

Electronic Supplementary Information

Hierarchical Cu pillar electrode for electrochemical CO₂ reduction to formic acid with low overpotential

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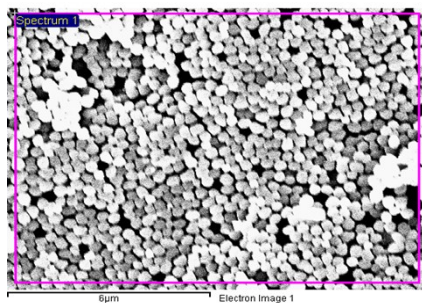
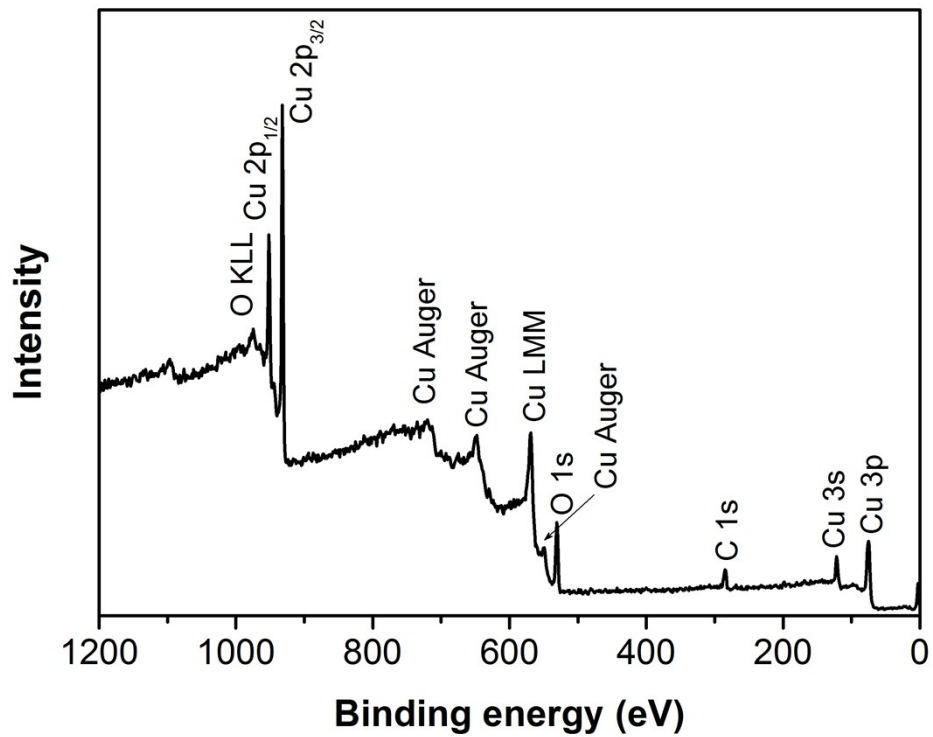
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		foil	Cu-2.5 h	Cu-5 h
Absolute intensity at each facet	(111)	6893	6310	6005
	(200)	12917	2959	1641
	(220)	1022	718	647
Relative ratio	(111) / (200)	0.53	2.13	3.66
	(111) / (220)	6.74	8.79	9.28

Table. S1 Absolute intensity of XRD result at each facet and their relative ratio of (111) / (200) and (111) / (220) facet



Element	Weight%	Atomic%
O K	1.13	4.33
Cu L	98.87	95.67
Totals	100.00	

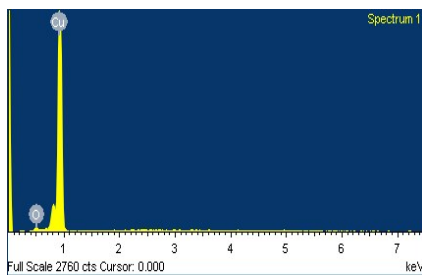


Fig. S1 (a) Survey XPS and (b) EDS result of a Cu pillar electrode after cathodic electrode deposition

for 5 hours (Cu-5 h). Atomic ratio of Cu, O and C are 39 %, 31 % and 30 %, respectively.

Voltage (V)	j_{tot} (mA/cm ²)	Production rate (μmol/h)			Faradaic efficiency (%)			
		H ₂	CO	HCOOH	H ₂	CO	HCOOH	Total
-0.3	3.01	2.25	0	0.18	87.53	0.00	6.95	93.78
-0.4	5.70	3.95	0.005	0.79	80.40	0.11	16.15	96.66
-0.5	9.78	6.4	0.009	1.93	75.64	0.21	22.85	98.70
-0.6	17.5	11	0.086	3.76	72.59	1.14	24.81	98.54
-0.7	25.8	15.9	0.335	5.4	71.29	3.01	24.21	98.51
-0.8	34.2	21	0.558	5.95	71.06	3.78	20.12	94.95
-0.9	41.9	28	0.397	7.03	77.34	2.20	19.41	98.95

Table S2. Summary of total current densities and faradaic efficiencies for all products at various potentials on Cu-2.5 h

