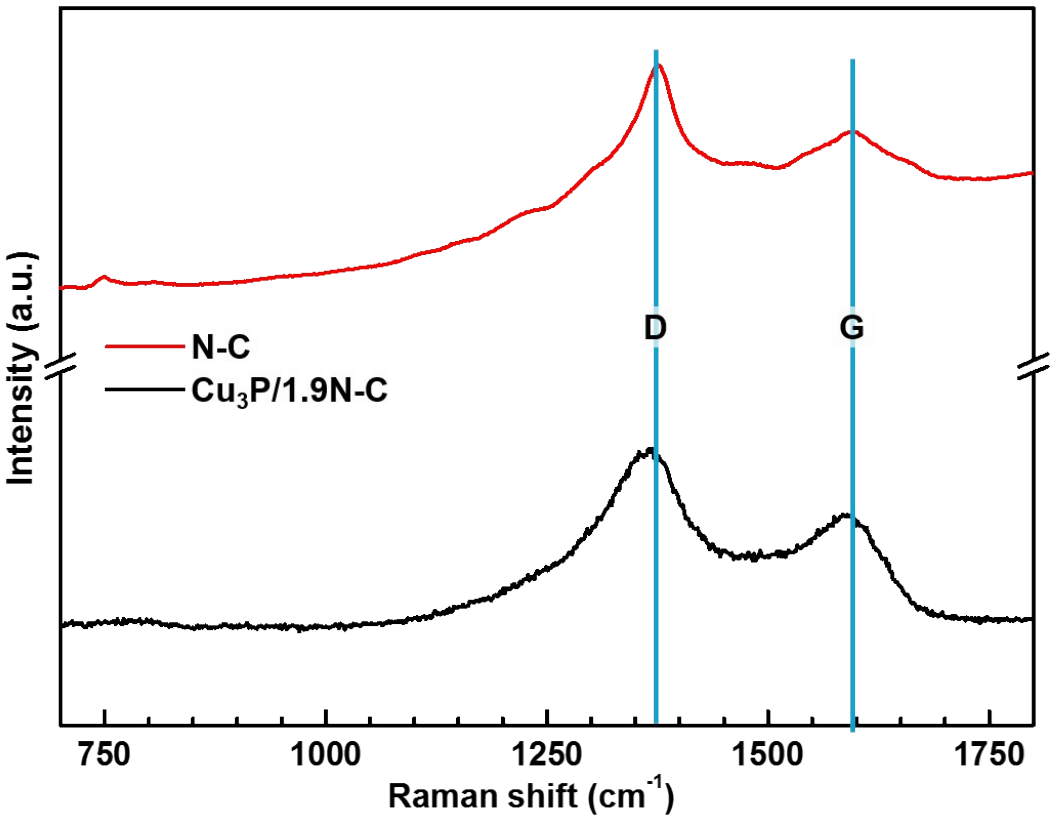

Figure S7. Raman spectra of the Cu_3P/1.9N-C and N-C.

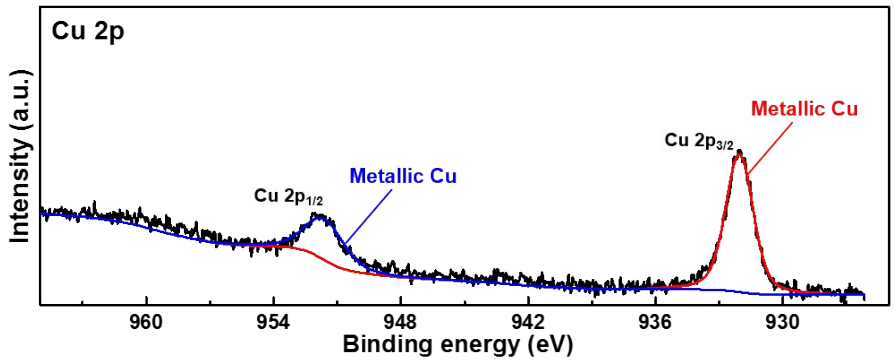

Figure S8. XPS spectra of Cu 2p for Cu substrate (Cu film).

