

Supporting information (SI)

Efficient electrocatalysts for biomass quasi-solid-state Li-O₂ batteries: porous nanocages with nickel-cobalt-N/C active species

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Experimental section

Materials preparation

Typically, cobalt (II) nitrate hexahydrate (2 mmol) was dissolved ultrasonically in 50 mL of methanol to form a clear purple solution. Next, 50 mL of methanol containing 2-Methylimidazole (2-MeIM, 8 mmol) was added dropwise into the solution above under mild stirring treatment. After continuing stirring for 20 min, the resulting solution was transferred and kept at 25 °C for 24 hours. The ZIF-67 nanoparticles were then collected by symmetric centrifugation, washed with methanol several times to remove the excess ions and residues, and dried at 80 °C under vacuum. As for the carbonization, the solid-precursor was kept under an Ar atmosphere for 5 min in a furnace before elevating the temperature, then performed the carbonization at 750 °C for 3 h with a heating rate of

5 °C min⁻¹. Finally, after washed with 0.5 M H₂SO₄ solution to remove unstable metal species, a fine black powder (the CNC sample) was obtained after drying at 60 °C under vacuum.

Characterization

The TG studies were carried out using a NETZSCH TG 209F1 thermogravimetric analyzer.

The crystal structure was characterized by X-ray diffraction (XRD, Bruker D8 Advance X-ray diffractometer) with high-intensity Cu-K α radiation ($\lambda=0.15406$ nm). Scanning electron microscopy (FESEM, Hitachi S-4800, Hitachi Corp., Japan) and transmission electron microscopy (TEM, JEM-2100F) were used to observe the morphology. X-ray photoelectron spectroscopy (XPS) analysis was performed with an RBD-equipped PHI-5000C ESCA system (Perkin-Elmer Co., USA) using monochromatic Al K α radiation ($h\nu = 1486.6$ eV). Raman spectra were recorded using a Raman spectrometer (InVia Reflex, Renishaw Corp., UK) coupled to a microscope in reflection mode with a 633 nm excitation laser source. The specific surface area was evaluated using the Brunauer-Emmett-Teller equation (BET) on a Tristar 3020 instrument (Micromeritics Corp., USA) at the temperature of liquid nitrogen. The pore size distribution was investigated using the Barrett-Joyner-Halenda (BJH) method derived from the desorption isotherm.

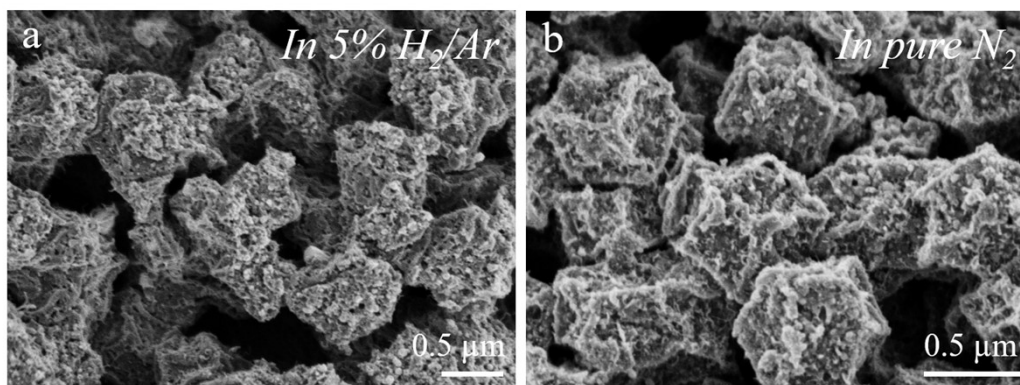


Fig. S1 SEM images of NC-ZIFs after annealing in (a) 5% H₂/Ar mixed atmosphere and (b) pure N₂ atmosphere.

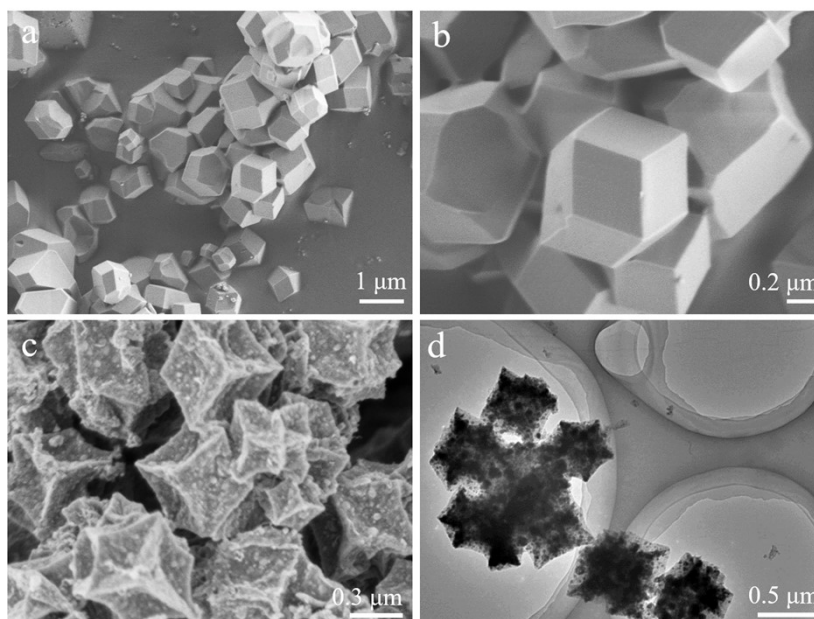


Fig. S2 (a) Low- and (b) high-magnified FESEM images of ZIF-67; (c) FESEM image and (d) low TEM image of CNC sample, respectively.

