Supporting information

The Activity Origin of C-N-Cu Electrocatalysts for Ethanol Formation in CO_2 Reduction Reaction under Working Condition

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1.Computational Details

1.1 Free energy calculations

The Gibbs free energy change (ΔG) is calculated as $\Delta G = \Delta E + \Delta ZPE - T\Delta S$. ΔE is the DFT energy difference, and ΔZPE and TΔS are the change of zero point energies and entropy calculated by the following equations:

$$ZPE = \frac{1}{2}\sum_i h\nu_i$$

$$S_{vib}(T) = R\sum_i \{\frac{h\nu_i}{kT}\frac{e^{-\frac{h\nu_i}{kT}}}{1-e^{-\frac{h\nu_i}{kT}}} - \ln(1-e^{-\frac{h\nu_i}{kT}})\}$$

The T is set to be 298.15K. The calculated data of reactants are listed in Table.

1.2 Binding energy

The binding energy expressed as

$$E_{binding}(Cu_N) = E(C\text{-}N\text{-}Cu_N) - E(C\text{-}N\ substrate) - E(Cu_N)$$

where right three terms represent total energy of C-N-Cu_N, clean C-N substrate and pure Cu_N cluster. The more negative the value, the easier the corresponding structure can be combined with the substrate.

1.3 Second-order difference of the total energies

The second-order difference of the total energies is used to evaluate the stability of the cluster structure. Its value is expressed as

$$\Delta^2 E = E(Cu_{N+1}) + E(Cu_{N-1}) - 2E(Cu_N)$$

. And the structure corresponding to the maximum value is considered stable.

1.4 D-band center

To analyze the adsorption ability of catalysts quantitatively, the d-band center are calculated as follows

$$\varepsilon_d = \frac{\int_{-\infty}^{\infty}\varepsilon\rho_d d\varepsilon}{\int_{-\infty}^{\infty}\rho_d d\varepsilon}$$

where ε represents energy and ρ_d is the d partial electronic density of states. Take the value as an indicator, the adsorption capacity is proportional to the value of d-band-center.

1.5 CO_2 reduction to CO

The Conversion of CO_2 to CO is a two-proton-coupled electron transfer process involving intermediates (*CO_2, *COOH and *CO) where * represents catalysts. The elementary reaction can be expressed as followed:

$$* + CO_2 \rightarrow *CO_2$$
$$*CO_2 + H^+ + e^- \rightarrow *COOH$$
$$*COOH + H^+ + e^- \rightarrow *CO + H_2O$$
$$*CO \rightarrow * + CO$$

The free energy calculations based on CHE model can be written as:

$$\Delta G_1 = E_{*CO_2} + ZPE_{*CO_2} - TS_{*CO_2} - (E_{(*+CO_2)} + ZPE_{(*+CO_2)} - TS_{(*+CO_2)})$$

$$\Delta G_2 = E_{*COOH} + ZPE_{*COOH} - TS_{*COOH} - (E_{CO_2} + ZPE_{CO_2} - TS_{CO_2} + \frac{E_{H_2}}{2} + \frac{ZPE_{H_2}}{2} - \frac{TS_{H_2}}{2})$$

$$\Delta G_3 = E_{*CO} + ZPE_{CO} - TS_{*CO} + E_{H_2O} + ZPE_{H_2O} - TS_{H_2O} - (E_{(*COOH)} + ZPE_{(*COOH)} - TS_{(*COOH)} + \frac{E_{H_2}}{2} + \frac{ZPE_{H_2}}{2} - \frac{TS_{H_2}}{2})$$

$$\Delta G_4 = E_{(*+CO)} + ZPE_{(*+CO)} - TS_{(*+CO)} - (E_{*CO} + ZPE_{*CO} - TS_{*CO})$$

Table S1. Calculated ZPE and TS for CO_2RR to CO on C-N-Cu_3 and C-N-Cu_5

		ZPE	TS
C-N-Cu_3	*CO_2	0.28	0.24
	*COOH	0.60	0.23
	*CO	0.18	0.21
C-N-Cu_5	*CO_2	0.29	0.24
	*COOH	0.59	0.15
	*CO	0.19	0.20

Table S2. Calculated ZPE and TS for CO_2RR to ethanol on C-N-Cu_5

	ZPE	TS
*COCO	0.37	0.35
*OCOCH	0.62	0.40
*COCHO	0.70	0.29
*CHOCHO	0.87	0.44
*OCHOCH	1.03	0.27
*$OCHOCH_2$	1.29	0.33
*$OCHOHCH_2$	1.61	0.32
*$OCHCH_2$	1.20	0.23
*$OCHCH_3$	1.49	0.31
*OCH_2CH_3	1.82	0.34

