

Supplementary Information

An integrated cathode-electrolyte architecture with Cu dual active-sites for all-solid-state Li–CO₂ batteries

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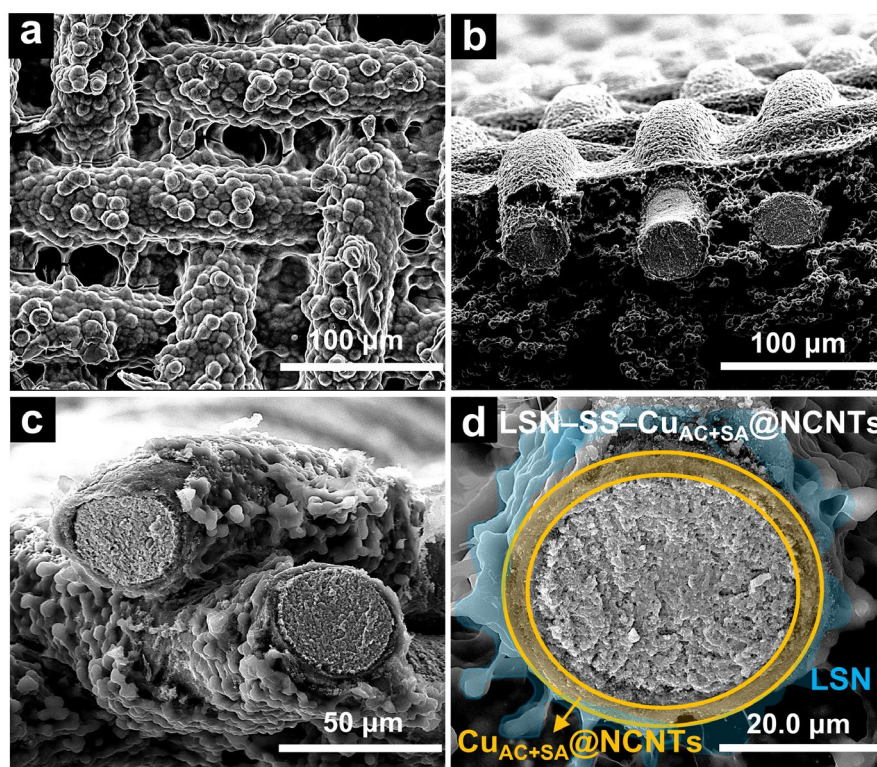
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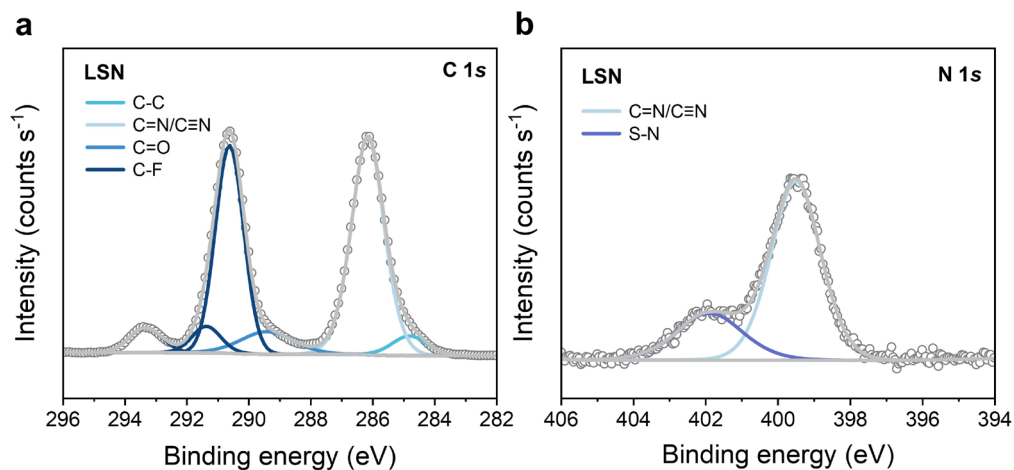
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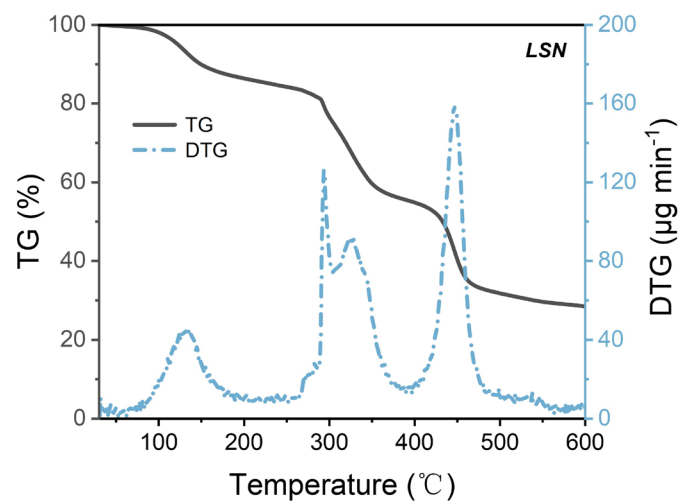
Supplementary figures and tables



Supplementary Fig. 1 Morphology characterization of the integrated cathodes. **a** Top-view and **b** cross-sectional scanning electron microscopy (SEM) images of the LSN-SS-NCNTs cathode. **c**, **d** Cross-sectional SEM images of the LSN-SS- $\text{Cu}_{\text{AC+SA}}@\text{NCNTs}$ cathode at different magnifications. The false-colored SEM image in **d** highlights the conformal LSN solid electrolyte (blue area) coating the $\text{Cu}_{\text{AC+SA}}@\text{NCNTs}$ active layer (yellow boundary) on the stainless-steel microfibers. LSN, lithium-salt-containing succinonitrile; SS, stainless steel; $\text{Cu}_{\text{AC+SA}}$, Cu atomic clusters and single atoms; NCNTs, nitrogen-doped carbon nanotubes.

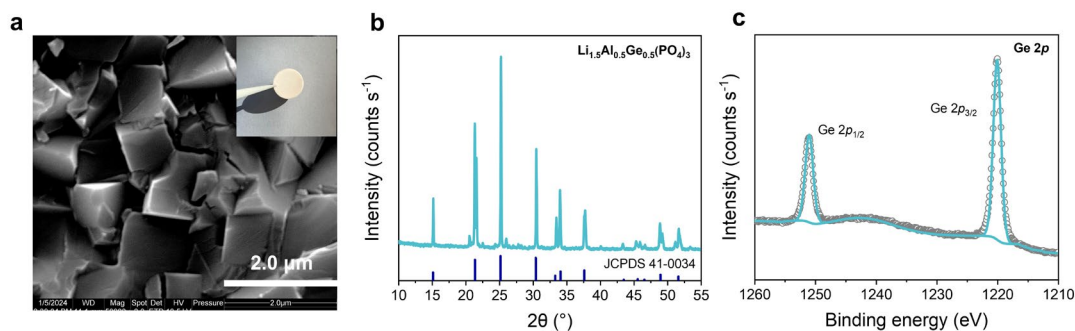


Supplementary Fig. 2 X-ray photoelectron spectroscopy characterization of the LSN solid electrolyte. High-resolution deconvoluted **a** C 1s and **b** N 1s spectra. LSN, lithium-salt-containing succinonitrile. Source data are provided as a Source Data file.

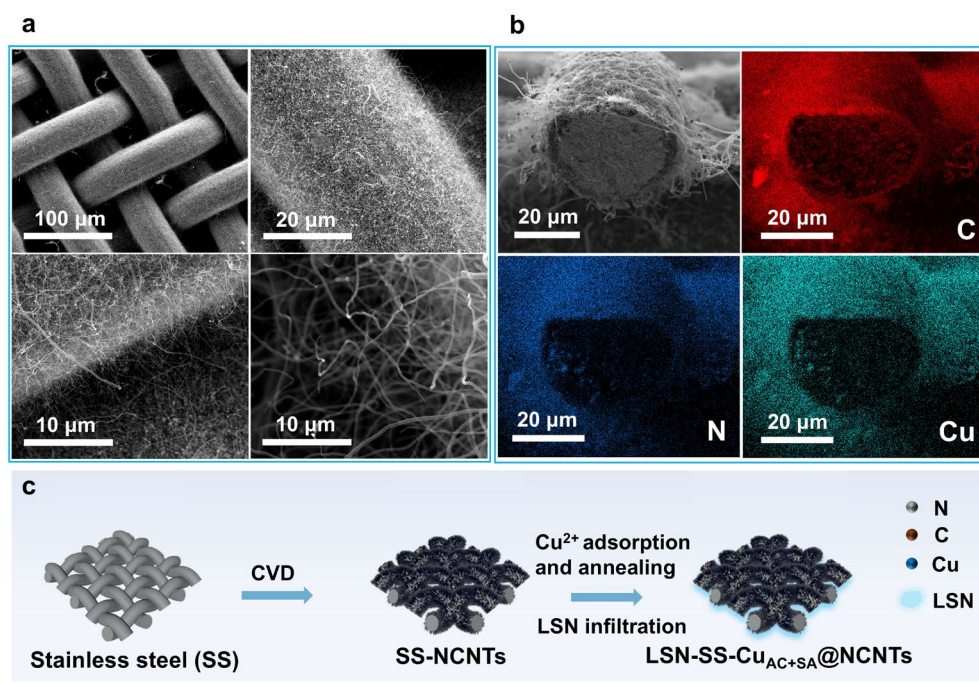


Supplementary Fig. 3 Thermal stability analysis of the LSN solid electrolyte.

