A hierarchical monolithic Co-single-atom electrode for efficient hydrogen peroxide production in acid

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Preparation of Co_1/NC. A typical 3-electrode cell was constructed with graphene nanosheets/carbon paper as a working electrode, a graphite rod as a counter electrode, and a saturated calomel electrode (SCE) as a reference electrode. The electrolyte is a mixture solution containing 4.5 mL of HNO_3, 3.4 mL of aniline, and 42.1 mL of water. Aniline was polymerized onto the surface of graphene nanosheets by a potentiostatic method (0.7 V, 120s) in the cell, and PANI/GN was obtained. Then, PANI/GN was washed thoroughly and dried at 60 ℃ overnight. Next, PANI/GN was vertically placed in the $K_3[Co(CN)_6]$ solution at 45 ℃ for 4h under stirring to trap Co atoms. Again, this precursor should be washed thoroughly and dried. Calcination process was conducted at 750 ℃ under Ar atmosphere with a ramp rate of 1.5 ℃/min and the temperature was kept for 2h, followed by acid leaching. The obtained sample was denoted as Co_1/NC.

Preparation of NC. The synthesis procedure of NC is the same as the preparation of Co_1/NC except the step of introduction of Co atoms.

Characterization. The morphology was collected by FESEM (JEOL JSM-6700F) and TEM (JEOL JEM-2100F). Sub-angstrom-resolution high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) was performed on a JEOL JEMARM200F STEM/TEM. The crystal structure was examined by XRD (Bruker AXS D8 Advance). The mass content of Co in Co_1/NC was measured by ICP-OES (PerkinElmer). XPS was conducted on an ESCALAB 250 photoelectron spectrometer (Thermo Fisher Scientific) using a monochromatic Al Kα X-ray beam (1486.6 eV). All binding energies were calibrated to the C 1s peak (284.6 eV) arising from the adventitious carbon-containing species. X-ray absorption spectroscopy (XAS) was collected by employing synchrotron radiation light source at BL14W1 beamline of Shanghai Synchrotron Radiation Facility (SSRF) at room temperature. Energy calibration was performed with a Co foil standard by shifting all spectra to a glitch in the incident intensity.

Electrochemical measurements. A three-electrode system was employed to measure the electrochemical performance in an H-type cell. The measurements were conducted on CHI 660E workstation with a graphite rod as a counter electrode and a saturated Ag/AgCl as a reference electrode. 0.1 M O_2-saturated $HClO_4$ was used as the electrolyte.

Device assembly. The flow cell contains three components: the cathode part, the anode part, and the membrane. The whole cell is filled with 0.1 M $HClO_4$.

