Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Supporting Information

An Efficient, Bifunctional Catalyst for Lithium-Oxygen Battery through Tuning Exterior Co^{2+}/Co^{3+} Ratio of CoO_x on N-doped Carbon Nanofibers

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Experimental Methods

Synthesis of CoO_x nanoparticles Decorated N-doped Carbon Nanofibers (CoO_x@NCF): The CoO_x@NCF was synthesized via an electrospinning method combined with subsequent heat treatment. Briefly, 2 g $Co(CH_3COO)_2\cdot 4H_2O$ and 2.1 g polyacrylonitrile (PAN, Mw=150,000) were added into 15 mL N, N-dimethylformamide (DMF) under vigorous stirring to form a homogeneous solution overnight. Then the prepared solution was transferred into 20 mL plastic syringe with a 24-gauge metal nozzle. In the electrospinning process, a flow rate of 0.6 mL h^{-1} was used for the solution and the distance between the collector of aluminum foil and the needle was kept 20 cm. The applied negative and positive voltage was fixed to -2.0 kV and 20.0 kV, respectively. After that, the obtained nanofiber film was stabilized at 250 ºC for 2 h in air and was maintained at 800 ºC for 1 h in Ar atmosphere for carbonization (named as CoO_x@NCF-800). Finally, the carbonized product was further reoxidized to 280 ºC and remained for 1 h (denoted as CoO_x@NCF). Additionally, the pure N-doped carbon nanofibers was prepared without adding the $Co(CH_3COO)_2\cdot 4H_2O$ and named as NCF.

Materials characterization: Powder X-ray diffraction (XRD) was used to characterize the crystal structure of samples on a PANalytical X'Pert^3 Powder diffractometer with Cu Kα radiation (λ = 1.5418, 40 kV, 40 mA) in the 2θ range of 10-80°. Morphologies of CoO_x@NCF, NCF and cathodes were performed on a field-emission scanning electron microscope (FESEM, NOVA NANOSEM 450) and transmission electron microscope (TEM, Tecnai G2 F20). Nitrogen adsorption-desorption measurements were carried out to investigate the porous structure at 77 K with a Micromeritcs ASAP-2046 analyzer. The pore diameter distribution and pore volume were determined from adsorption branches of the isotherms by the Barrett-Joyner-Halenda (BJH) model. The thermal stability was evaluated by Simultaneous Thermal Analyzer (STA 449F3, NETZSCH, Germany) ranging from 25 ºC to 600 ºC with a heating rate of 10 ºC min^{-1} in hybrid atmosphere of Ar and O_2 (volume ratio of 1:1). X-ray photoelectron spectroscopy (XPS) spectra were analyzed by Thermo escalab 250Xi with C1s value of 284.7 eV. The Raman spectra were recorded (HORIBA, LabRAM HR Evolution) with an exciting wavelength of 532 nm. The conductivity of products was characterized by RTS-9 four-point probe method referred to aluminum foil value of 4.532 S cm^{-1}.

Electrochemical Measurement: The typical 2032 coin cells with a few of holes were used to investigate the electrochemical performance of Li-O_2 batteries. The Li-O_2 cells were assembled in an argon-filled glove box with water and oxygen levels less than 0.01 ppm. The oxygen cathodes were prepared by mixing 60 wt% CoO_x@NCF or NCF, 30 wt% super P, and 10 wt% polyvinylidene fluoride (PVDF) in N-methyl-2-pyrrolidone (NMP), then the slurry was casted onto carbon paper with a diameter of 12 mm as current collector. Subsequently, the prepared carbon papers were put in an oven at 80 °C for 2 h, then dried at 120 °C for 12 h under vacuum. The total loading cathode mass was about 0.7±0.1 mg cm^{-2}. Tetraethlene glycol dimethyl ether (TEGDME) containing 1 M lithium bis-(trifluoromethanesulfony)-imide (LiTFSI) was served as electrolyte. In addition, glass fiber filters (Whatman GF/D) and lithium foils were acted as separator and anode, respectively. Finally, a dry plastic box filled with pure oxygen atmosphere was used to test the Li-O_2 cells. Galvanostatic discharge-charge tests were performed on LAND battery system in the voltage range of 2.2-4.4 V (vs. Li^+/Li) and the Li-O_2 cells were rested at least 4 hours at room temperature before measurements. Both linear sweep voltammograms (LSV) and cyclic voltammetry (CV) measurements were carried out on a CHI 660E electrochemical workstation at a scan rate of 1 mV s^{-1}. The specific capacity of the electrodes were normalized based on the total mass of super P and CoO_x@NCF or NCF.