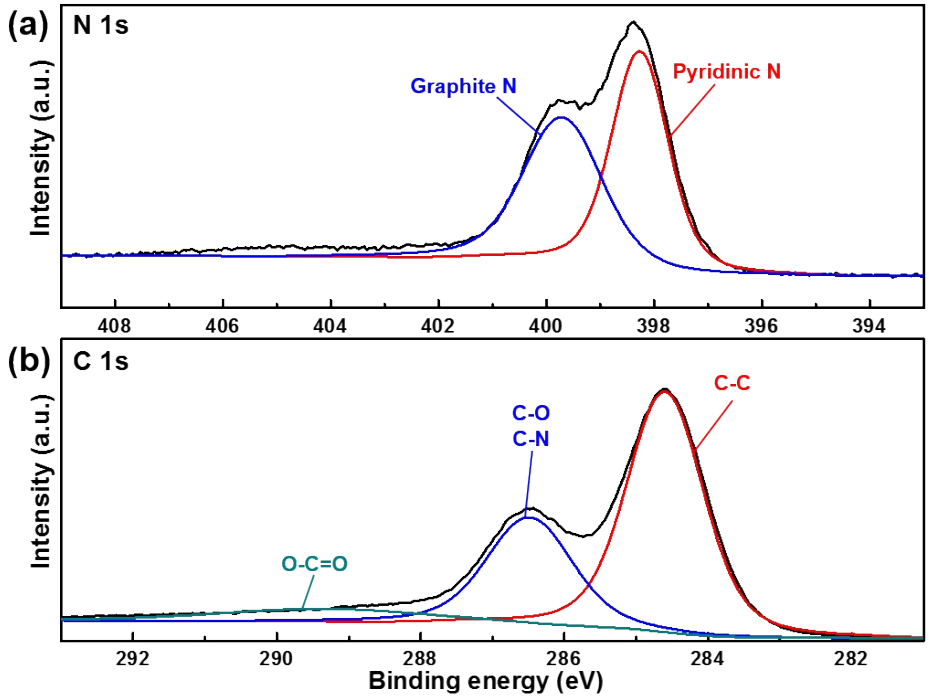

Figure S9. XPS spectra of N 1s and C 1s for N-C.

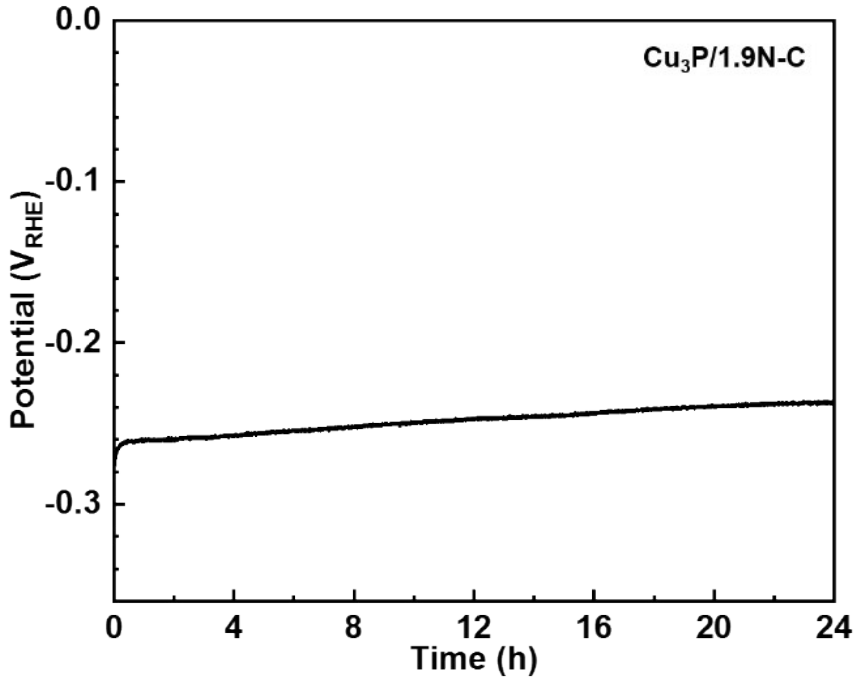

Figure S10. Potential-time response (V-t) result of the Cu_3P/1.9N-C in a 1 M KOH solution at a HER current density of -10 mA/cm^2.