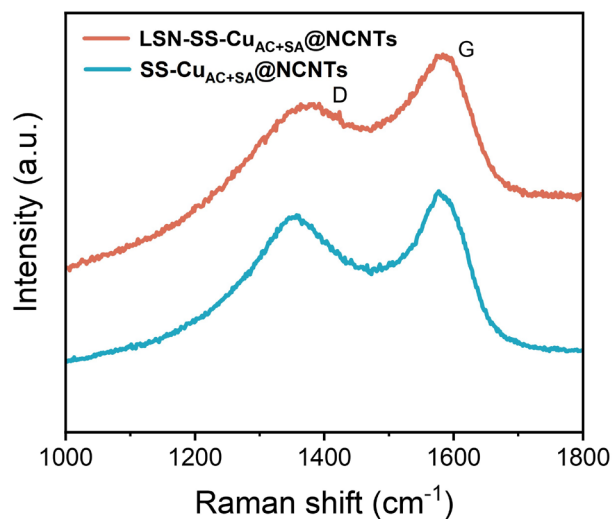
Thermogravimetric and the corresponding derivative thermogravimetric profiles of the LSN electrolyte, recorded under a nitrogen atmosphere. LSN, lithium-salt-containing succinonitrile. Source data are provided as a Source Data file.



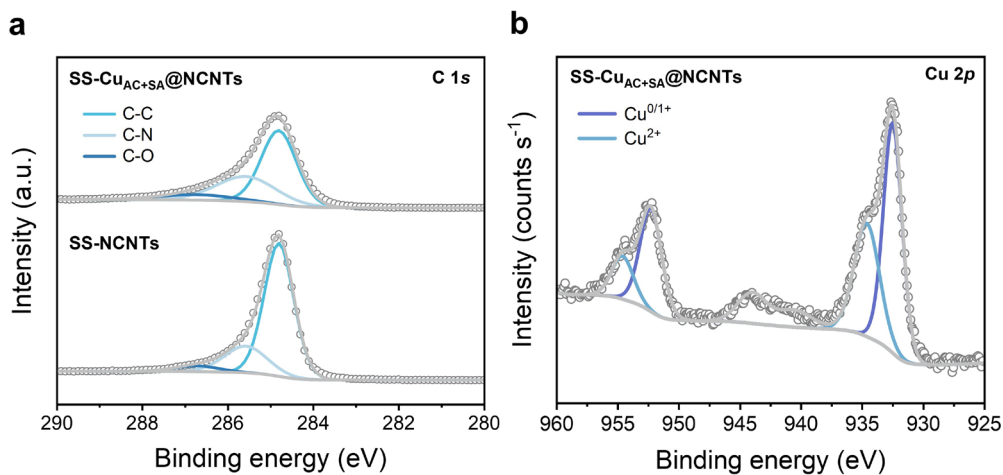
Supplementary Fig. 4 Morphological and structural characterization of the LAGP electrolyte. **a** Cross-section scanning electron microscopy image of an LAGP pellet. Inset shows the corresponding digital photograph. **b** X-ray diffraction pattern and **c** Ge $2p$ X-ray photoelectron spectroscopy spectrum of the LAGP electrolyte. LAGP, lithium aluminium germanium phosphate, $\text{Li}_{1+x}\text{Al}_y\text{Ge}_{2-y}(\text{PO}_4)_3$. Source data are provided as a Source Data file.



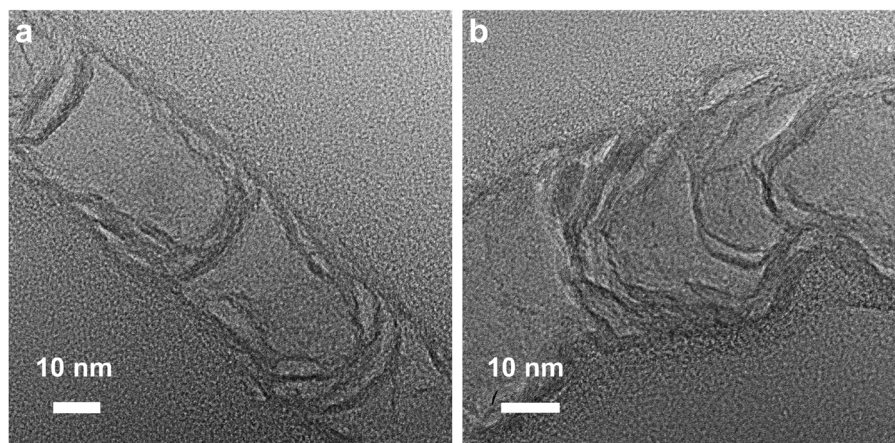
Supplementary Fig. 5 Morphology and synthesis of the designed cathodes. **a** scanning electron microscopy (SEM) images of SS-NCNTs at different magnifications. **b** Cross-section SEM image and corresponding energy-dispersive X-ray spectroscopy elemental maps of SS-Cu_{AC+SA}@NCNTs, showing the distribution of C, N and Cu across the freestanding cathode. **c** Schematic illustration of the fabrication of LSN-SS-Cu_{AC+SA}@NCNTs through CVD growth of NCNTs on SS, Cu²⁺ adsorption followed by annealing, and subsequent infiltration with the LSN solution and drying. CVD, chemical vapour deposition. LSN, lithium-salt-containing succinonitrile; SS, stainless steel; Cu_{AC+SA}, Cu atomic clusters and single atoms; NCNTs, nitrogen-doped carbon nanotubes.



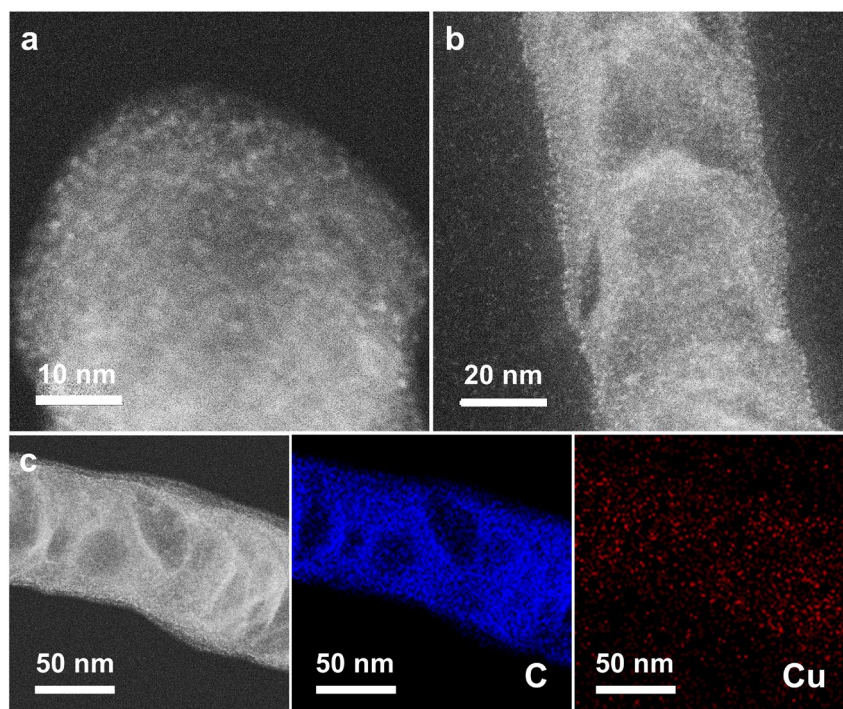
Supplementary Fig. 6 Raman spectra of the designed composite cathodes. Raman spectra comparing LSN-SS-Cu_{AC+SA}@NCNTs and SS-Cu_{AC+SA}@NCNTs. LSN, lithium-salt-containing succinonitrile; SS, stainless steel; Cu_{AC+SA}, Cu atomic clusters and single atoms; NCNTs, nitrogen-doped carbon nanotubes. Source data are provided as a Source Data file.



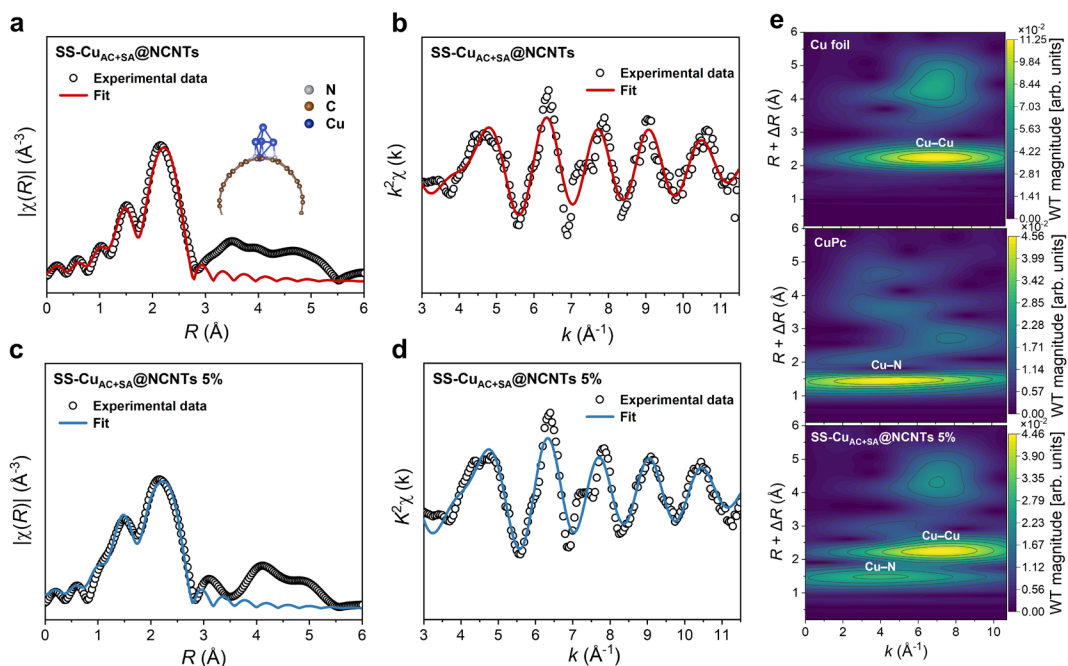
Supplementary Fig. 7 High-resolution X-ray photoelectron spectroscopy spectra of the electrocatalysts. a C 1s spectra of SS-Cu_{AC+SA}@NCNTs and the SS-NCNTs. **b** Cu 2p spectrum of SS-Cu_{AC+SA}@NCNTs. SS, stainless steel; Cu_{AC+SA}, Cu atomic clusters and single atoms; NCNTs, nitrogen-doped carbon nanotubes. Source data are provided as a Source Data file.