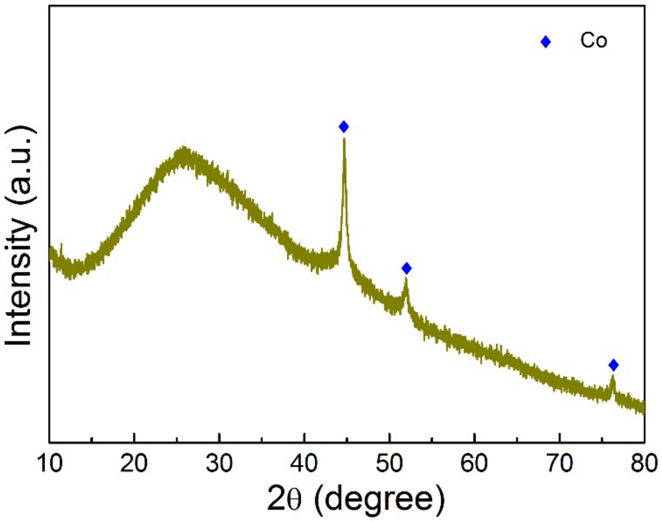

Fig. S1 The XRD patterns of CoO_x@NCF after 800 ºC in Ar.

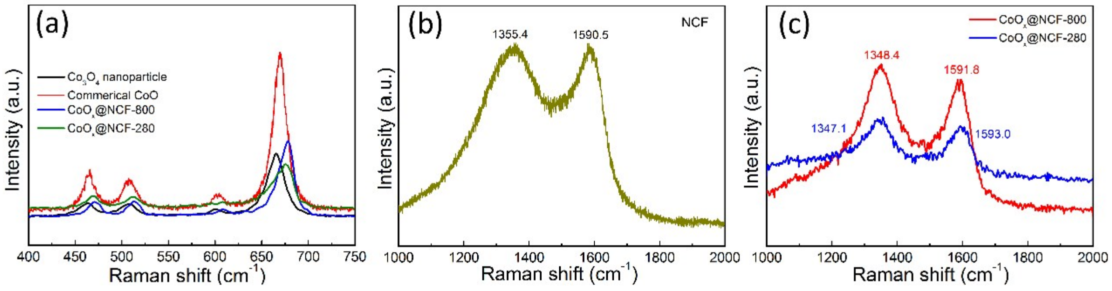

Fig. S2 Raman spectra of Co_3O_4 nanoparticle with 35 nm, commercial CoO, CoO_x@NCF-800 and CoO_x@NCF-280 from 400-750 cm^{-1}(a). Raman spectra of NCF, CoO_x@NCF-800 and CoO_x@NCF-280 from 1000-2000 cm^{-1}(b) and (c), respectively.

