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Electronic Supplementary Information

In-situ formed Copper Nanoparticles via Strong Electronic Interaction with Organic Skeleton for pH-Universal Electrocatalytic CO_2 Reduction

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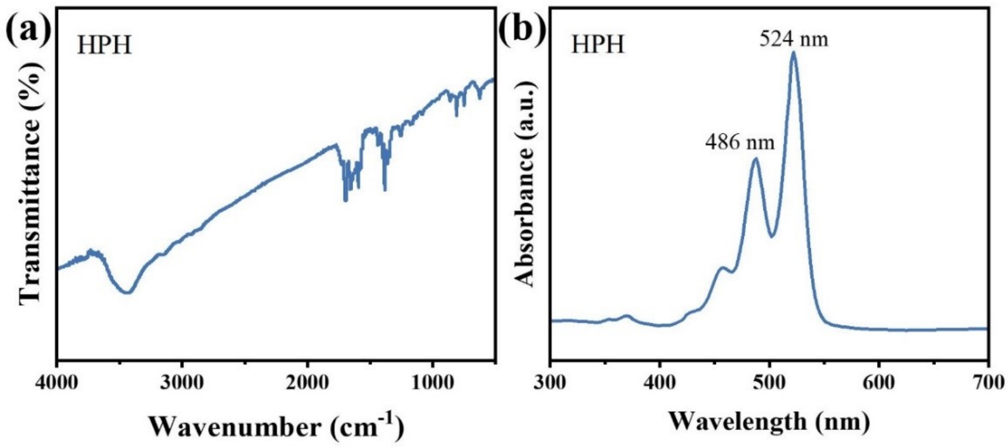
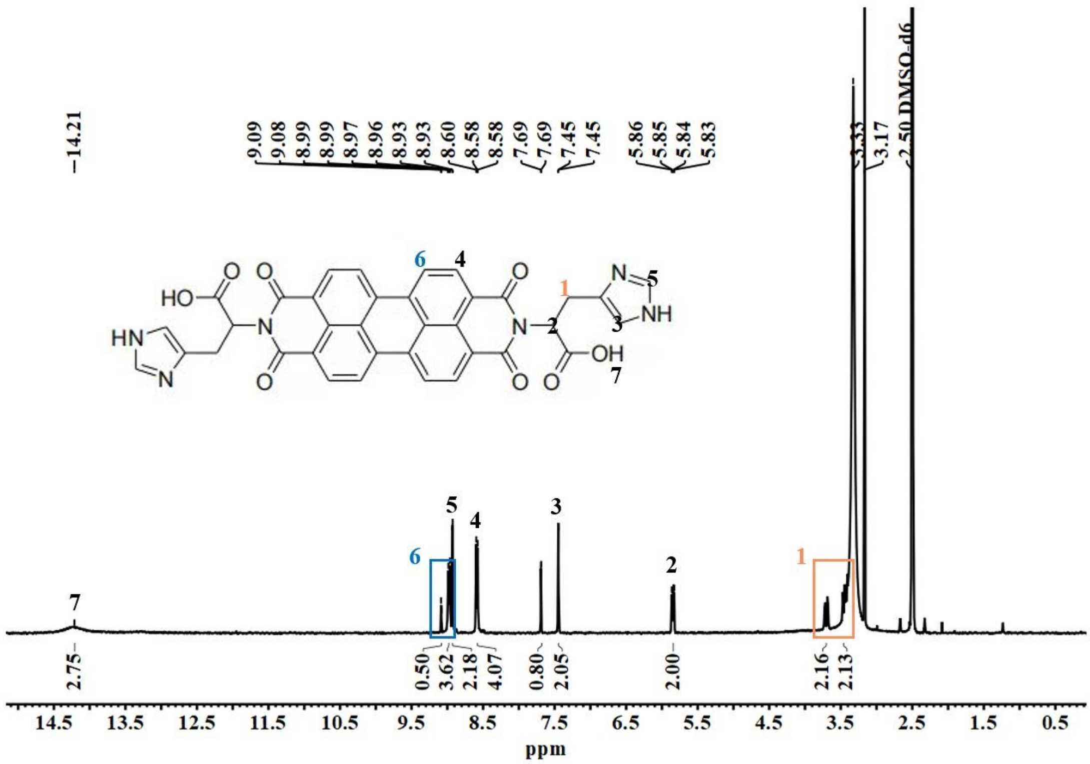
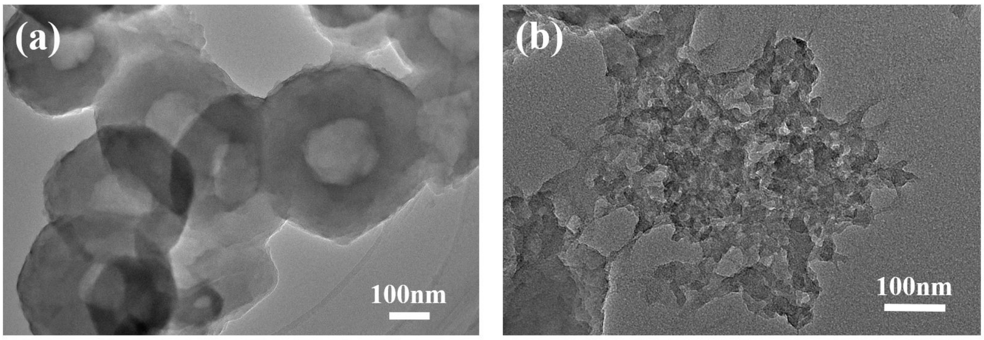