Supplementary Fig. 8 Microstructural characterization of the SS- $\text{Cu}_{\text{AC+SA}}\text{@NCNTs}$. **a, b** High-resolution Transmission electron microscopy images showing the detailed morphology of the composite. $\text{Cu}_{\text{AC+SA}}$, Cu atomic clusters and single atoms; NCNTs, nitrogen-doped carbon nanotubes.

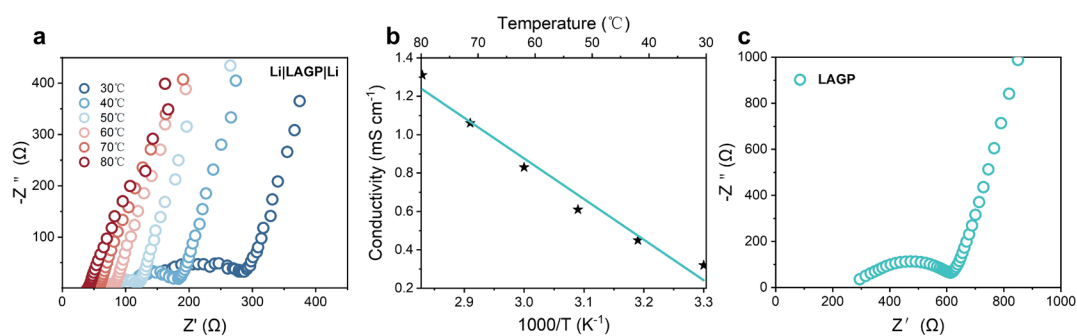


Supplementary Fig. 9 High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) and elemental analysis of the designed catalyst. a, b High-resolution HAADF-STEM images of the SS-Cu_{AC+SA}@NCNTs at different magnifications. **c** A representative HAADF-STEM image and EDS elemental maps of C and Cu. SS, stainless steel; Cu_{AC+SA}, Cu atomic clusters and single atoms; NCNTs, nitrogen-doped carbon nanotubes.



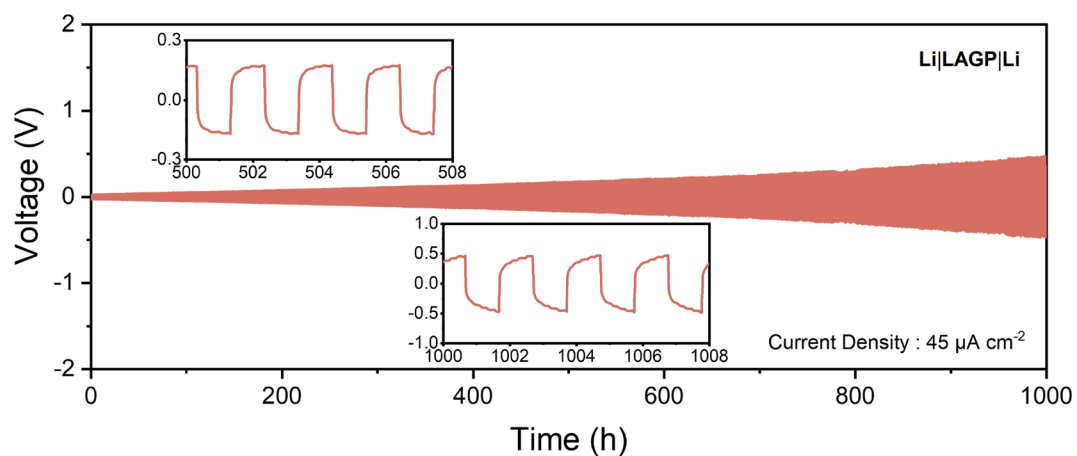
Supplementary Fig. 10 Local coordination environment of the catalysts. Extended X-ray absorption fine structure (EXAFS) fitting curves of the SS-Cu_{AC+SA}@NCNTs in **a** *R*-space and **b** *k*-space. The inset in **a** shows the corresponding atomic configuration model of the SS-Cu_{AC+SA}@NCNTs. EXAFS fitting curves of the SS-Cu_{AC+SA}@NCNTs-5% in **c** *R*-space and **d** *k*-space. **e** Wavelet-transform EXAFS maps of Cu foil, CuPc, and SS-Cu_{AC+SA}@NCNTs-5%. Brown, blue, and gray spheres represent C, Cu, and N atoms, respectively. SS, stainless steel; Cu_{AC+SA}, Cu atomic clusters and single atoms; NCNTs, nitrogen-doped carbon nanotubes; CuPc, copper phthalocyanine. Source data are provided as a Source Data file.

The Cu_{AC+SA}@NCNTs model shown in the inset of Supplementary Fig. 10a was constructed based on the X-ray absorption spectroscopy evidence for coexisting Cu–N coordination and Cu–Cu interactions. This pyramid-like Cu cluster model serves as a chemically representative local structure that captures low-coordination Cu sites, Cu–N/Cu–Cu interactions, and interfacial coupling with the N-doped carbon substrate. It is intended to describe the essential local coordination environment of the catalyst, rather than to reproduce the full size and morphology of experimentally formed Cu aggregates.

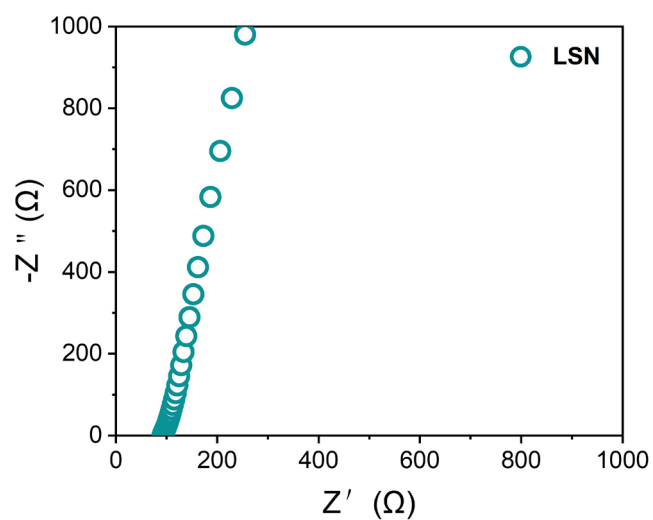


Supplementary Fig. 11 Electrochemical characterization of the LAGP electrolyte.

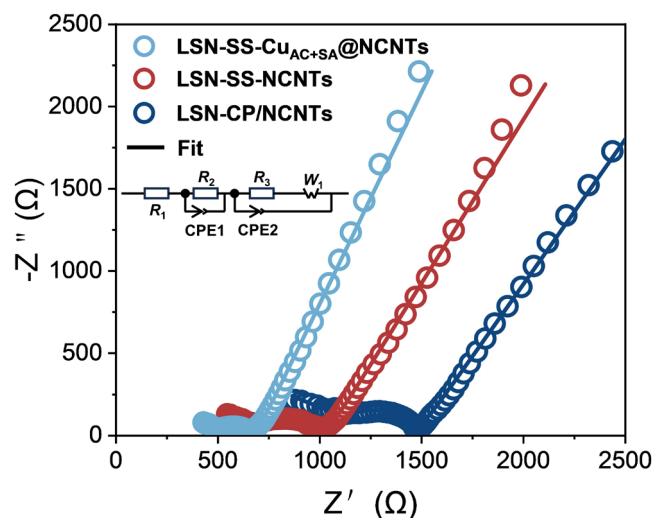
a Temperature-dependent Nyquist plots of the LAGP electrolyte measured from 30 to 80 °C. **b** The corresponding Arrhenius plot of ionic conductivity. **c** Nyquist plot of the LAGP electrolyte measured at 28 ± 1 °C. LAGP, lithium aluminium germanium phosphate. Source data are provided as a Source Data file.



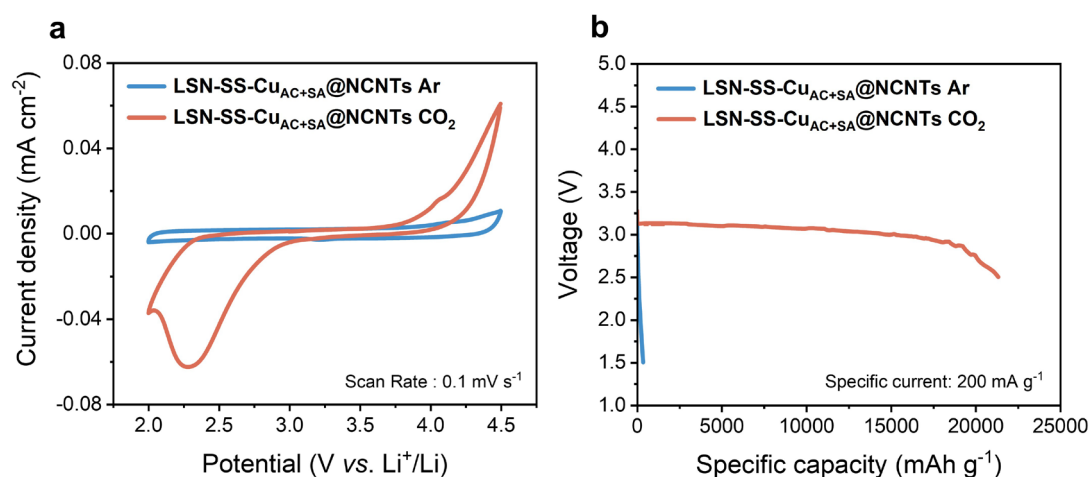
Supplementary Fig. 12 Galvanostatic Li plating/stripping profile of the Li|LAGP|Li symmetric cell. The test was conducted at a constant current density of 45 $\mu\text{A cm}^{-2}$. Insets show the enlarged voltage profiles at 500–508 and 1000–1008 h. The coin cells were performed at 28 ± 1 °C. LAGP, lithium aluminium germanium phosphate. Source data are provided as a Source Data file.