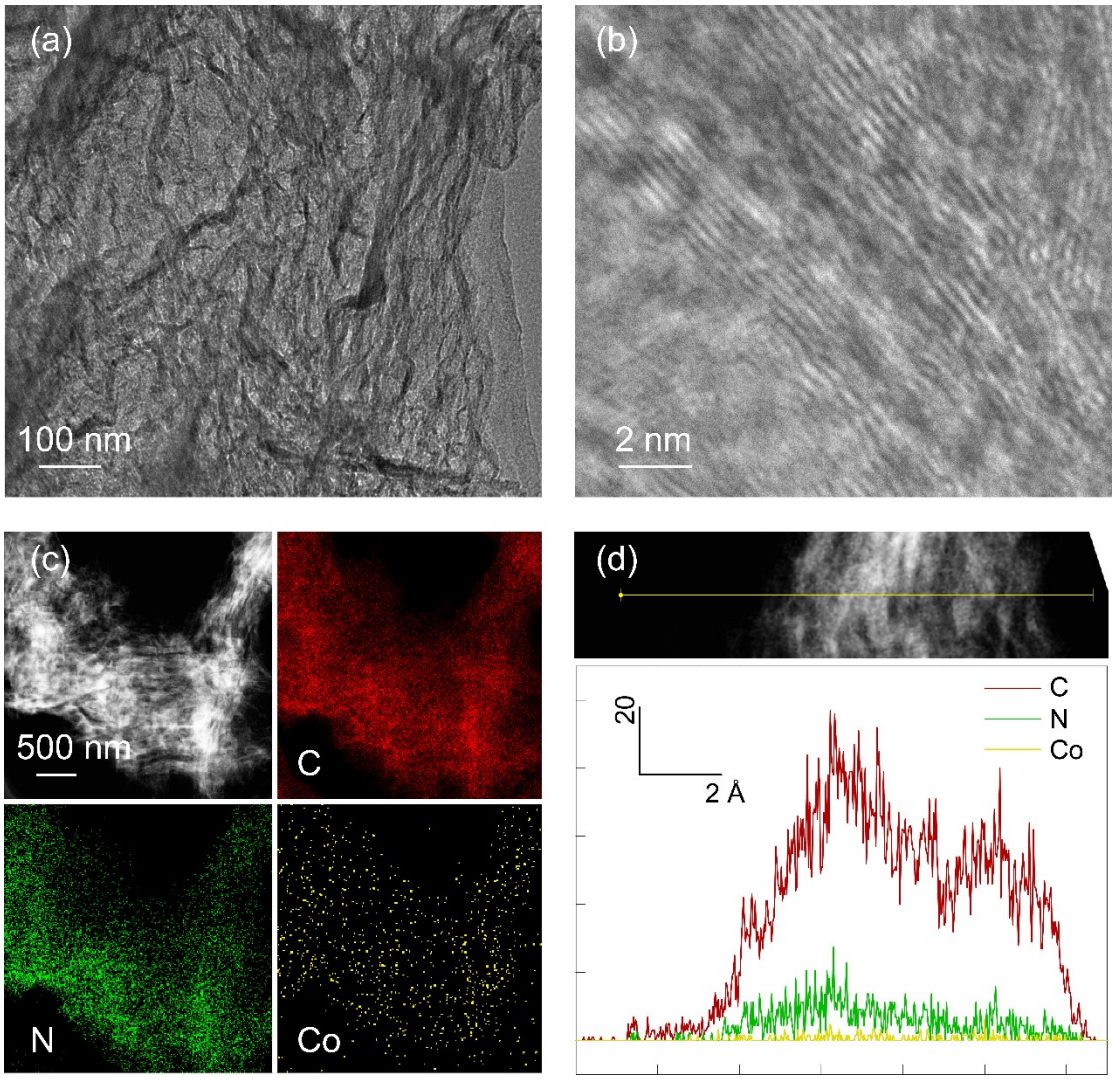

Figure S1 (a-b) TEM images of Co_1/NC. (c) EDS elemental mappings of Co_1/NC. (d) Line scans of Co_1/NC.

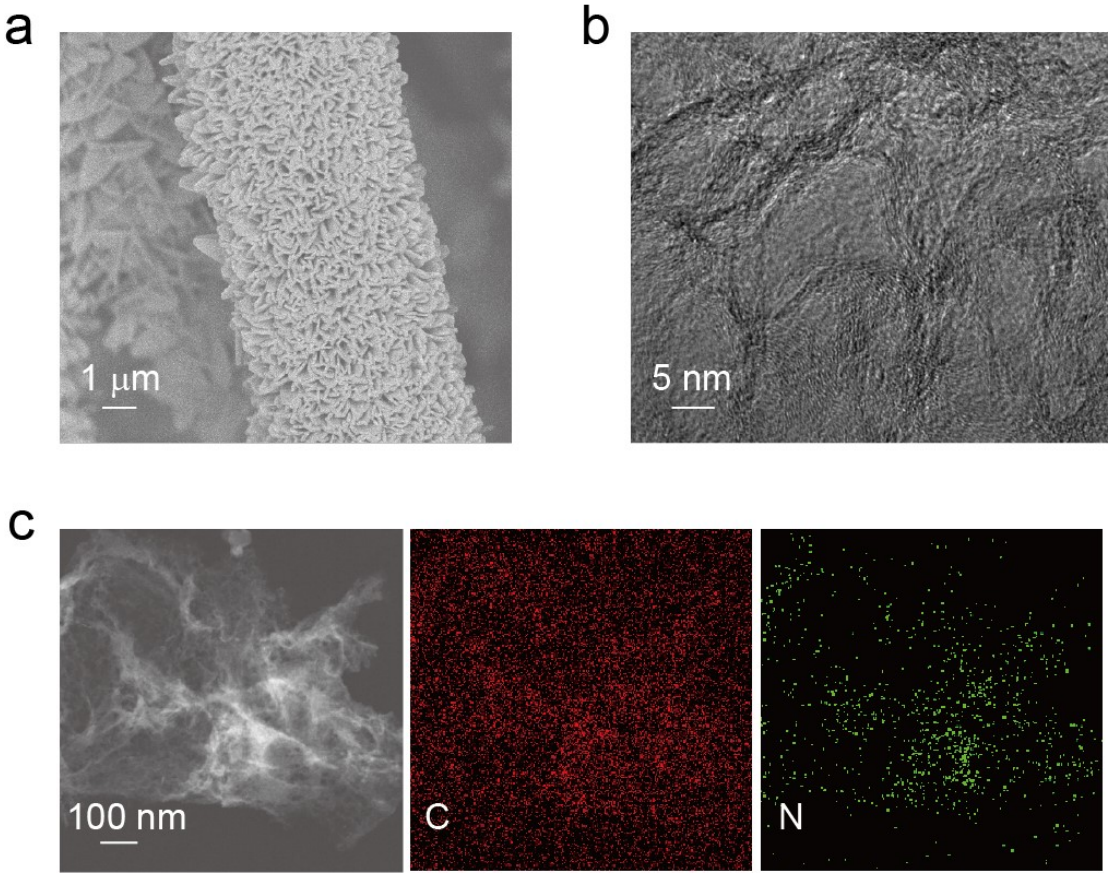

Figure S2. SEM (a), HR-TEM (b) and EDS elemental mappings (c) images of NC.