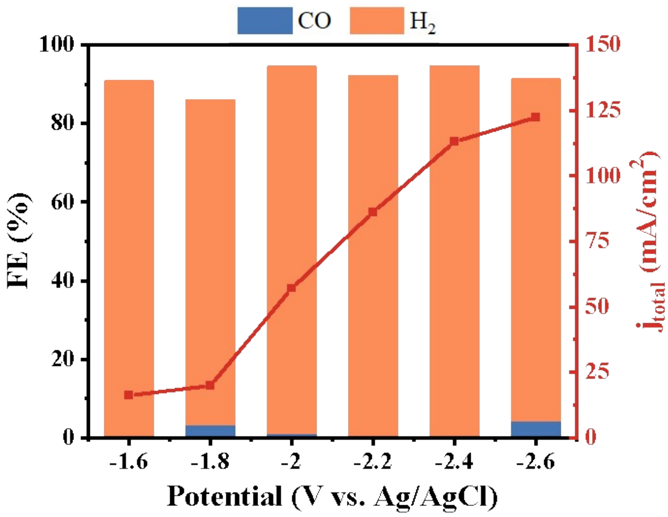
Supplementary Figure S1. (a) FTIR spectrum and (b) UV-vis absorption spectrum of HPH.



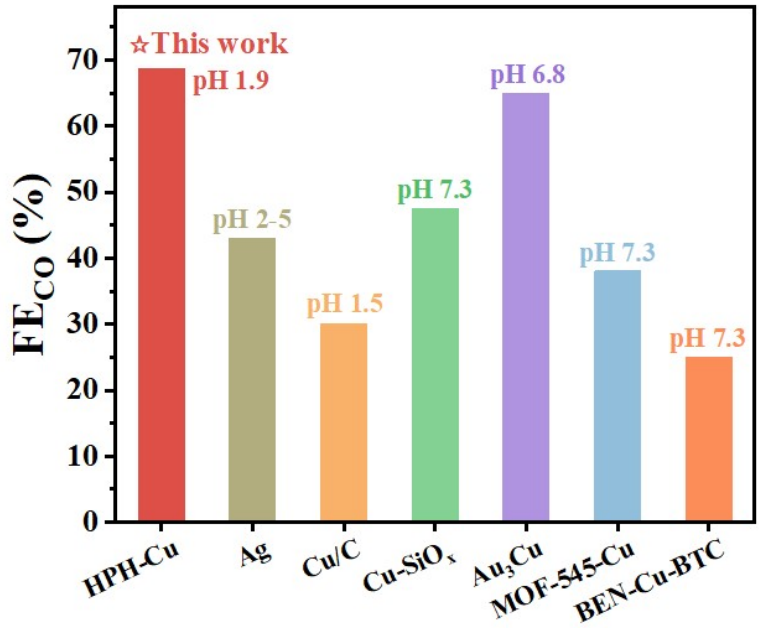
Supplementary Figure S2. ^{1}H-NMR spectrum of HPH in DMSO-d_6.