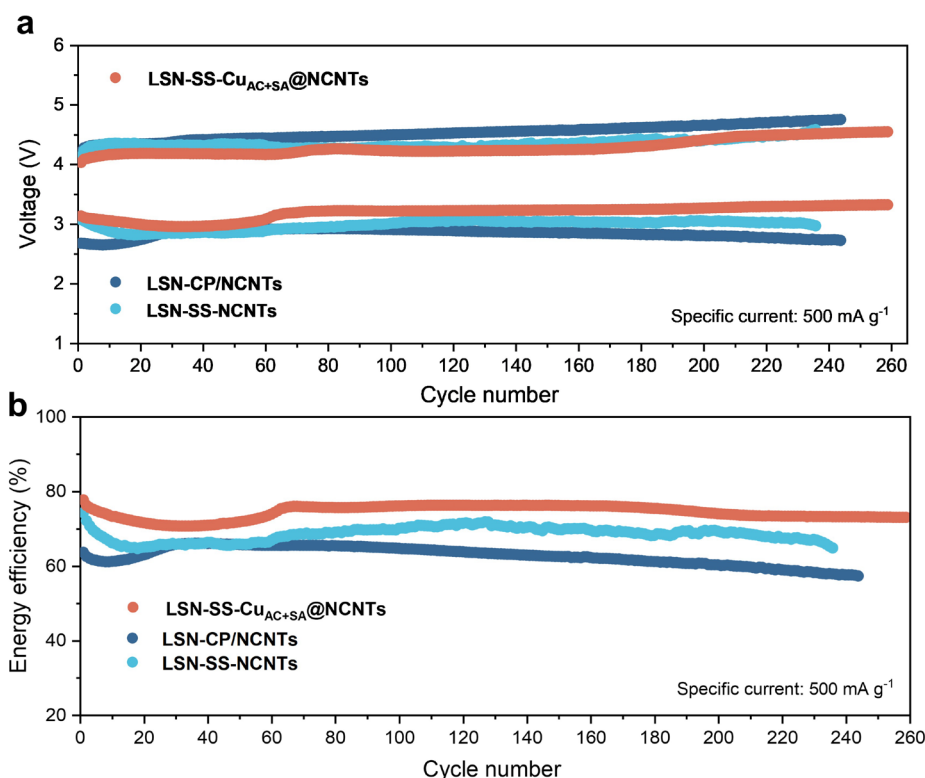
Supplementary Fig. 13 Ionic conductivity of the LSN electrolyte at 28 ± 1 °C. Nyquist plot of the LSN electrolyte. The fitted resistance corresponds to an ionic conductivity of 0.16 mS cm^{-1} . LSN, lithium-salt-containing succinonitrile. Source data are provided as a Source Data file.



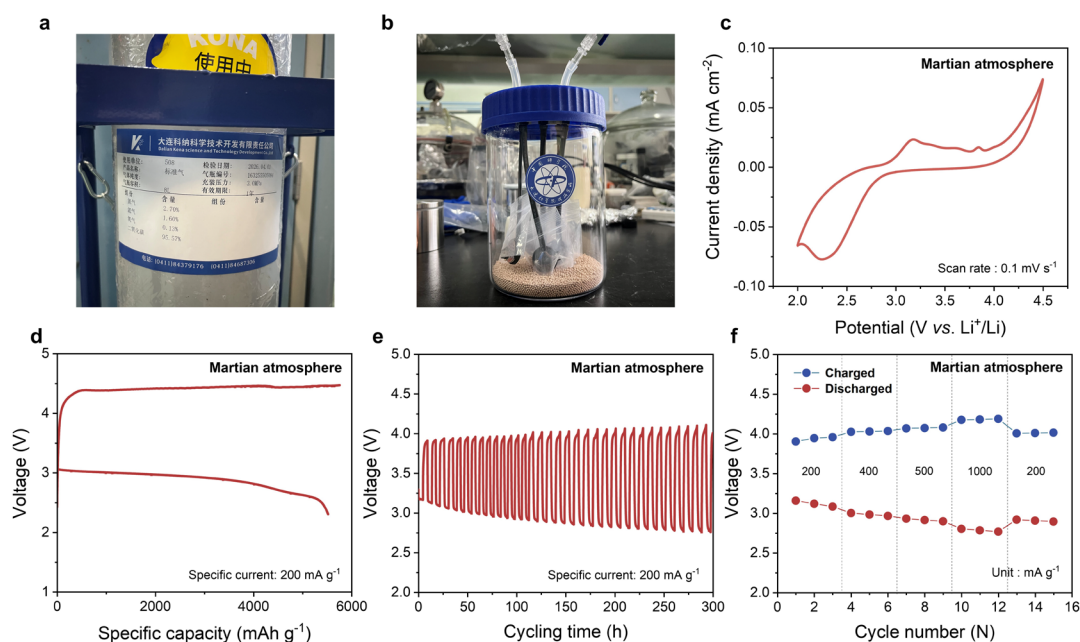
Supplementary Fig. 14 Electrochemical impedance spectra of the Li-CO₂ batteries. Nyquist plots of batteries assembled with LSN-CP/NCNTs, LSN-SS-NCNTs, and LSN-SS-Cu_{AC+SA}@NCNTs cathodes, obtained at 28 ± 1 °C. Light-blue, red and dark-blue open circles represent experimental data for LSN-SS-Cu_{AC+SA}@NCNTs, LSN-SS-NCNTs and LSN-CP/NCNTs, respectively, and the corresponding solid lines represent fitted curves. The inset shows the equivalent circuit used for fitting, in which R_1 – R_3 represent resistance elements, CPE₁ and CPE₂ represent constant-phase elements, and W_1 represents a Warburg diffusion element. The corresponding equivalent-circuit fitting parameters are provided in Supplementary Table 2. LSN, lithium-salt-containing succinonitrile; SS, stainless steel; Cu_{AC+SA}, Cu atomic clusters and single atoms; CP, carbon paper; NCNTs, nitrogen-doped carbon nanotubes. Source data are provided as a Source Data file.



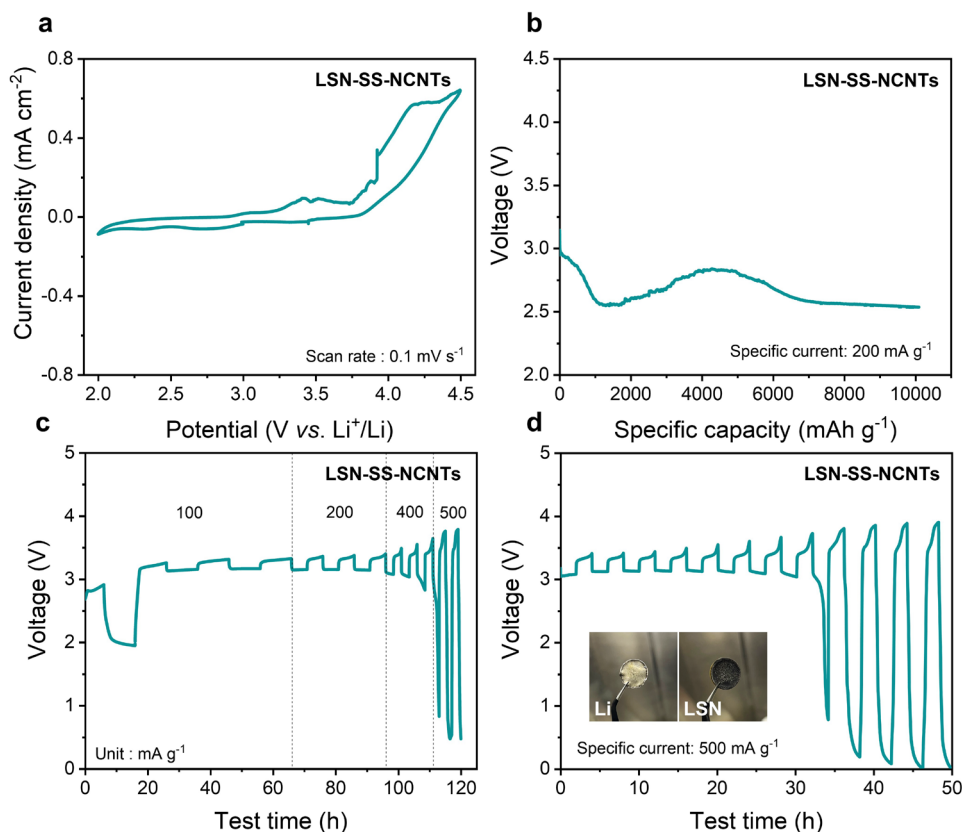
Supplementary Fig. 15 Electrochemical performance of the Li–CO₂ battery using LSN-SS-Cu_{AC+SA}@NCNTs cathodes under CO₂ and Ar atmospheres. **a Cyclic voltammetry curves of the battery tested at a scan rate of 0.1 mV s⁻¹. **b** Full discharge profiles of the battery at a constant specific current. All electrochemical measurements were performed at 28 ± 1 °C. LSN, lithium-salt-containing succinonitrile; SS, stainless steel; Cu_{AC+SA}, Cu atomic clusters and single atoms; NCNTs, nitrogen-doped carbon nanotubes. Source data are provided as a Source Data file.**