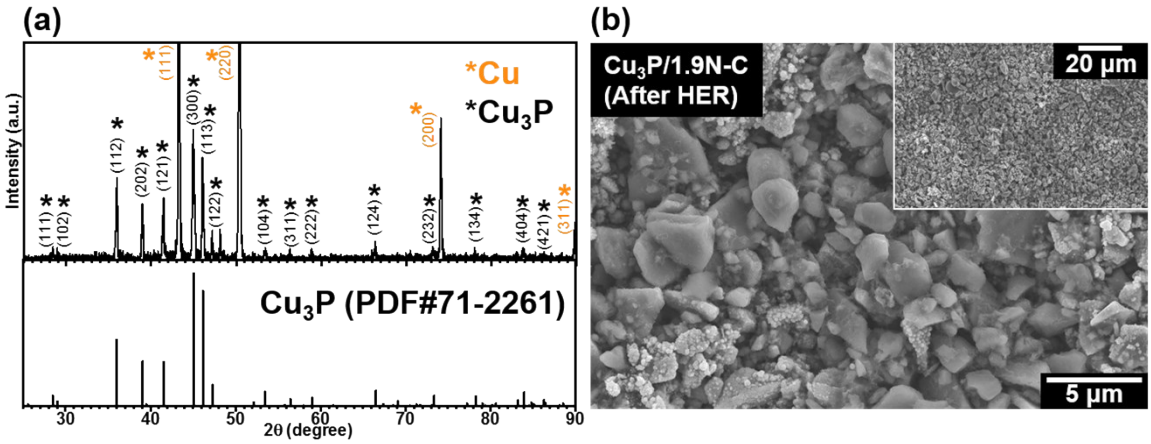

Figure S11. (a) XRD pattern and (b) SEM image of the Cu_3P/1.9N-C after the HER stability test.

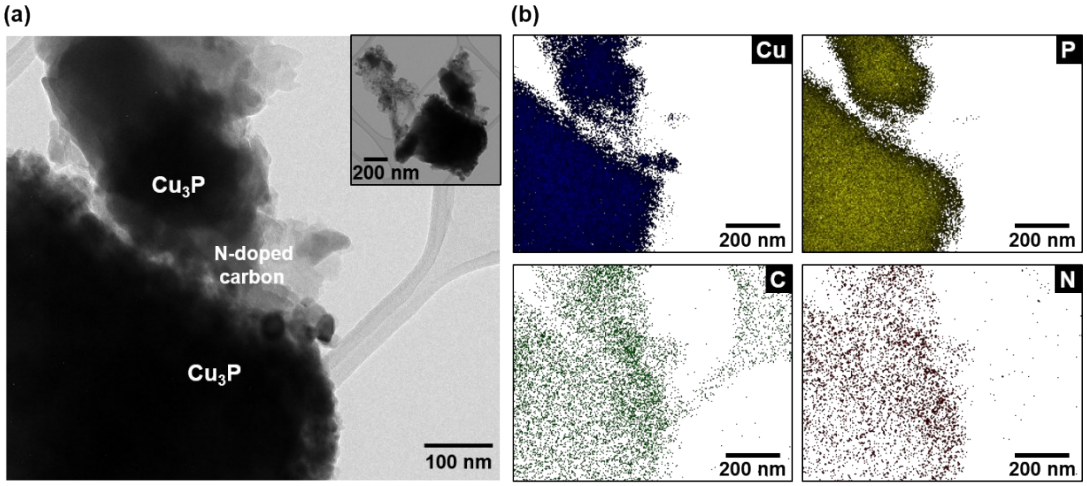

Figure S12. (a) TEM and (b) TEM-EDS mapping images of Cu_3P/1.9N-C after the HER stability test.