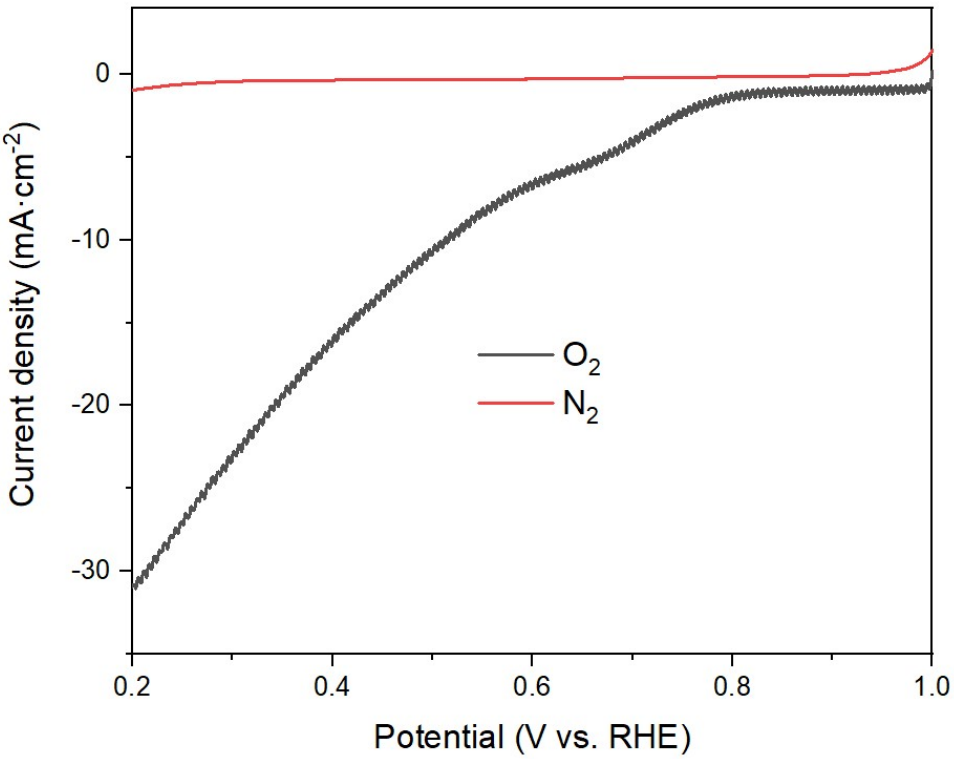

Figure S3 LSV curves of Co_1/NC measured in N_2-saturated and O_2-saturated solution.

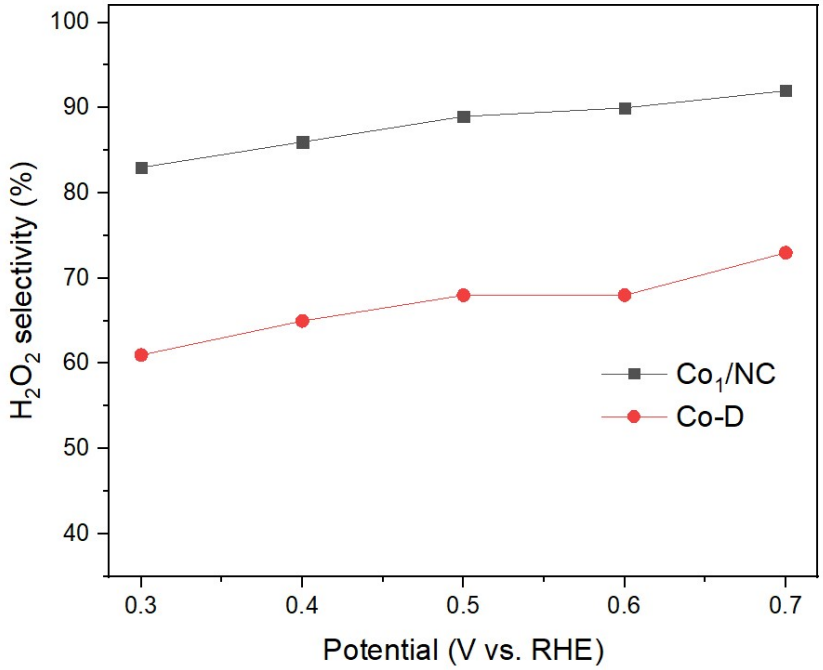

Figure S4 H_2O_2 selectivity of Co_1/NC and Co-D.

Table S1 Fitting parameters of the EXAFS of the Co_1/NC.

name	N	S02	sigma^2	e0	delr	Reff	R
Co(K)-N	0.900	4.020	0.00793	-5.573	-0.01989	1.90000	1.88011
name	ei	third	fourth				
Co(K)-N	0.00000	0.00000	0.00000				

Table S2 Performance of various H_2O_2 flow cells.

Catalyst	Production rate (mol/kg_{cat}/h)	Ref
Co_1/NC	606	This work
CoN_2C_x	117	[1]
2.5% Pd/XC-72	129	[2]
Au@SiO_2	24.8	[3]

References

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