Supplementary Information

Thermodynamically driven self-formation of copper-embedded nitrogen-doped carbon nanofiber catalysts for a cascade electroreduction of carbon dioxide to ethylene

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**Fig. S1** Digital images of (a, d, g) electrospinning solution, (b, e, h) as spun nanofibers, and (c, f, i) calcinated nanofibers of (a, b, c) Cu30/N-CNF, (d, e, f) Cu50/N-CNF, and (g, h, i) Cu50/CNF
**Fig. S2** Electrical conductivity and nitrogen concentration of Cu50/CNF and Cu50/N-CNF catalysts
Fig. S3 Raman spectrum of Cu30/N-CNF, Cu50/N-CNF, and Cu50/CNF catalyst
Fig. S4 Ellingham diagram of N, C, and Cu and morphological change of Cu50/N-CNf as O\textsubscript{2} partial pressure increases
Fig. S5 Particle size distribution of (a) Cu30/N-CNF and (b) Cu50/N-CNF, and (c) Cu50/CNF
Fig. S6 (a) XRD pattern (b) Cu2p spectra, and (c) Cu LMM spectra of Cu/N-CNF catalysts.
Fig. S7 HRTEM image and FFT diffraction pattern of (a, c) Cu30/N-CN, (b, d) Cu50/N-CN, and (c, f) Cu50/CN.
**Fig. S8** Brunauer-Emmett-Teller (BET) specific surface area measured by (a) N₂ and (b) CO₂ gas.
Fig. S9 TGA curves of PAN and PVA nanofibers.
Fig. S10 Map of Cu radius – Cu mass fraction of Cu/(N)-CNF catalyst.

Assuming that the copper particle is sphere, surface area of copper particle and mass of copper are given as below: 

\[ S = n(4\pi r^2) \]  \hspace{1cm} (Eq. 1)

\[ M_\alpha = n\mu \left(\frac{4}{3}\pi r^3\right) = \alpha M \]  \hspace{1cm} (Eq. 2)

and Eq. 3 can be derived by Eq. 2. Moreover, Eq.4 and Eq.5 formed by Eq. 1 and Eq. 3 which is derived by Eq.2 as follows:

\[ n = \frac{3\alpha M}{4\mu\pi r^3} \]  \hspace{1cm} (Eq. 3)

\[ S = \frac{3\alpha M}{\mu r} \]  \hspace{1cm} (Eq. 4)

\[ \alpha = \left(\frac{\mu S}{3M}\right) r = kr \]  \hspace{1cm} (Eq. 5)

When we plot the mass fraction of copper and radius of copper particle, it is confirmed that the slope is proportional to the total surface area of copper particle.

\[ k = \frac{\mu}{3M} S \]  \hspace{1cm} (Eq. 6)
Fig. S11 Cyclic voltammograms of (a) Cu30/N-CNF, (b) Cu50/N-CNF, and (c) Cu50/CNF, and (d) determination of double layer capacitance of Cu30/N-CNF, Cu50/N-CNF, and Cu50/CNF.
**Fig. S12** Electrochemical surface area of Cu/N-CNF and Cu/CNF catalysts

\[ \text{ECSA} = \frac{C_{\text{cal}}}{C_r} \]

\[ C_r = 29 \, \mu F \, \text{(polycrystalline Cu)} \]
Fig. S13 (a) XPS survey spectra, (b) deconvolution of XPS N1s spectra of Cu30/N-CNF and Cu50/N-CNF, and (c) pyridinic N/Cu ratio of Cu30/N-CNF, Cu50/N-CNF
Fig. S14 Pyridinic N concentration of N-CNF, Cu30/N-CNF, and Cu50/N-CNF catalysts
Fig. S15 SEM images of (a) bare and (b) Cu50/N-CN coated GDE
**Fig. S16** Images of (a) CO$_2$ reduction system and (b) flow cell reactor. (c) Schematics of flow cell reactor for electrochemical CO$_2$ reduction system
Fig. S17 Faradaic efficiency of liquid products during CO$_2$RR by (a) Cu50/N-CN and (b) Cu50/CNF catalyst
Fig. S18 (a,c) Faradaic efficiency and (b,d) geometric partial current density of (a, b) CO and (c, d) C₂H₄ as a function of potential.
**Fig. S19** Faradaic efficiency of H\textsubscript{2} as function of potential.
Fig. S20 Dimerization energy barrier as function of number of CO* per unit cell
Fig. S21 (a, b) HRTEM image and (c) FFT analysis of Cu50/N-CNF after 2 hour of CO$_2$ RR
**Fig. S22** SEM image of commercial Cu powder (a) before reaction, and (b) after 2 hour of CO$_2$ RR
Fig S23 (a) Schematics and (b) image of carbon black/Cu/CuNCNF/PTFE
Fig. S24 Potential profile of carbon black/CuNCNF/Cu/PTFE and carbon black/Cu/PTFE for 20 hours of reactions.