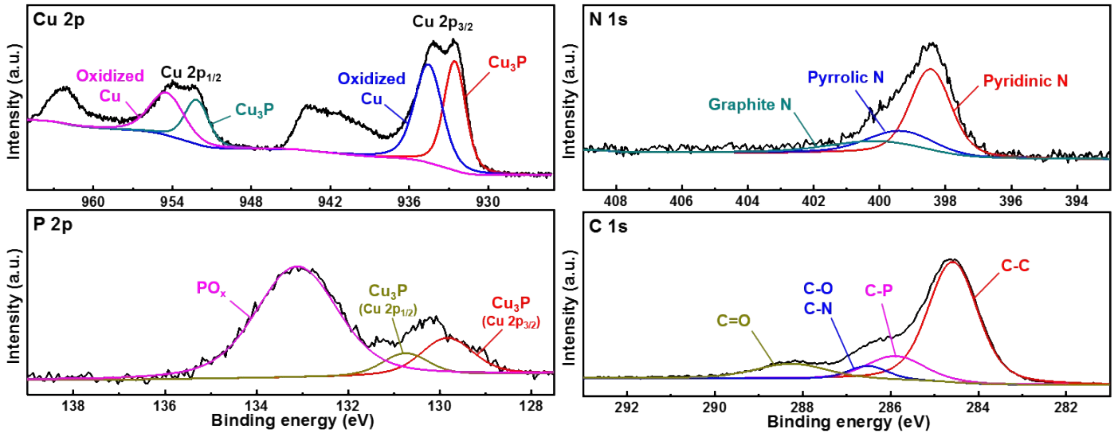

Figure S13. XPS spectra of Cu_3P/1.9N-C after the HER stability test.

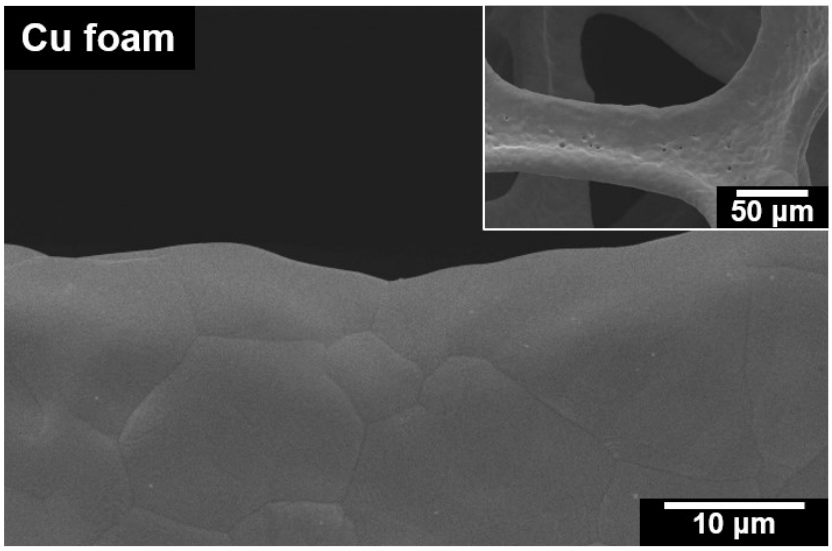

Figure S14. SEM images of the Cu foam.