Table S3. Calculated E_{DFT}, ZPE, TS for molecular in CO_2RR

	E_{DFT}	ZPE	TS
H_2	-6.77	0.30	0.40
H_2O	-14.23	0.58	0.67
CO_2	-23.00	0.31	0.67
CO	-14.80	0.14	0.62
C_2H_5OH	-46.88	2.11	0.36

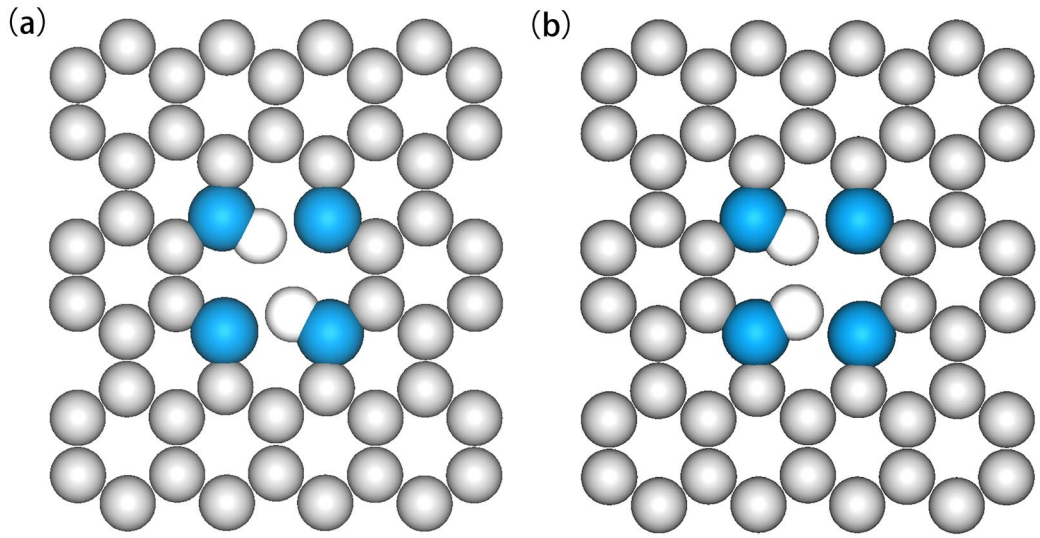

Figure S1. C_N substrate with two hydrogens adsorbed: a) diagonal hydrogen atoms; b) adjacent hydrogen atoms

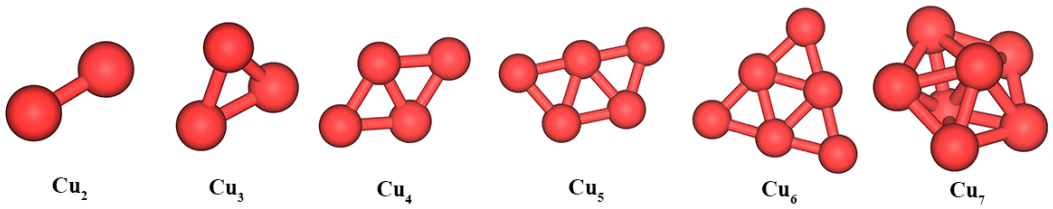

Figure S2. The configurations of Cu_N in the air.

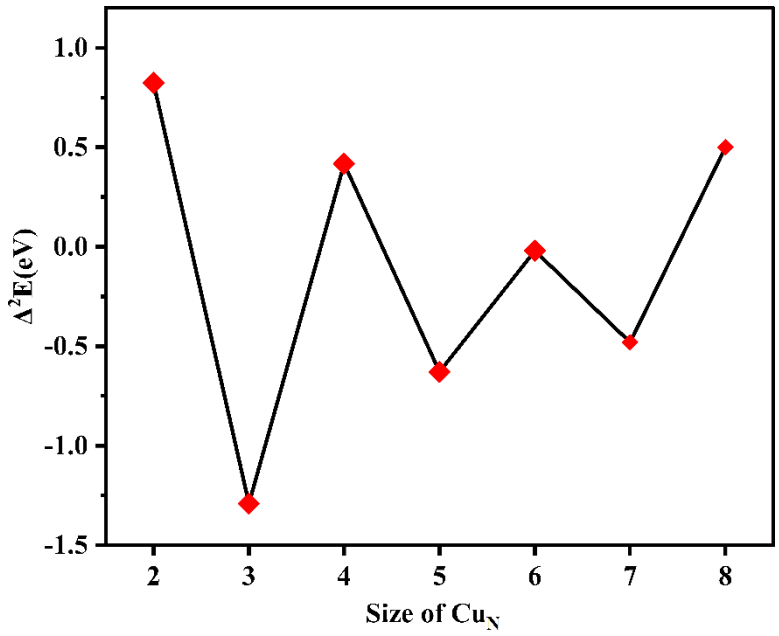

Figure S3. Second-order difference of total energies of Cu_N cluster in the air.