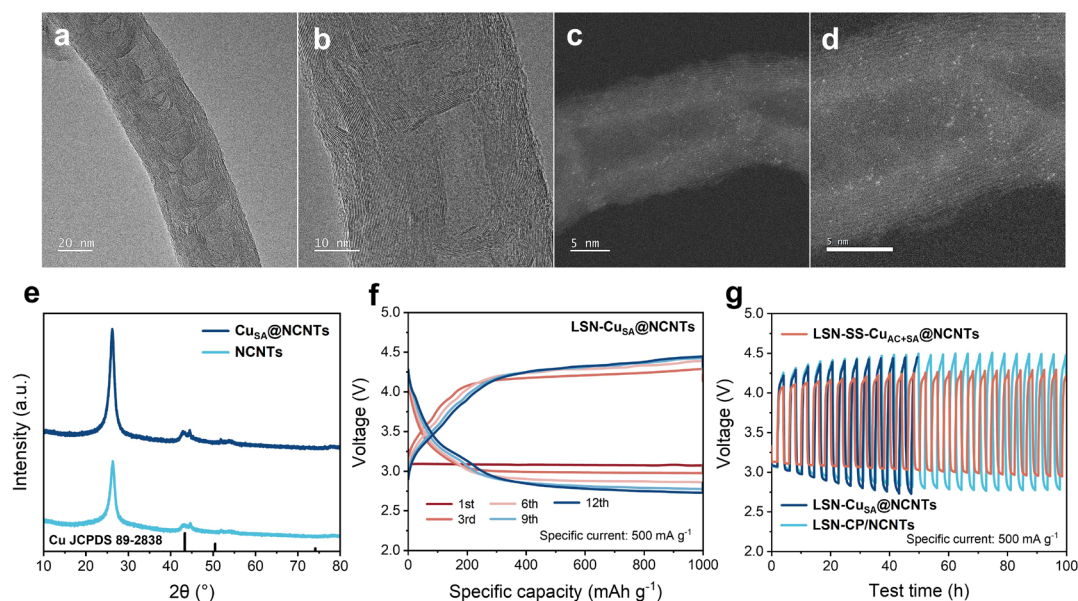
Supplementary Fig. 16 Long-term cycling stability of the all-solid-state Li-CO₂ batteries. Evolution of **a** mid-discharge/charge voltages and **b** corresponding energy efficiencies of batteries employing LSN-CP/NCNTs, LSN-SS-NCNTs, and LSN-SS-Cu_{AC+SA}@NCNTs cathodes. The coin cells were tested at a specific current of 500 mA g⁻¹ and a capacity limit of 1000 mAh g⁻¹ at 28 ± 1 °C. LSN, lithium-salt-containing succinonitrile; SS, stainless steel; Cu_{AC+SA}, Cu atomic clusters and single atoms; CP, carbon paper; NCNTs, nitrogen-doped carbon nanotubes. Source data are provided as a Source Data file.



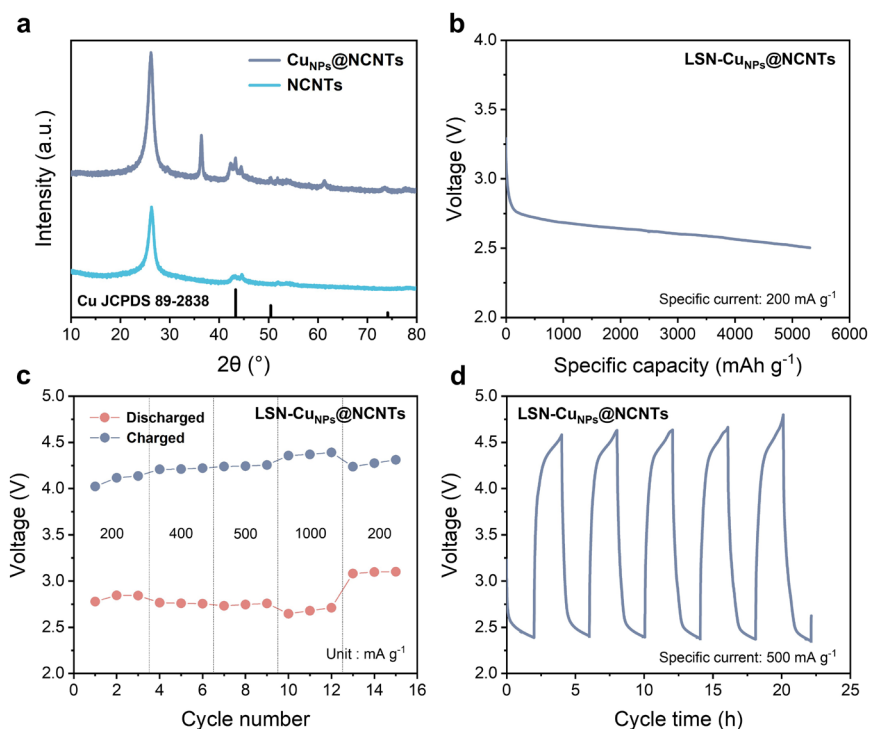
Supplementary Fig. 17 Electrochemical evaluation of the Li-CO₂ battery under a simulated Martian gas composition. Digital photographs of **a** the simulated-gas cylinder and **b** the custom-built testing setup. Electrochemical performance of the LSN-SS-Cu_{AC+SA}@NCNTs cathode under the mixed gas: **c** Cyclic voltammetry curve at 0.1 mV s⁻¹; **d** galvanostatic discharge-charge profiles at 200 mA g⁻¹; **e** voltage evolution during continuous cycling at 200 mA g⁻¹; **f** rate capability at different specific currents. The cycling measurements in **e** were performed using coin cells. Electrochemical measurements in **c-f** were performed at 28 ± 1 °C. Source data are provided as a Source Data file.



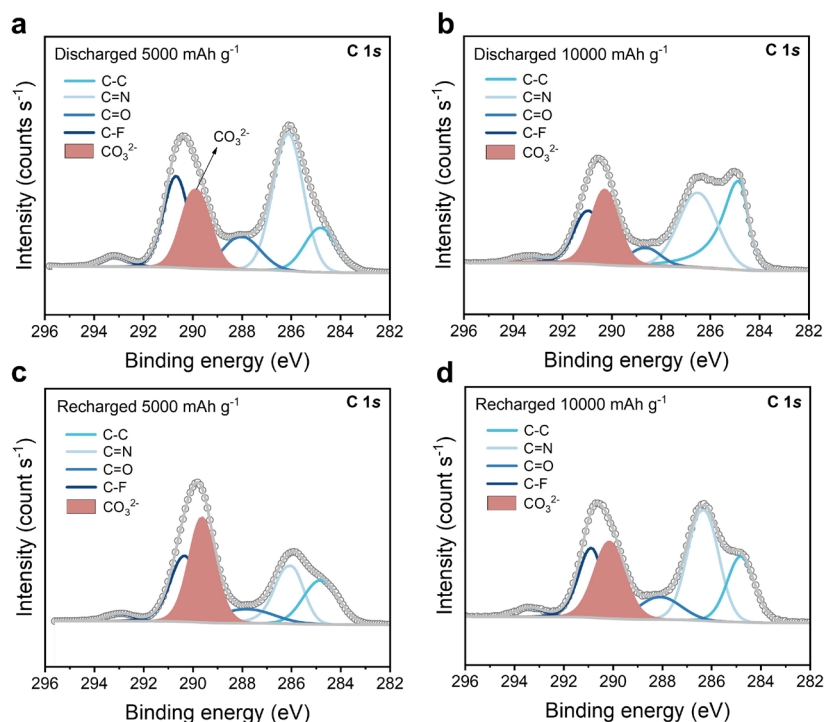
Supplementary Fig. 18 Electrochemical performance of the Li–CO₂ battery using the LSN-based electrolyte and LSN-SS-NCNTs cathode. **a** Cyclic voltammetry curve, **b** full discharge voltage profile at a specific current of 200 mA g^{−1}. **c** Rate capability evaluated at different specific currents. **d** Cycling stability at 500 mA g^{−1}. The insets in **d** show optical images of the Li anode and LSN solid-state electrolyte after cell failure. Photographs of the anode and separator taken in an Ar-filled glovebox after cell disassembly following 50 h of cycling. All electrochemical tests were conducted at 28 ± 1 °C. The cycling measurements in **d** were performed using coin cells. LSN, lithium-salt-containing succinonitrile; SS, stainless steel; NCNTs, nitrogen-doped carbon nanotube. Source data are provided as a Source Data file.