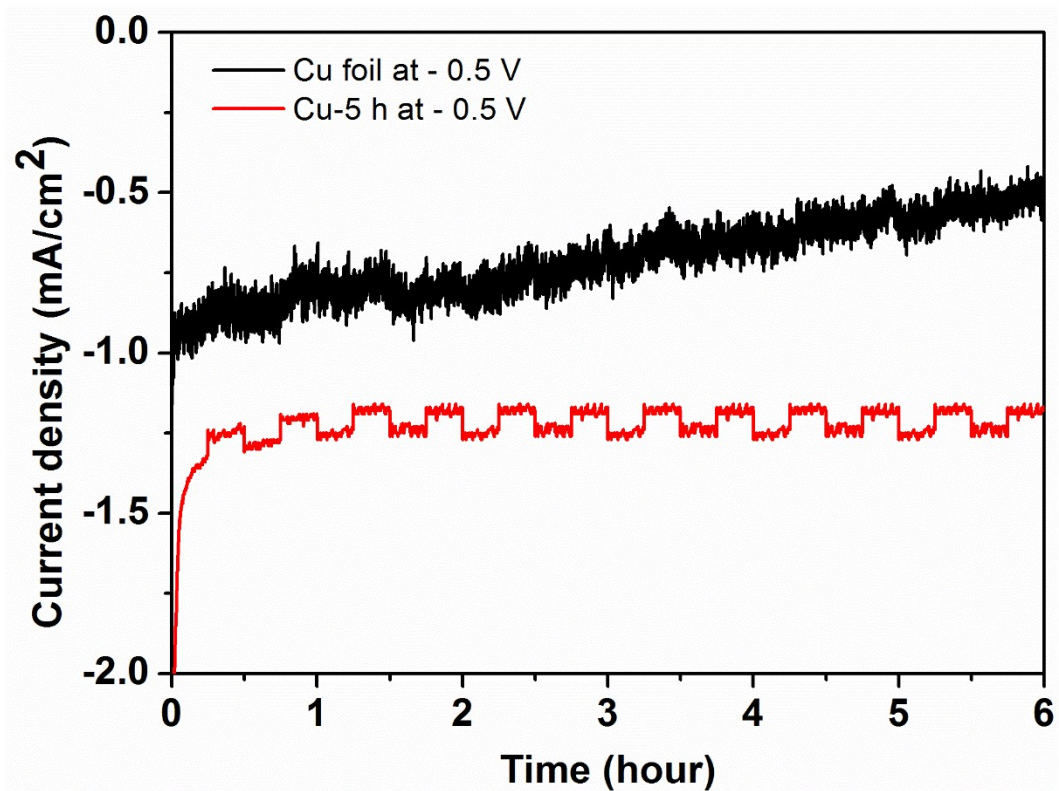


Fig. S2 Chronoamperometry curve of Cu-5 h (red) and Cu foil (black) electrode for 6 hours at -0.5 V in saturated 0.1 M KHCO_3 .

Applied Potential	Cu foil			Cu-2.5 h			Cu-5 h		
	Electrolyte resistance	Ohmic resistance	Charge transfer resistance	Electrolyte resistance	Ohmic resistance	Charge transfer resistance	Electrolyte resistance	Ohmic resistance	Charge transfer resistance
- 0.4 V	48.35	162.7	15350	42.92	112.8	373.4	38.77	82.74	486.6
- 0.5 V	50.38	166.5	5065	43.18	111.5	203.1	39.14	83.58	186.7
- 0.6 V	48.84	163.4	2542	43.95	110.9	114	39.14	83.02	96.08
- 0.7 V	43.07	172.8	646.4	40.35	103.8	59.25	41.96	80.5	65.88

Table S3. Summary of EIS measurement for all products at various applied potentials on Cu-5 h, Cu-2.5 h and Cu foil.

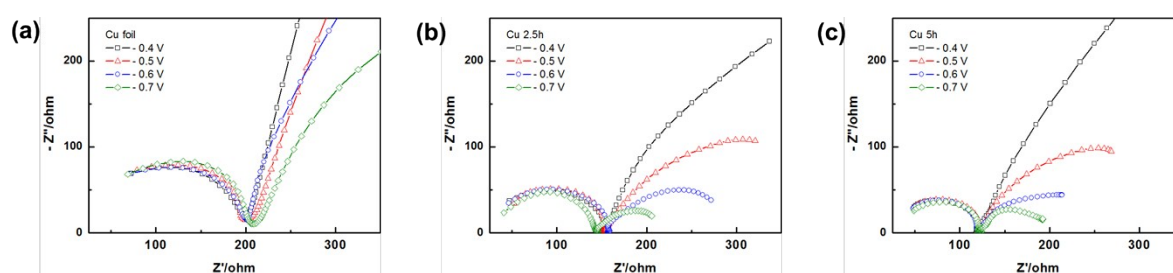


Fig. S3 Result of EIS measurement of (a) Cu-5 h, (b) Cu-2.5 h and (c) Cu foil at various applied potential

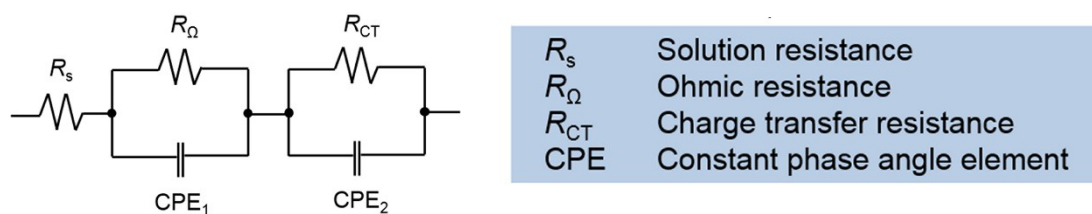


Fig. S4 An equivalent circuit model and its parameters used for the EIS simulations