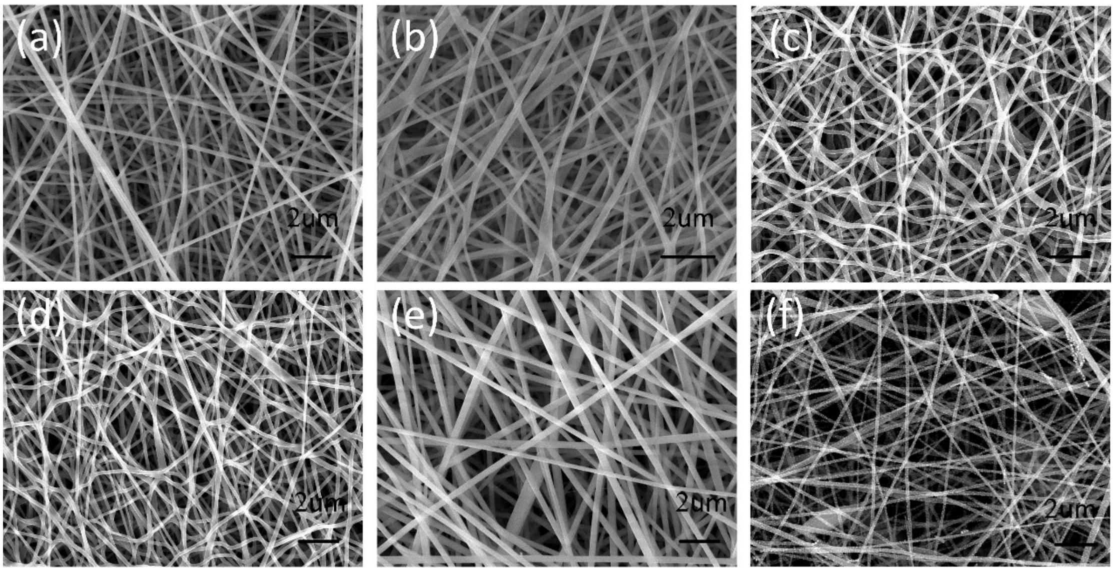

Fig. S3 The SEM images of NCF at initial electrospun film (a), 250 ºC (b), 800 ºC (c), 280 ºC (d) and CoO_x@NCF at 250 ºC (e), 800 ºC (f).

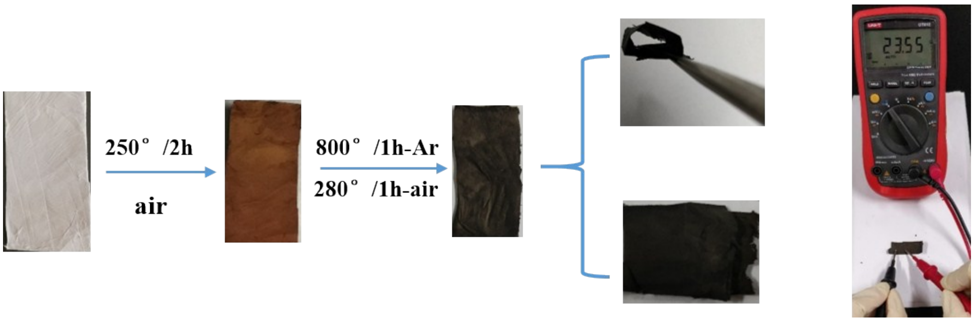

Fig. S4 The optical photographs of products at different states and the exhibition of flexible and conductivity performance.