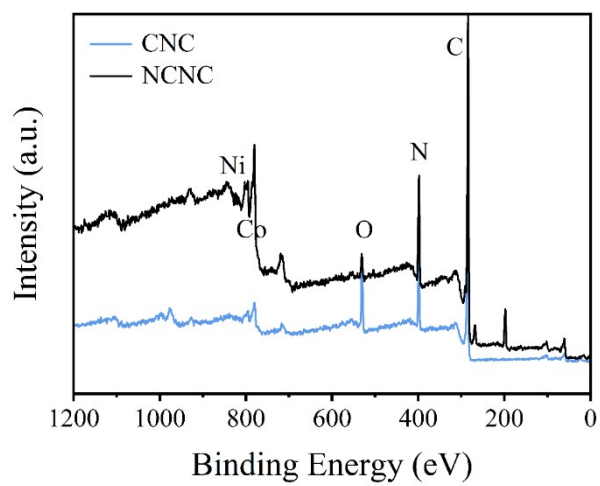


Fig. S3 The XPS survey spectrum of NCNC and CNC catalysts.

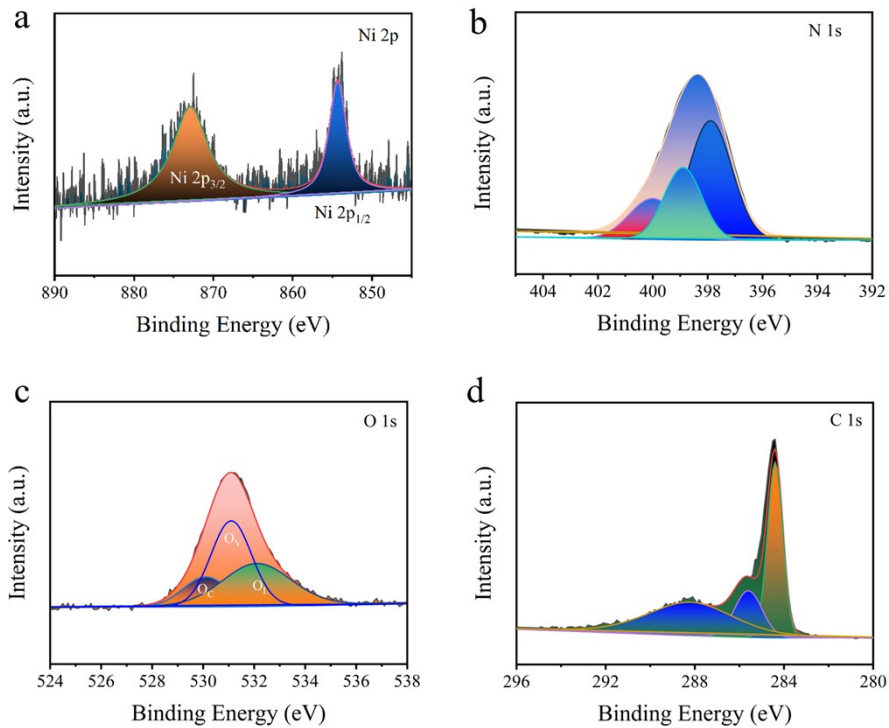


Fig. S4 The high-resolution XPS spectra of (a) Ni 2p, (b) N 1s, (c) O 1s and (d) C 1s in NCNC catalyst, respectively.

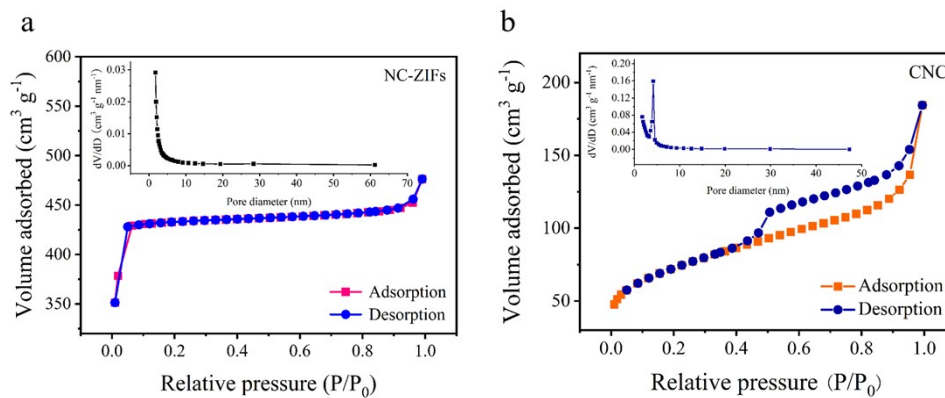


Fig. S5 N₂ adsorption–desorption isotherms and pore-size distribution of (a) NC-ZIFs and (b) CNC sample, respectively.