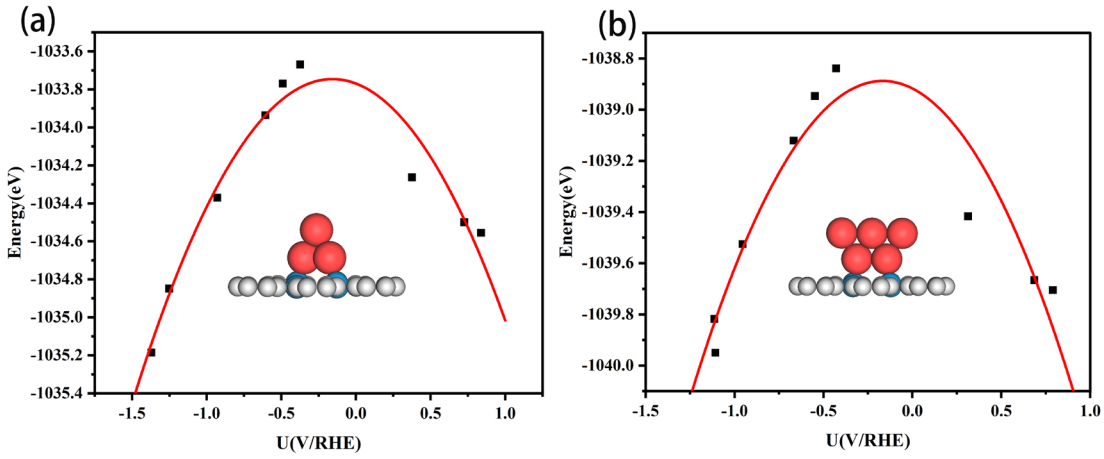

Figure S4. Fitted Energy-potential curve for (a) C-N-Cu_3 and (b) C-N-Cu_5 with constant potential method.

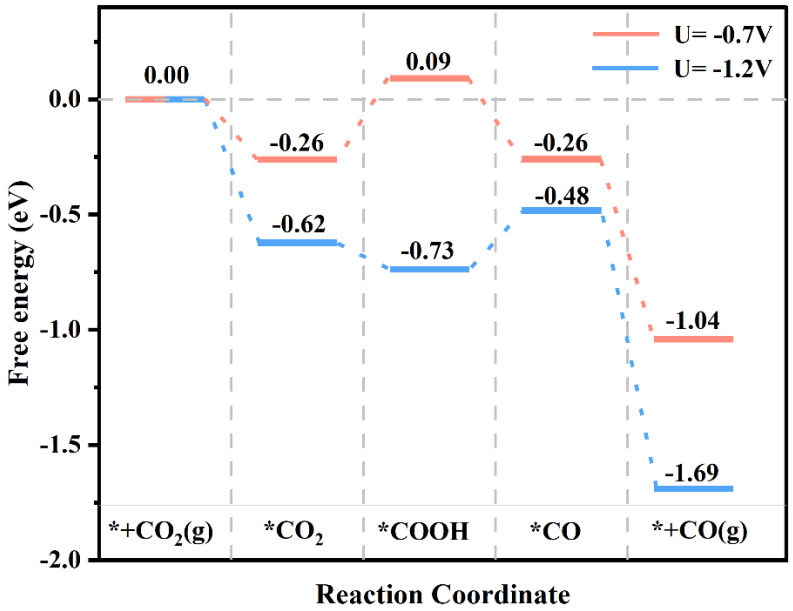

Figure S5. The free energy step diagram of CO_2 reduction to CO under specific potentials.

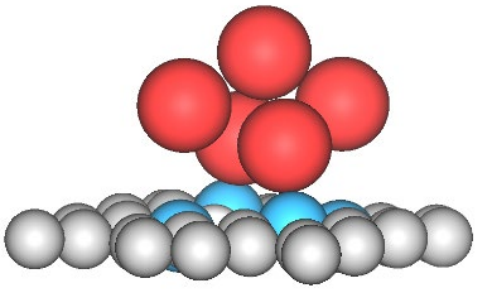

Figure S6. The stable hexahedral structure of C-N-Cu_5 which is optimized under non-aqueous environment.