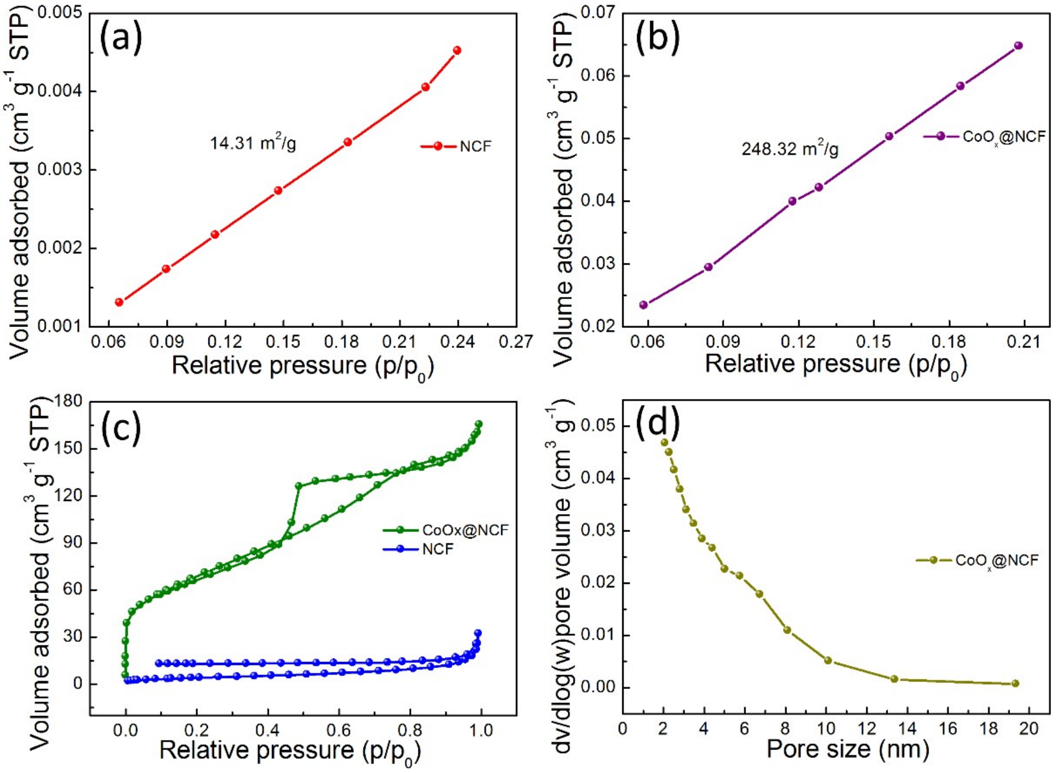

Fig. S5 S_{BET} curves of NCF (a) and CoO_x@NCF (b); Nitrogen adsorption-desorption isotherms of two samples (c); The pore size distribution of CoO_x@NCF (d).

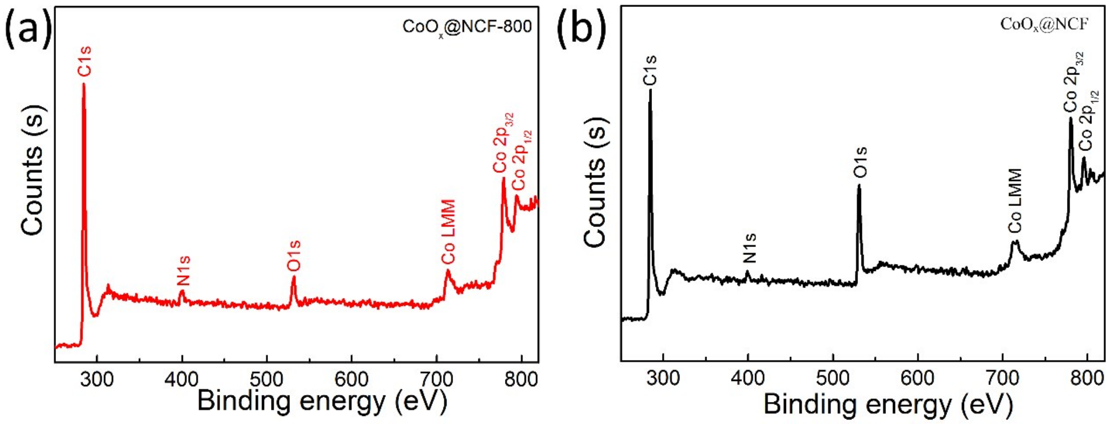

Fig. S6 XPS spectra of CoO_x@NCF-800 (a) and CoO_x@NCF (b) for full spectrum.

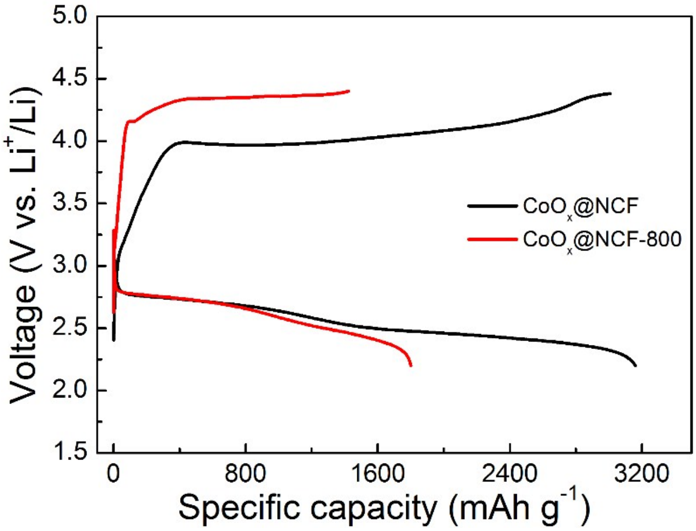

Fig. S7 The discharge-charge curves of Li-O_2 cells with CoO_x@NCF and CoO_x@NCF-800 at a current density of 50 mA g^{-1} (with catalyst:PVDF=9:1).