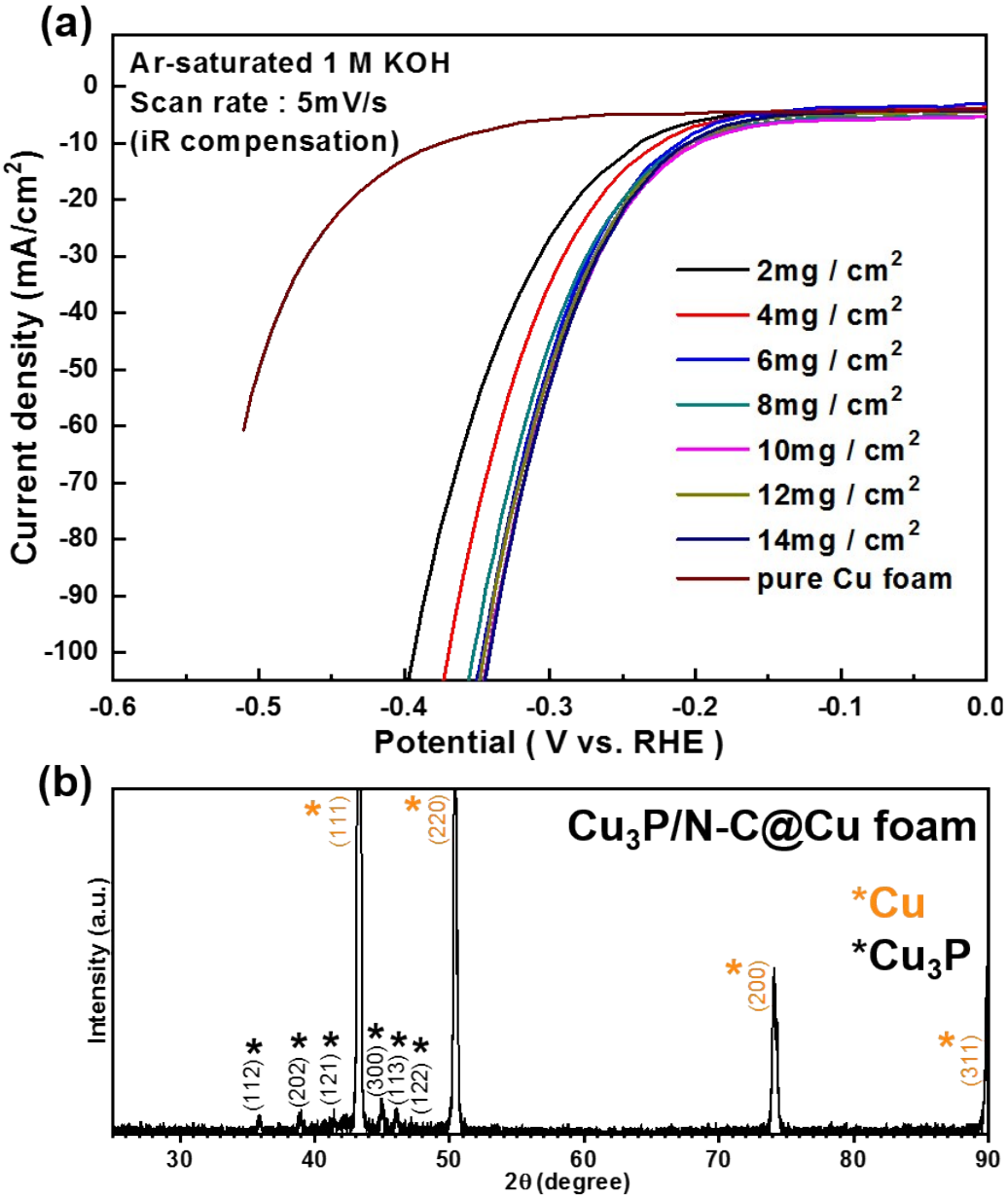

Figure S15. (a) HER polarization curves in 1 M KOH solution for Cu_3P/N-C@Cu foam with different P/PAN loading amount in 1 M KOH solution. (b) XRD pattern for Cu_3P/N-C@Cu foam.

Table S1. Precursor composition for synthesis of Cu_3P, Cu_3P/N-C and N-C.