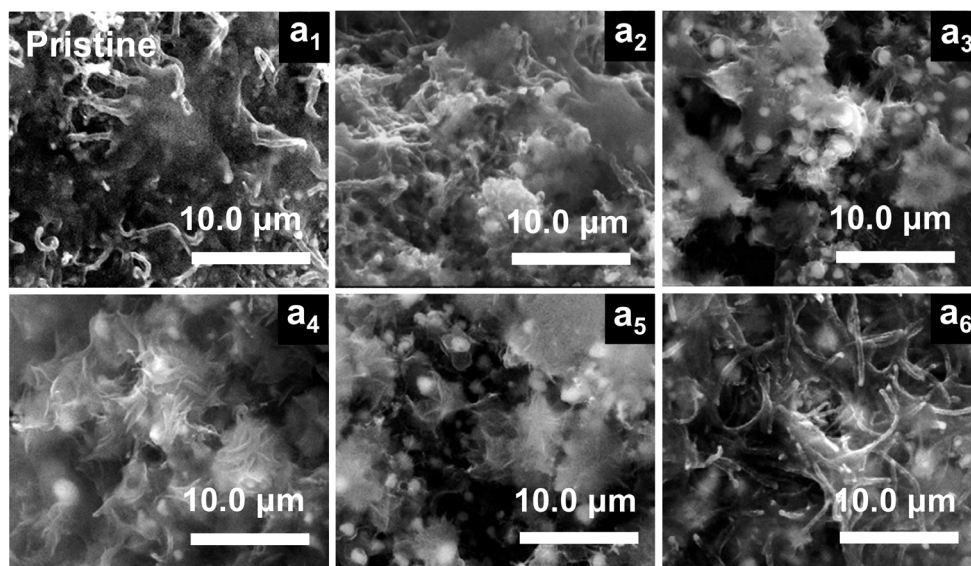
Supplementary Fig. 19 Structural characterization and electrochemical performance of the CuSA control cathode. **a, b** Transmission electron microscopy images and **c, d** High-angle annular dark-field scanning transmission electron microscopy images of CuSA@NCNTs at different magnifications. **e** X-ray diffraction patterns of pristine NCNTs and CuSA@NCNTs. Electrochemical performance of the Li–CO₂ battery with the LSN-CuSA@NCNTs cathode at 500 mA g⁻¹: **f** selected voltage profiles and **g** cycling stability compared with the LSN-SS-CuAC+SA@NCNTs and LSN-CP/NCNTs cathodes. Electrochemical measurements in **f** and **g** were performed at 28 ± 1 °C. The cycling measurements in **g** were performed using coin cells. LSN, lithium-salt-containing succinonitrile; SS, stainless steel; CuSA, Cu single atoms; CuAC+SA, Cu atomic clusters and single atoms; CP, carbon paper; NCNTs, nitrogen-doped carbon nanotube. Source data are provided as a Source Data file.



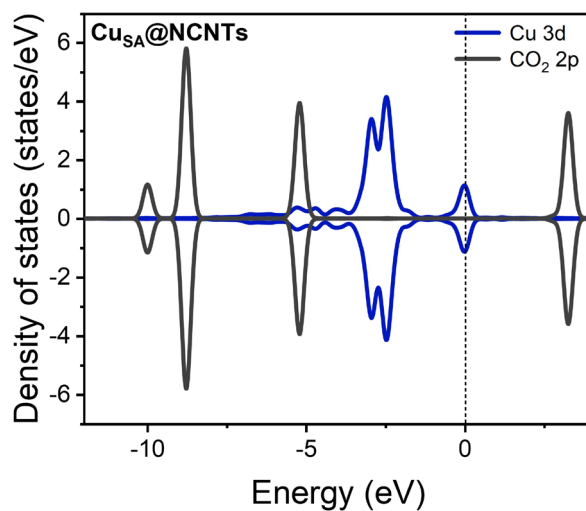
Supplementary Fig. 20 Structural characterization and electrochemical performance of the Cu nanoparticle control cathode. **a** X-ray diffraction patterns of NCNTs and $\text{Cu}_{\text{NPs}}@\text{NCNTs}$. Electrochemical performance of the Li- CO_2 battery with the LSN- $\text{Cu}_{\text{NPs}}@\text{NCNTs}$ cathode: **b** full discharge profile at 200 mA g^{-1} , **c** rate capability, and **d** galvanostatic cycling profile at 500 mA g^{-1} . The measurements shown in **b–d** were conducted at 28 ± 1 $^{\circ}\text{C}$. The cycling measurements in **d** were performed using coin cells. LSN, lithium-salt-containing succinonitrile; Cu_{NPs} , Cu nanoparticles; NCNTs, nitrogen-doped carbon nanotube. Source data are provided as a Source Data file.



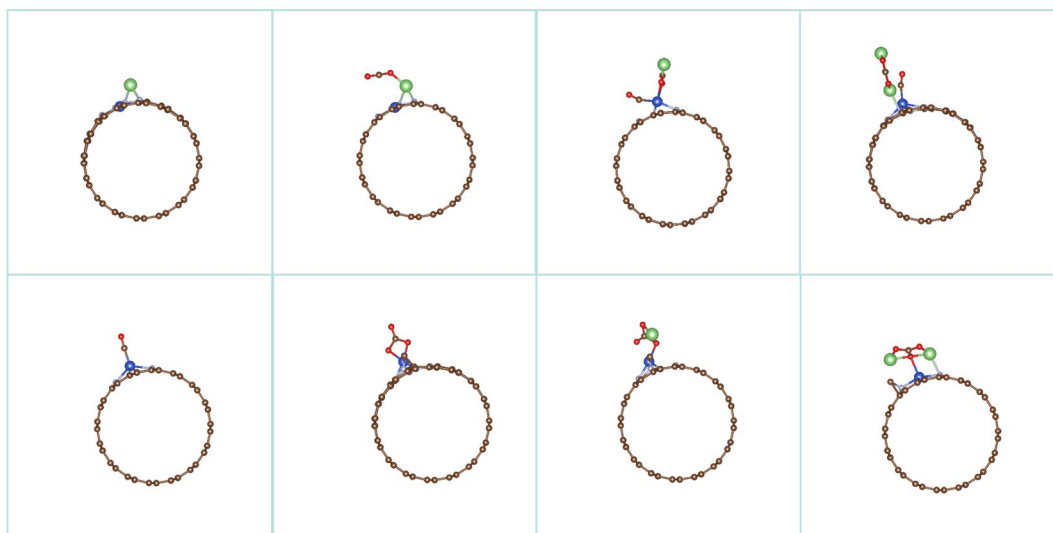
Supplementary Fig. 21 C 1s XPS spectra of the cathode at selected discharge and recharge capacities. Spectra of the LSN-SS-Cu_{AC+SA}@NCNTs cathode collected after the first discharge to **a** 5000 mAh g⁻¹ and **b** 10000 mAh g⁻¹, and after subsequent charging to **c** 5000 mAh g⁻¹ and **d** 10000 mAh g⁻¹. Samples for XPS analyses were obtained from cells operated at 200 mA g⁻¹ and 28 ± 1 °C. LSN, lithium-salt-containing succinonitrile; SS, stainless steel; Cu_{AC+SA}, Cu atomic clusters and single atoms; NCNTs, nitrogen-doped carbon nanotube. Source data are provided as a Source Data file.



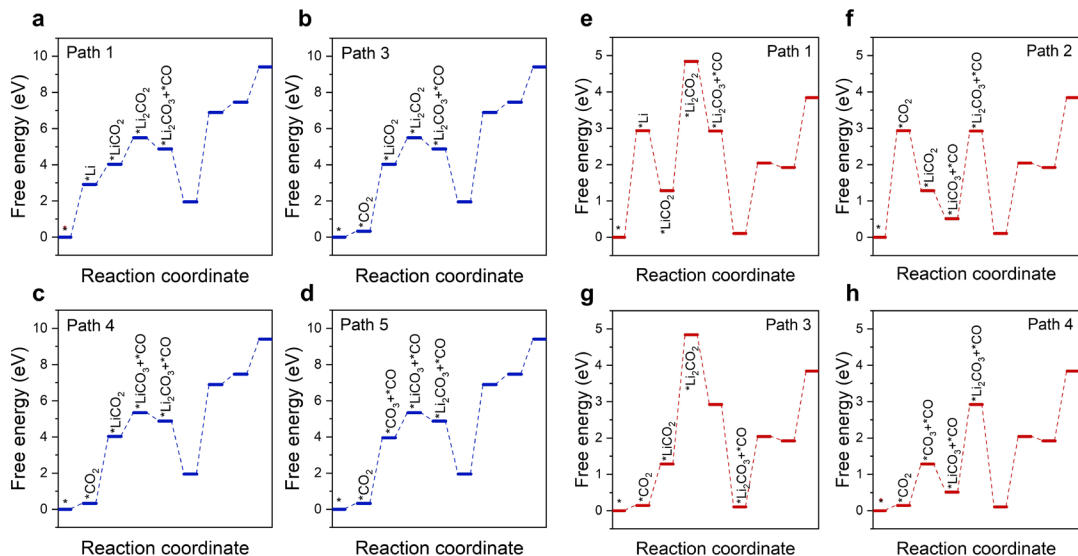
Supplementary Fig. 22 Morphological evolution of the LSN-SS-Cu_{AC+SA}@NCNTs cathode during cycling. **a₁** Scanning electron microscopy (SEM) image of the pristine cathode. **a₂–a₄** SEM images after discharge to 5000, 10000, and 15000 mAh g^{−1}, respectively, showing flake-like discharge products. **a₅, a₆** SEM images after subsequent charging to 5000 and 10000 mAh g^{−1}, respectively, showing the progressive removal of the flake-like products from the cathode surface. The discharged and recharged cathodes for SEM imaging were collected from cells operated at 200 mA g^{−1} and 28 ± 1 °C. LSN, lithium-salt-containing succinonitrile; SS, stainless steel; Cu_{AC+SA}, Cu atomic clusters and single atoms; NCNTs, nitrogen-doped carbon nanotube.