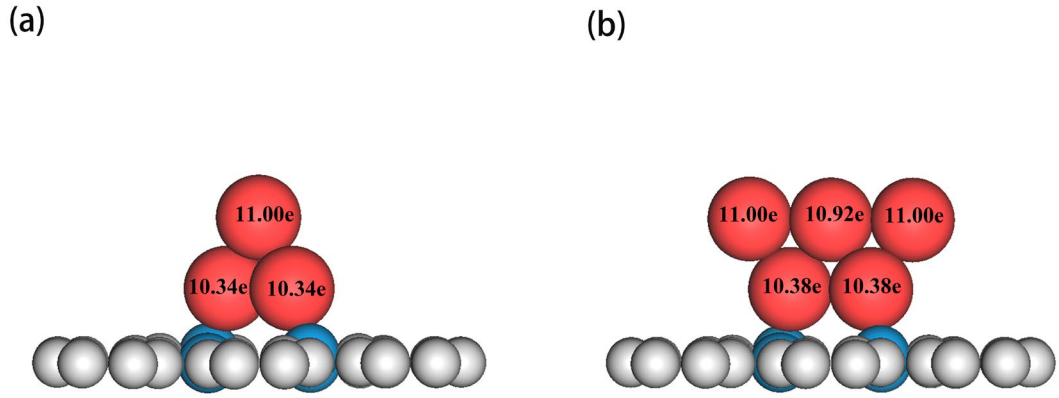

Figure S7. The valance electron of (a) Cu_3 and (b) Cu_5 calculated by Bader Change analysis. The copper atoms at the bottom of the C-N-Cu_3 and C-N-Cu_5 molecules that are interacting with nitrogen lose 0.66e and 0.62e, respectively. The electrons of the up-middle copper atom in C-N-Cu_5 are losing 0.08e, whilst the electrons of the other two coppers at the angle of C-N-Cu_5 and the top copper in C-N-Cu_3 stay constant.

The atomic coordinates

(1) Cu2

0.5868773130720107	0.5739136741989520	0.6411131991654587	Cu1
0.4797726599279932	0.5171163268010409	0.6782767998345361	Cu2

(2) Cu3

0.4765529828924561	0.5153189683147229	0.6793395461257844	Cu1
0.5485435924203922	0.4514785388246503	0.6029010363062729	Cu2
0.4341434136871556	0.3891425368606200	0.6431394085679356	Cu3

(3) Cu4

0.5905745141101002	0.5758749142849661	0.6398360314395012	Cu1
0.4760851347895466	0.5151606498228131	0.6795522594292216	Cu2
0.5484963717255620	0.4510009480944903	0.6026865302571841	Cu3
0.4346639853747958	0.3897834927977299	0.6431451768740896	Cu4

(4) Cu4

0.5905745141101002	0.5758749142849661	0.6398360314395012	Cu1
0.4760851347895466	0.5151606498228131	0.6795522594292216	Cu2
0.5484963717255620	0.4510009480944903	0.6026865302571841	Cu3
0.4346639853747958	0.3897834927977299	0.6431451768740896	Cu4

(5) Cu5

0.5229067505353442	0.5691594356362142	0.6025722924641930	Cu1
0.4975631714627709	0.5030272610178949	0.7052637632322465	Cu2
0.4687153352258888	0.4408944043473386	0.6013108595565002	Cu3
0.5491885021544856	0.6290384973715287	0.7059125326140649	Cu4
0.4439062266215122	0.3779504476270177	0.7036505221329959	Cu5

(6) Cu6

0.5164201387324489	0.5698754811208806	0.5984686142468754	Cu1
0.4935945099241920	0.5031587917263848	0.7025141915498631	Cu2
0.4711373546443335	0.4408352193712413	0.6003956699786841	Cu3
0.5407887115532555	0.6357662601141921	0.7026450106561251	Cu4
0.5171092086946455	0.5693689596634373	0.8026842219504147	Cu5
0.5625801074511160	0.6985352430038527	0.6005722846180415	Cu6

(7) Cu7

0.5022112087416890	0.4910019038577218	0.5120480866703774	Cu1
0.5073726002968948	0.6107159163164543	0.5772702936515977	Cu2
0.6181898243299987	0.5242682156002018	0.5734070006793697	Cu3
0.5715674775986069	0.3903084596087101	0.5727302822996468	Cu4
0.4320605703070104	0.3938785187701778	0.5763148706633018	Cu5
0.3924309492961262	0.5300016472600704	0.5791585289221250	Cu6
0.5065273214296722	0.4886053585866618	0.6394909421135926	Cu6

(8) C-N-Cu

0.0000000008293323	0.0829534563774832	0.4999999903629910	C1
0.0714688928622983	0.2077540294978927	0.4999999808244401	C2
0.0000000005026329	0.1664338753720708	0.4999999807046589	C3
0.0716273048955180	0.0417753558335255	0.5000000061218159	C4

0.1431945021568964	0.0829585362819582	0.5000000125077487	C5
0.2143433456634119	0.2081455652321550	0.5000000081050336	C6
0.1429980031666078	0.1665786792612668	0.5000000019830164	C7
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0.3574738316822488	0.2098811196979171	0.5000000328971611	C10
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0.4291297884625572	0.0846692297220338	0.4999999991504139	C13
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