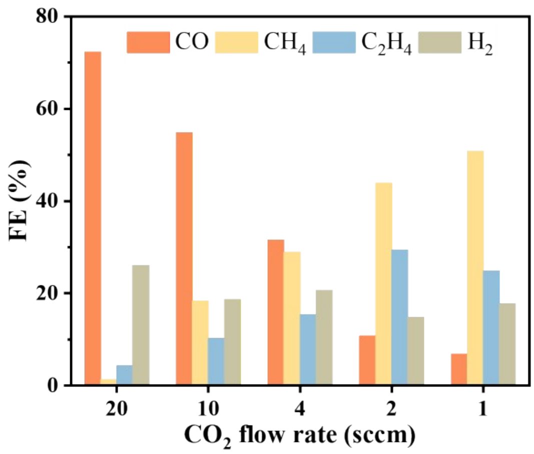
Supplementary Figure S3. TEM images of (a) HPH and (b) HPH-Cu.



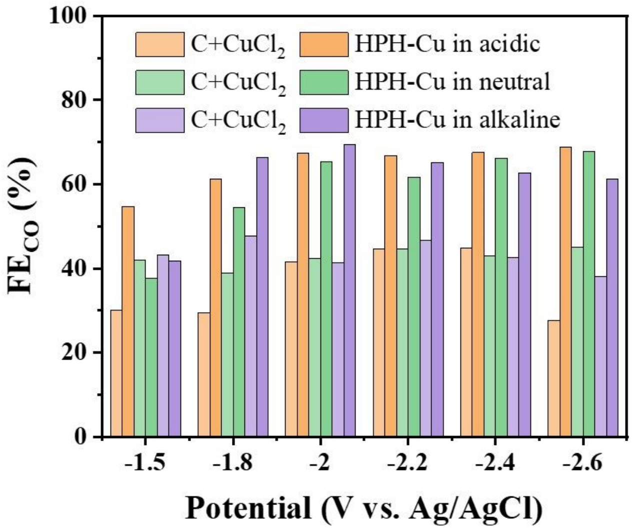
Supplementary Figure S4. FEs and current densities of HPH at different applied potential.



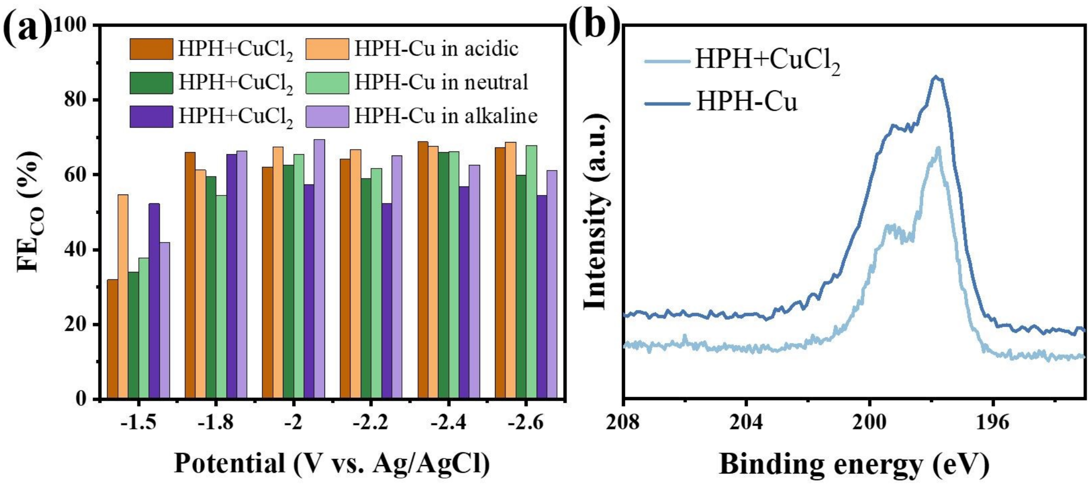
Supplementary Figure S5. Comparison of Faradaic efficiency of CO and pH of electrolyte with HPH-Cu and other reported CO_2RR catalysts.