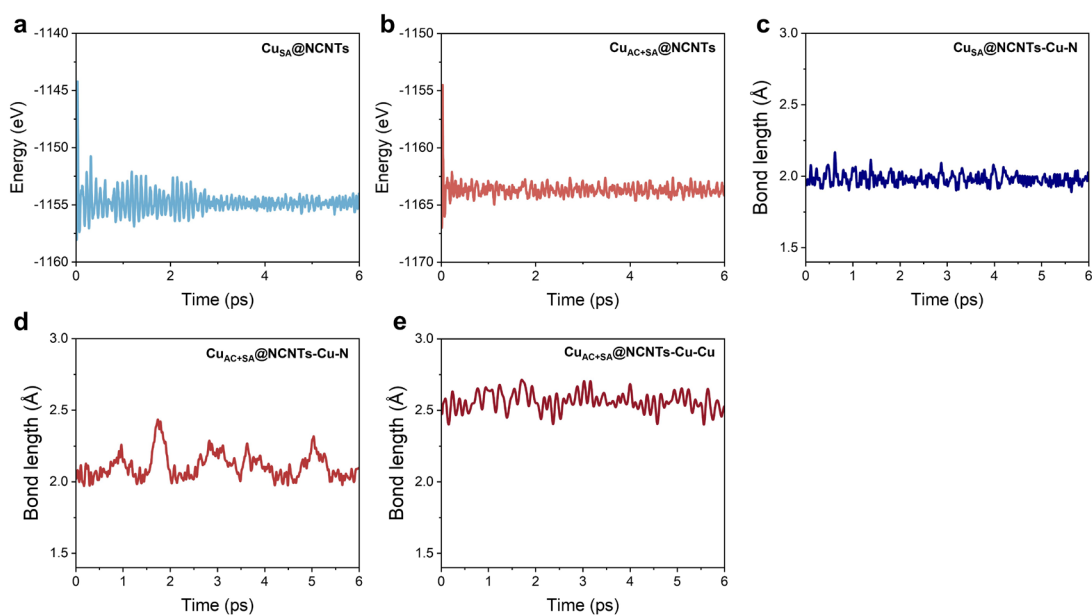
Supplementary Fig. 23 Electron density of state of the Cu_{SA}@NCNTs. Projected density of states of the Cu 3*d* and CO₂ 2*p* orbitals for CO₂ adsorbed on the SS-Cu_{SA}@NCNTs catalyst. The vertical dashed line indicates the Fermi level (set to 0 eV). Cu_{SA}, Cu single atoms; NCNTs, nitrogen-doped carbon nanotube. Source data are provided as a Source Data file.



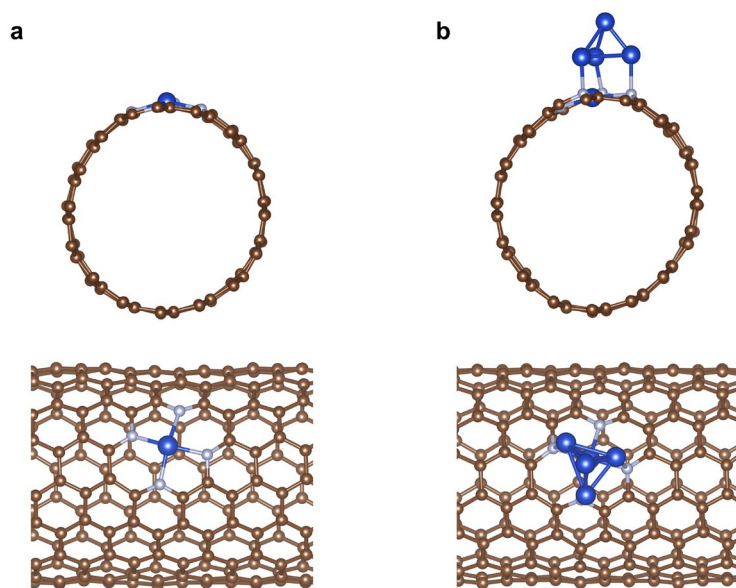
Supplementary Fig. 24 Calculated discharge pathways for Li_2CO_3 formation on $\text{Cu}_{\text{SA}}@\text{NCNTs}$. Brown, blue, grey, red, and green spheres represent C, Cu, N, O, and Li atoms, respectively. Cu_{SA} , Cu single atoms; NCNTs, nitrogen-doped carbon nanotube. Source data are provided as a Source Data file.



Supplementary Fig. 25 Gibbs free-energy diagrams of representative CO₂ reduction pathways on Cu_{SA}@NCNTs (blue profiles) and Cu_{AC+SA}@NCNTs (red profiles). a–d Free-energy profiles of Path 1, 3, 4, and 5 on SS-Cu_{SA}@NCNTs. **e–h** Free-energy profiles of Path 1, 2, 3, and 4 on SS-Cu_{AC+SA}@NCNTs. SS, stainless steel; Cu_{SA}, Cu single atoms; Cu_{AC+SA}, Cu atomic clusters and single atoms; NCNTs, nitrogen-doped carbon nanotube. Source data are provided as a Source Data file.



Supplementary Fig. 26 Total energy and bond-length evolution during *ab initio* molecular dynamics (AIMD) simulations. Total energy fluctuations of **a** $\text{Cu}_{\text{SA}}@\text{NCNTs}$ and **b** $\text{Cu}_{\text{AC+SA}}@\text{NCNTs}$, respectively, during 6 ps AIMD simulations. Evolution of the Cu–N bond length in **c** $\text{Cu}_{\text{SA}}@\text{NCNTs}$ and **d** $\text{Cu}_{\text{AC+SA}}@\text{NCNTs}$. **e** Evolution of the Cu–Cu bond length in $\text{Cu}_{\text{AC+SA}}@\text{NCNTs}$ during the AIMD simulation. Cu_{SA} , Cu single atoms; $\text{Cu}_{\text{AC+SA}}$, Cu atomic clusters and single atoms; NCNTs, nitrogen-doped carbon nanotube. Source data are provided as a Source Data file.



Supplementary Fig. 27 Final structural snapshots of $\text{Cu}_{\text{SA}}@\text{NCNTs}$ and $\text{Cu}_{\text{AC+SA}}@\text{NCNTs}$ after AIMD simulations. side and top views of **a** $\text{Cu}_{\text{SA}}@\text{NCNTs}$ and **b** $\text{Cu}_{\text{AC+SA}}@\text{NCNTs}$ after 6 ps of AIMD simulation. Brown, blue, and grey spheres represent C, Cu, and N atoms, respectively.

The average Cu–N bond length in $\text{Cu}_{\text{SA}}@\text{NCNTs}$ is 1.98 Å, the average Cu–N bond length in $\text{Cu}_{\text{AC+SA}}@\text{NCNTs}$ is 2.10 Å, and the average Cu–Cu bond length within the Cu clusters of $\text{Cu}_{\text{AC+SA}}@\text{NCNTs}$ is 2.56 Å. The Cu–N bond length in the $\text{Cu}_{\text{AC+SA}}@\text{NCNTs}$ model is slightly larger than that in the single-atom $\text{Cu}_{\text{SA}}@\text{NCNTs}$ configuration with equivalent Cu–N₄ coordination, which is ascribed to the increased number of inequivalent Cu–N bonds arising from the Cu–N bonding between the cluster Cu atoms and the N sites of the substrate.

Supplementary Table 1. The best-fitted EXAFS results of Cu sample^a.

Sample	Shell	CN	R (Å)	σ^2 (10^{-2} Å ²)	ΔE_0 (eV)	r-factor
Cu foil	Cu–Cu	12*	2.54 ± 0.003	0.9 ± 0.04	3.2 ± 0.4	0.001
SS-	Cu–N	1.9 ± 0.6	1.92 ± 0.03	0.6 ± 0.9	2.6 ± 2.9	0.012
Cu _{AC+SA} @NCN	Cu–Cu	3.7 ± 0.8	2.53 ± 0.02	0.6 ± 0.2	2.6 ± 2.9	
Ts						
SS-	Cu–N	2.7 ± 0.8	1.94 ± 0.03	0.7 ± 0.7	2.9 ± 3.1	0.01
Cu _{AC+SA} @NCN	Cu–Cu	4.2 ± 1.0	2.54 ± 0.02	0.7 ± 0.2	2.9 ± 3.1	
Ts 5%						

^aCN is the coordination number for the absorber-backscattered pair, R is the average absorber-backscatterer distance, σ^2 is the Debye-Waller factor, and ΔE_0 is the inner potential correction. S_0^2 was fixed to 0.79 as determined from Cu foil fitting. The data range used for data fitting in k -space (Δk) and R -space (ΔR) is 3.0–10.9 Å^{−1} and 1.0–2.8 Å, respectively.

Supplementary Table 2. Equivalent-circuit fitting parameters for the EIS spectra of Li-CO₂ batteries with different cathode configurations.

Sample	LSN-SS-Cu _{AC+SA} @NCNTs	LSN-SS-NCNTs	LSN-CP/NCNTs
R_1 (Ω)	241.9	299.8	3692
R_2 (Ω)	269.8	367.7	4954
CPE1- T	1.9033×10^{-7}	7.497×10^{-8}	1.5298×10^{-7}
CPE1- P	0.69985	0.7650	0.37143
R_3 (Ω)	118.8	307.2	227.7
CPE2- T	5.8514×10^{-6}	1.138×10^{-5}	1.7189×10^{-6}
CPE2- P	0.85414	0.6989	0.91785
W_1 - R (Ω)	187.9	201.9	37663
W_1 - T	0.57512	0.4733	195.4
W_1 - P	0.38205	0.3519	0.67217
χ^2	5.8×10^{-4}	3.8×10^{-4}	7.93×10^{-4}

Supplementary Table 3. Comparison of cell configurations, testing conditions and cycling performance of reported solid-state Li–CO₂ batteries.