Sample (P:PAN)	P (mg)	PAN (mg)	NMP (uL)	Doctor blade height (Thickness of coated P/PAN ink) (μm)	*Weight of coated P/PAN (Δw, mg/cm^2)	**Calculated Cu_3P weight (mg/cm^2)
P:PAN (10:0)	100	0	105	18.75	0.2863	**2.0456**
P:PAN (9:1)	90	10	186	25.00	0.3240	**2.0833**
P:PAN (8:2)	80	20	210	37.50	0.3616	**2.0671**
P:PAN (6:4)	60	40	350	50.00	0.4746	**2.0348**
P:PAN (0:10)	0	100	450	62.50	0.3466	-

* Weight of coated P and PAN (Δw) :

(Measured weight of P/PAN coated Cu film) - (Measured weight of Cu film)

**Cu_3P weight :

(Ratio of P) × (Δw) × (221.5/31)

Ex) P : PAN = 8 : 2 → Ratio of P = 0.8,

Molar mass → Cu_3P = 221.5, P = 31.0

Table S2. Material composition of Cu_3P, Cu_3P/N-C and N-C obtained by XPS analysis.

Sample (P:PAN)	Cu (at%)	P (at%)	C (at%)	N (at%)	**Cu_3P : C (molar ratio)	Notation
P:PAN (10:0)	72.4	27.6	-	-	-	**Cu_3P**
P:PAN (9:1)	61.2	21.0	*16.2	*1.6	1 : 0.8	**Cu_3P/0.8N-C**
P:PAN (8:2)	48.8	14.6	31.6	5.0	1 : 1.9	**Cu_3P/1.9N-C**
P:PAN (6:4)	19.7	12.5	58.1	9.7	1 : 8.8	**Cu_3P/8.8N-C**
P:PAN (0:10)	-	-	86.7	13.3	-	**N-C**

*In the case of P:PAN (9:1), the C-to-N ratio is slightly different, most likely due to the XPS fitting margin caused by the low composition of nitrogen.

**Cu_3P : C = (Cu/3, at%) : (C, at%)

Table S3. Resistance values obtained from the Nyquist plots fitted based on the 2TS circuit model.

Sample	$R_s(\Omega)$	$R_{ct}(\Omega)$	$R_1(\Omega)$
Cu_3P	7.566	28.791	9.312
Cu_3P/0.8N-C	7.777	26.560	3.918
Cu_3P/1.9N-C	7.061	22.911	2.574
Cu_3P/8.8N-C	7.019	30.930	4.269
N-C	11.062	10.267k	8.419k

***R_s**: Uncompensated solution resistance

Table S4. Comparison of catalytic activities (Cu_3P).

*Graph-derived value

Materials	Overpotential of HER in 1 M KOH			Journal	Substrate
	10 mA/cm^2	50 mA/cm^2	100 mA/cm^2		
Cu_3P/N-C	**211.1 mV**	**301.8 mV**	**346.4 mV**	**This work**	**Cu foam**
Cu_3P nanowires	266 mV	*344 mV	382 mV	*ACS Sustainable Chem. Eng.* 2018, 6, 380	Cu mesh
Cu_3P nanoarrays	222 mV (0.1 M KOH)	*364 mV (0.1 M KOH)		*ACS Appl. Mater. Interfaces.* 2016, 8, 23037	Cu foam
Cu_3P nanobush	252 mV	*390 mV		*ACS Omega* 2016, 1, 1367	Cu mesh
NiCuP foam		146 mV	*179 mV	*Nanoscale* 2017, 9, 4401	Stainless steel
Cu_3N-Cu_3P N,P,S doped carbon	68 mV	*130 mV		*ChemElectroChem* 2020, 7, 289	Ni foam
Cu_3P-Co_2P	*95 mV	*175 mV		*Nanoscale* 2019, 11, 6394	Ni foam
Cu_3P microsheets	130 mV	*200 mV	*255 mV	*Adv. Mater. Interfaces* 2016, 3, 1600236	Ni foam
CeO_2-Cu_3P		*227 mV	*273 mV	*Nanoscale* 2018, 10, 2213	Ni foam
Cu_3P nanosheets	105 mV	*235 mV		*ACS Appl. Mater. Interfaces* 2017, 9, 2240	Ni foam