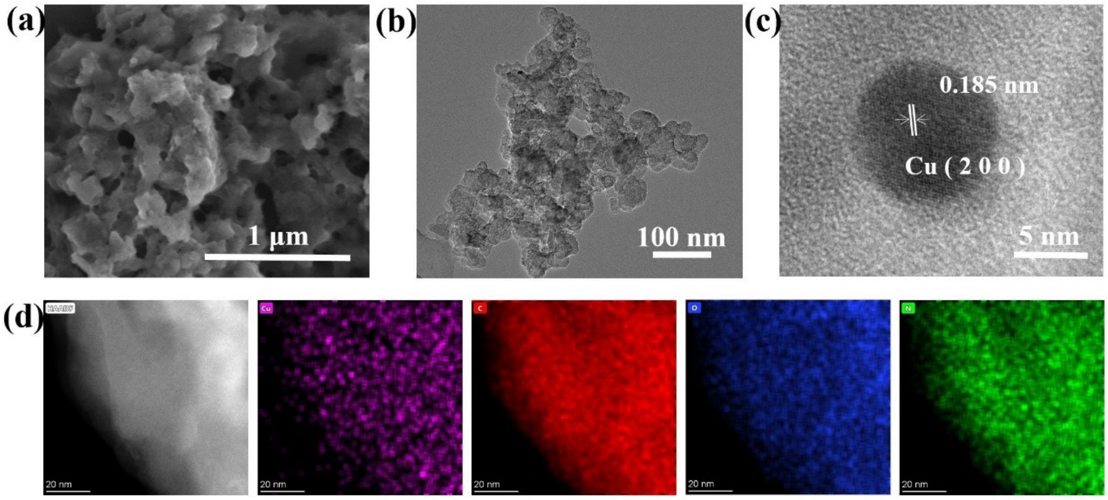
Supplementary Figure S6. FEs of HPH-Cu in acidic electrolytes at different CO_2 flow rates.



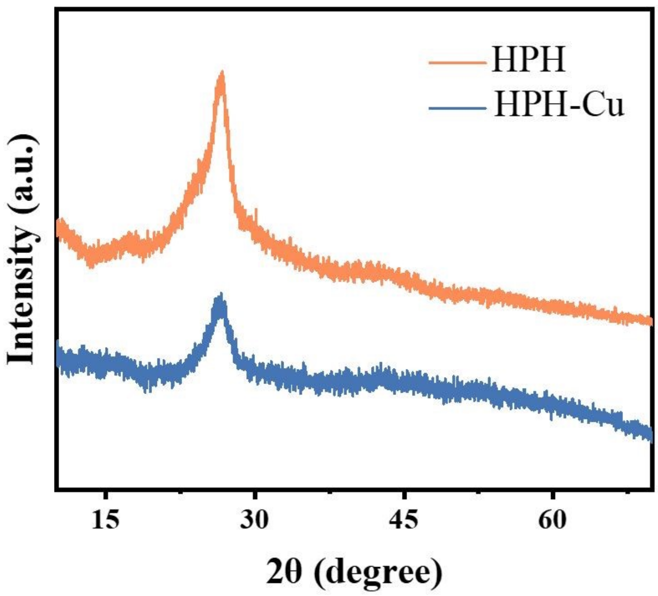
Supplementary Figure S7. FE_{CO} of HPH-Cu and C+$CuCl_2$ in acidic, alkaline and neutral electrolytes.