A. Cell configurations and cycling performance.

Cathode	Electrolyte type	Cell configuration	specific current (mA g ⁻¹)	Capacity limit (mAh g ⁻¹)	Cycle life (cycles)	Ref
LSN-SS-Cu _{AC} +SA@NC NTs	LSN/LAGP	CR2023 coin cell	500	1000	260	This work
CPE@CNTs	PMA/PEG–LiClO ₄ –3 wt% SiO ₂	CR2023 coin cell	NR	1000	100	20
MCNTs	PEO–LiTFSI–20 wt% LLZTO	CR2023 coin cell	100	1000	70	21
RuO ₂ /SWCNT	LAGP	Pouch cell	50	500	30	22
Ru/CNT	LAGP	CR2023 coin cell	100	500	45	23
MWCNT/PPy	LATP ceramic	NR	60	600	50	24
RuO ₂ /carbon black	PVDF-HFP/LLZTO/SN	NR	200	500	34	25
MWCNT/Ru	LATP	CR2023 coin cell	50	500	50	26
OM-ZIF-8/MWCNTs	OM-ZIF-8/PEO	CR2023 coin cell	NR	1000	133	27
Fe ₃ C/N-doped carbon tubes	LATP-3Zn	CR2025 coin cell	100	500 or 1000	180 or >120	28

B. Electrode specifications and test conditions.

Cathode	Mass loading	Electrode thickness (μm)	Electrolyte amount/thickness	CO ₂ pressure/flow	T (°C)	Ref
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LSN-SS- Cu _{AC+SA} @NC NTs	0.1–0.15 mg cm ⁻² (Cu _{AC+SA} @ NCNTs)	150	0.3–0.34 mg; 0.5 mm	CO ₂ -filled sealed container; pressure/flow NR	28	This work
CPE@CNTs	NR	NR	NR; 0.07– 0.1 mm	CO ₂ -filled sealed container; pressure/flow NR	55	20
MCNTs	0.05–0.1 mg cm ⁻² (MCNTs)	NR	NR	CO ₂ atmosphere; pressure/flow NR	70	21
RuO ₂ / SWCNT	0.3 mg per electrode; mass basis not further specified.	NR	NR; 1 mm	CO ₂ atmosphere; pressure/flow NR	60	22
Ru/CNT	0.15–0.20 mg (Ru/CNT)	NR	NR; 0.3 mm	CO ₂ -purged glass bottle; pressure/flow NR	RT	23
MWCNT/PPy	NR	NR	NR	CO ₂ atmosphere; pressure/flow NR	RT	24
RuO ₂ /carbon black	NR	NR	NR	CO ₂ atmosphere; pressure/flow NR	RT	25
MWCNT/Ru	NR	NR	NR	CO ₂ atmosphere; pressure/flow NR	RT	26
OM-ZIF-8 /MWCNTs	2.1 ± 0.1 mg cm ⁻² (OM-ZIF-8)	NR	NR; 0.1– 0.11 mm	CO ₂ -filled sealed container; pressure/flow NR	60	27
Fe ₃ C/N- doped carbon tubes	0.6 mg of active carbon tube material	NR	NR; 1.0 mm	CO ₂ -filled container; pressure/flow NR	RT	28

T, operating temperature; RT, room temperature. NR, not reported. Exact temperature values for RT measurements were not provided in the original references. Loading refers to the mass of Cu_{AC+SA}@NCNTs per unit geometric electrode area.”

Supplementary Table 4. Comparison of the adsorption energies of all reactants and intermediates on Cu_{SA}@NCNTs. Configurations that led to calculation failures because of potentially unreasonable structures are denoted as “not converged”.

Cu _{SA} @NCNTs	Configuration 1	Configuration 2	Configuration 3
Li	-1159.271	-1159.124	-1159.046
CO ₂	-1180.311	-1180.149	-1180.149
Li ₂ CO ₃	-1193.837	-1193.238	not converged
LiCO ₂	-1181.501	-1181.243	-1181.299
CO ₃ +CO	-1199.890	-1199.566	-1199.381
Li ₂ CO ₂	-1184.873	-1183.240	not converged
LiCO ₃ +CO	-1203.490	not converged	-1203.478
Li ₂ CO ₃ +CO	-1208.884	-1208.258	-1208.390
CO	-1171.668	-1171.467	-1170.615
CO ₃ +C	-1190.063	-1189.645	-1189.373
LiCO ₃ +C	-1194.420	not converged	not converged
Li ₂ CO ₃ +C	-1197.395	-1195.884	not converged

Supplementary Table 5. Comparison of the adsorption energies of all reactants and intermediates on Cu_{AC+SA}@NCNTs. Configurations that led to calculation failures because of potentially unreasonable structures are denoted as “not converged”.

Cu_{AC+SA}@NCNTs	Configuration 1	Configuration 2	Configuration 3
Li	-1168.191	-1168.335	-1168.360
CO ₂	-1189.358	-1189.392	-1189.368
Li ₂ CO ₃	-1203.611	-1203.984	-1203.689
LiCO ₂	-1192.173	-1193.182	-1192.220
CO ₃ +CO	-1212.930	-1212.207	-1212.290
Li ₂ CO ₂	-1194.511	-1194.221	-1194.219
LiCO ₃ +CO	-1217.296	-1216.901	-1216.874
Li ₂ CO ₃ +CO	-1219.891	-1219.809	-1219.841
CO	-1182.206	-1182.404	-1181.114
CO ₃ +C	-1203.872	-1202.753	-1203.885
LiCO ₃ +C	-1207.812	-1207.600	not converged
Li ₂ CO ₃ +C	not converged	-1210.789	not converged

Supplementary Table 6. Calculated Gibbs free energy changes (ΔG , eV) for the reaction steps along the discharge pathway.

	$\Delta G1$	$\Delta G2$	$\Delta G3$	$\Delta G4$	$\Delta G5$	$\Delta G6$	$\Delta G7$	$\Delta G8$
Cu _{AC+SA} NCNTs	0.146	-0.166	0.531	2.412	-2.816	1.937	-0.123	1.919
Cu _{SA} @NCNTs	2.918	1.112	1.310	-0.466	-2.924	4.943	0.573	1.946

$\Delta G1$: Gibbs free energy change for the initial adsorption of CO₂ molecule onto the bare catalyst surface. $* + \text{CO}_2 \rightarrow *\text{CO}_2$ for Cu_{AC+SA}@NCNTs, and $* + \text{Li}^+ + \text{e}^- \rightarrow *\text{Li}$ for Cu_{SA}@NCNTs.

$\Delta G2$: Free energy change for the first C–O bond cleavage and molecular coupling, forming $*\text{CO}_3$ and $*\text{CO}$ intermediates. $*\text{CO}_2 + \text{CO}_2 \rightarrow *\text{CO}_3 + *\text{CO}$ for Cu_{AC+SA}@NCNTs, and $*\text{Li} + \text{CO}_2 \rightarrow *\text{LiCO}_2$ for Cu_{SA}@NCNTs.

$\Delta G3$: Free energy change for the first lithiation step of the carbonate intermediate. $*\text{CO}_3 + *\text{CO} + \text{Li}^+ + \text{e}^- \rightarrow *\text{LiCO}_3 + *\text{CO}$ for Cu_{AC+SA}@NCNTs, $*\text{LiCO}_2 + \text{CO}_2 \rightarrow *\text{LiCO}_3 + *\text{CO}$ for Cu_{SA}@NCNTs.

$\Delta G4$: Free energy change for the second lithiation step, yielding the first formula unit of solid $*\text{Li}_2\text{CO}_3$. $*\text{LiCO}_3 + *\text{CO} + \text{Li}^+ + \text{e}^- \rightarrow *\text{Li}_2\text{CO}_3 + *\text{CO}$ for both Cu_{AC+SA}@NCNTs and Cu_{SA}@NCNTs.

$\Delta G5$: Free energy change for the precipitation/desorption of the formed Li₂CO. $*\text{Li}_2\text{CO}_3 + *\text{CO} \rightarrow *\text{CO} + \text{Li}_2\text{CO}_3$ for both Cu_{AC+SA}@NCNTs and Cu_{SA}@NCNTs.

$\Delta G6$: Free energy change for the deep reduction of $*\text{CO}$ to form solid C alongside the generation of a second $*\text{CO}_3$. $*\text{CO} + \text{CO}_2 \rightarrow *\text{CO}_3 + *\text{C}$ for both Cu_{AC+SA}@NCNTs and Cu_{SA}@NCNTs.

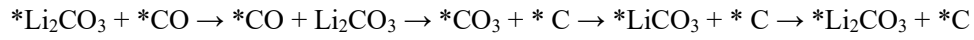
$\Delta G7$: Free energy change for the third lithiation step, acting on the newly formed carbonate intermediate. $*\text{CO}_3 + *\text{C} + \text{Li}^+ + \text{e}^- \rightarrow *\text{LiCO}_3 + *\text{C}$ for both Cu_{AC+SA}@NCNTs and Cu_{SA}@NCNTs.

$\Delta G8$: Free energy change for the final lithiation step, generating the second Li₂CO₃ unit

and completing the discharge product formation. $*LiCO_3 + *C + Li^+ + e^- \rightarrow *Li_2CO_3 + *C$ for both $Cu_{AC+SA}@NCNTs$ and $Cu_{SA}@NCNTs$.

Supplementary Table 7. The reaction pathways of Li_2CO_3 and C as discharge products in Li- CO_2 battery.

Path 1	$* \rightarrow * \text{Li} \rightarrow * \text{LiCO}_2 \rightarrow * \text{Li}_2\text{CO}_2 \rightarrow * \text{Li}_2\text{CO}_3 + * \text{CO}$
Path 2	$* \rightarrow * \text{Li} \rightarrow * \text{LiCO}_2 \rightarrow * \text{LiCO}_3 + * \text{CO} \rightarrow * \text{Li}_2\text{CO}_3 + * \text{CO}$
Path 3	$* \rightarrow * \text{CO}_2 \rightarrow * \text{LiCO}_2 \rightarrow * \text{Li}_2\text{CO}_2 \rightarrow * \text{Li}_2\text{CO}_3 + * \text{CO}$
Path 4	$* \rightarrow * \text{CO}_2 \rightarrow * \text{LiCO}_2 \rightarrow * \text{LiCO}_3 + * \text{CO} \rightarrow * \text{Li}_2\text{CO}_3 + * \text{CO}$
Path 5	$* \rightarrow * \text{CO}_2 \rightarrow * \text{CO}_3 + * \text{CO} \rightarrow * \text{LiCO}_3 + * \text{CO} \rightarrow * \text{Li}_2\text{CO}_3 + * \text{CO}$



Competing interests

The authors declare no competing interests.