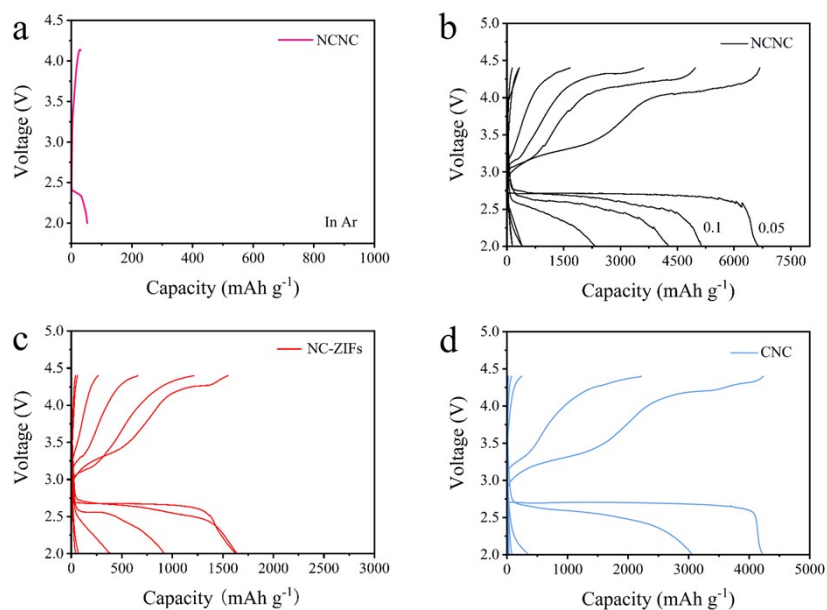


Fig. S6 (a) the discharge-charge profiles at 0.05 mA cm^{-2} of NCNC cathode-based cell in pure Ar; the rate performance of the discussed cathodes from 0.05 mA cm^{-2} to 0.5 mA cm^{-2} : (b) NCNC, (c) NC-ZIFs, and (d) CNC cathodes.

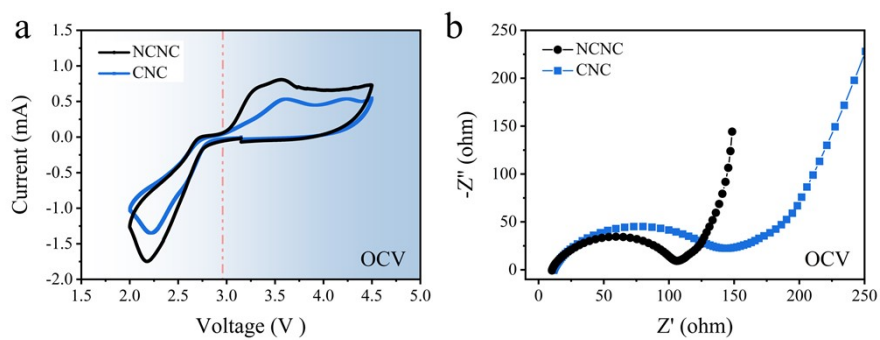


Fig. S7 Electrochemical performance of NCNC and CNC cathodes. (a) CV curves at a scan rate of 0.5 mV/s and (b) Nyquist plots of the NCNC electrode (in black) and CNC electrode (in blue) before discharge.

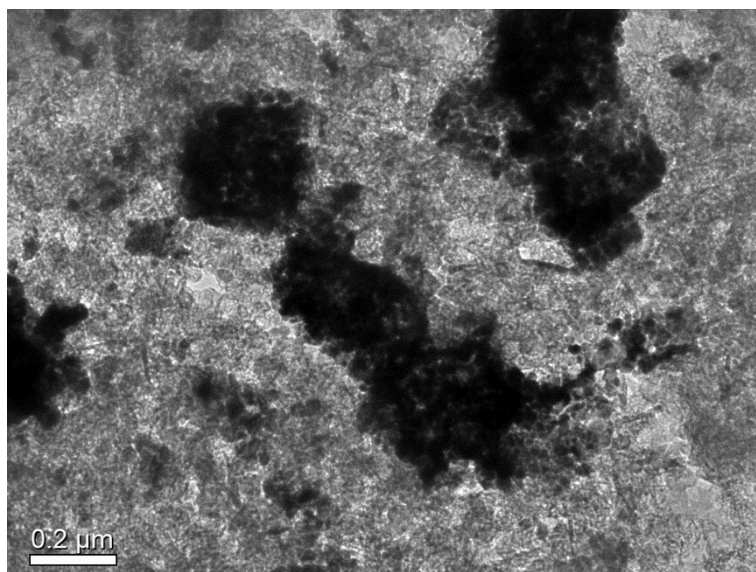


Fig. S8 The TEM image of NCNC cathode after full discharge