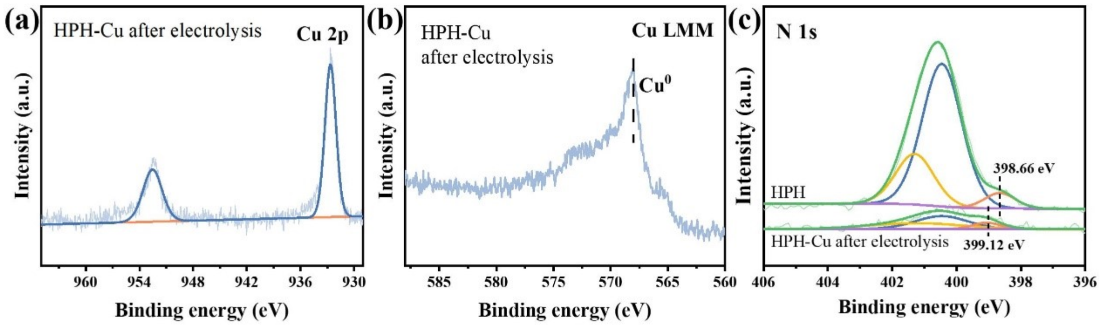
Supplementary Figure S8. (a) FE_{CO} of HPH-Cu and HPH+$CuCl_2$ in acidic, alkaline and neutral electrolytes; (b) Cl 2p XPS spectrum of HPH-Cu and HPH+$CuCl_2$.



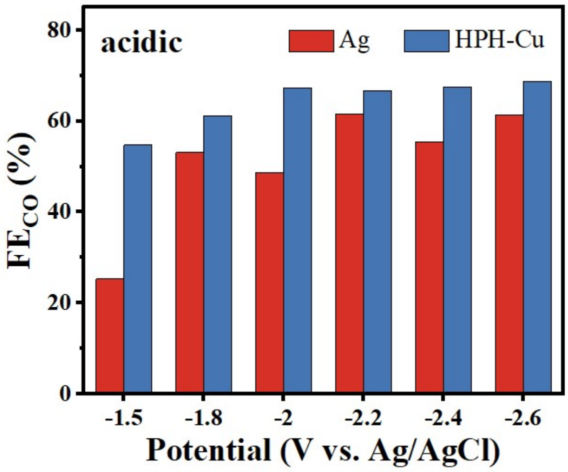
Supplementary Figure S9. (a) SEM image, (b) TEM image, (c) High-resolution TEM image and (d) Elemental mapping images of HPH-Cu after electrolysis.



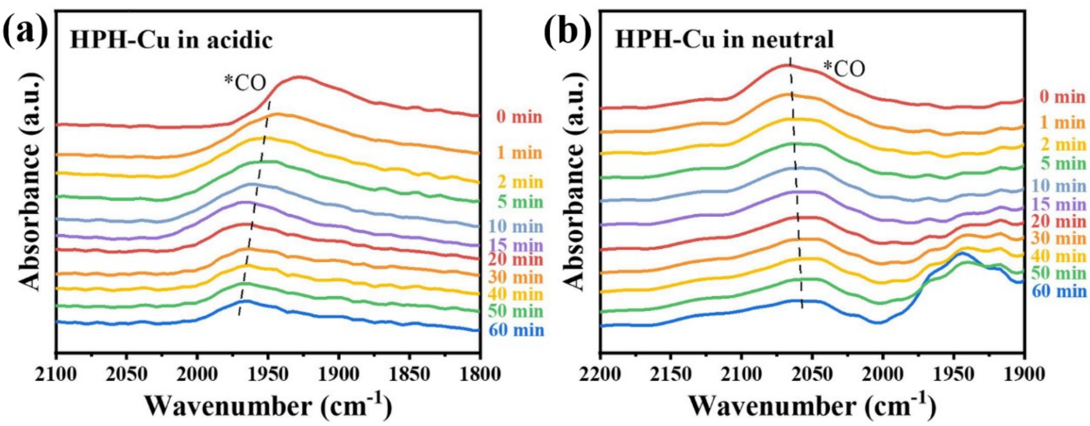
Supplementary Figure S10. XRD patterns of HPH and HPH-Cu.



Supplementary Figure S11. (a) Cu 2p and (b) Cu LMM XPS spectra of HPH-Cu after electrolysis; (c) XPS N 1s spectra of HPH and HPH-Cu after electrolysis.



Supplementary Figure S12. The FE_{CO} of HPH-Cu and Ag in acidic electrolyte.



Supplementary Figure S13. In situ ATR-SEIRAS spectra of CO desorption after -1.2 V vs. Ag/AgCl electrolysis in CO_2-saturated (a) acidic and (b) neutral electrolytes.

Supplementary Table S1. E (V vs. Ag/AgCl) after iR correction and E (V vs. RHE) after iR correction of HPH-Cu in acidic, alkaline, and neutral electrolytes.

	E (V vs. Ag/AgCl)	I/mA	R/Ω	E (V vs. Ag/AgCl) after 80% iR correction	E (V vs. RHE) after 80% iR correction
acidic	-1.5	28.19	3	-1.43	-1.13
	-1.8	84.82	3	-1.60	-1.30
	-2.0	102.70	3	-1.75	-1.45
	-2.2	147.30	3	-1.85	-1.55
	-2.4	180.98	3	-1.97	-1.67
	-2.6	207.36	3	-2.10	-1.80
alkaline	-1.5	44.59	1	-1.46	-0.46
	-1.8	127.29	1	-1.70	-0.70
	-2.0	193.93	1	-1.84	-0.84
	-2.2	250.23	1	-2.00	-1.00
	-2.4	378.37	1	-2.10	-1.10
	-2.6	408.63	1	-2.27	-1.27
neutral	-1.5	19.55	3	-1.45	-0.85
	-1.8	59.50	3	-1.66	-1.06
	-2.0	88.18	3	-1.79	-1.19
	-2.2	123.85	3	-1.90	-1.30
	-2.4	200.58	3	-1.92	-1.32
	-2.6	160.68	3	-2.21	-1.61

Supplementary Table S2. Cu content analysis result of HPH-Cu.

Sample	m_0(g)	Test element	Element content W (%)
HPH-Cu	0.0659	Cu	7.12%

Supplementary Table S3. Detailed comparison of Faradaic efficiency of CO and pH of electrolyte with HPH-Cu and other reported CO_2RR catalysts.

Catalyst	**Electrolyte**	**pH**	**Faradaic efficiency of CO [%]**	**Reference**
HPH-Cu	0.45 M K_2SO_4 + 0.05 M H_2SO_4	1.9	68	☆this work
Ag	polymer electrolytes	2~5	43	*Nat Chem*, 2021, **13**, 33-40.
Cu/C	0.4 M K_2SO_4 + 0.1 M H_2SO_4	1.5	30	*Nat Catal*, 2022, **5**, 268-276.
Cu-SiOx	0.1 M $KHCO_3$	7.3	47.5	*Nat commun*, 2021, **12**, 2808.
Au_3Cu NPs	0.1 M $KHCO_3$	6.8	65	*Nat commun*, 2014, **5**, 4948.
MOF-545-Cu	0.1 M $KHCO_3$	7.3	38	*Chin Chem Lett*, 2023, **34**, 107458.
BEN-Cu-BTC	0.1 M $KHCO_3$	7.3	25	*Catal Sci Technol*, 2019, **9**, 5668-5675.