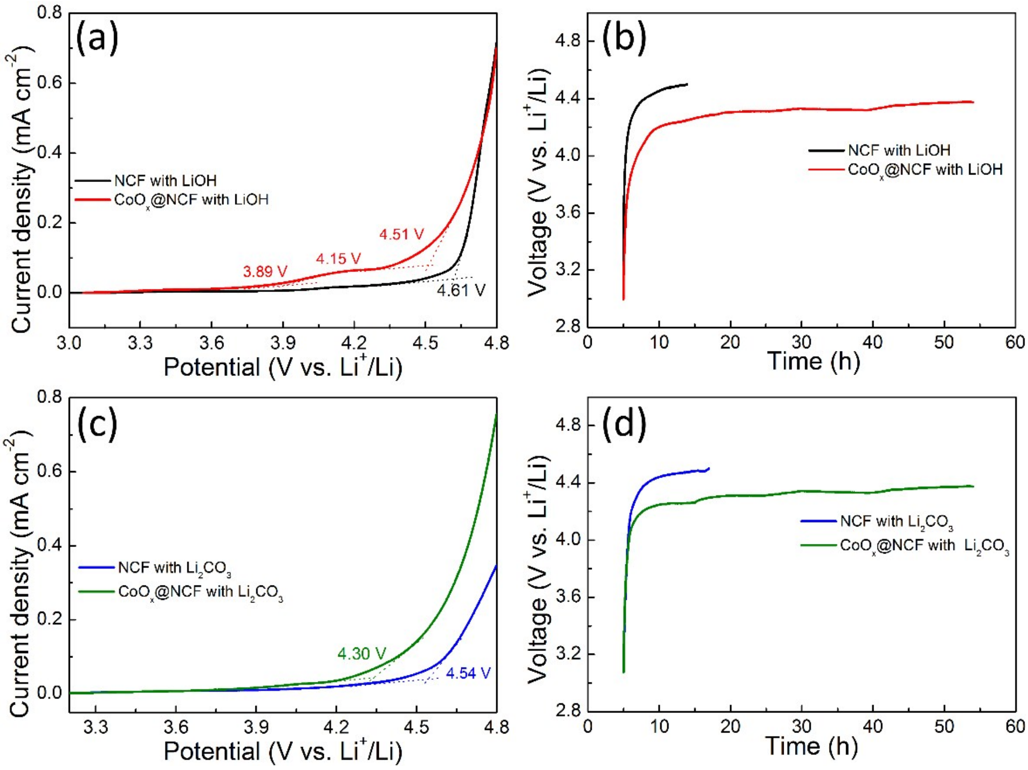

Fig. S8 Anodic LSV curves of the cells with NCF and CoO_x@NCF based electrodes from open potential to 4.8 V at a scan rate of 0.5 mV s^{-1} to show the oxidation of LiOH and Li_2CO_3 (a, c); Only charge profiles of the Li-O_2 cells with the NCF and CoO_x@NCF based cathodes at a current density of 100 mA g^{-1} by adding LiOH and Li_2CO_3 (b, d).

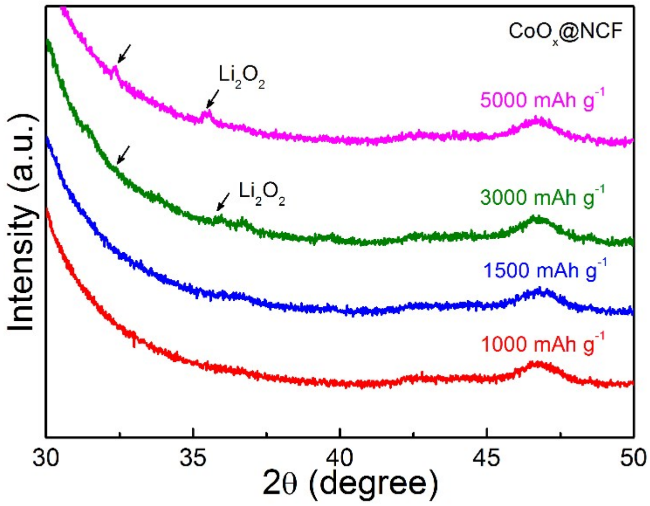

Fig. S9 XRD patterns CoO$_x$@NCF based cathode of the Li-O_2 cells at different discharge capacity states.

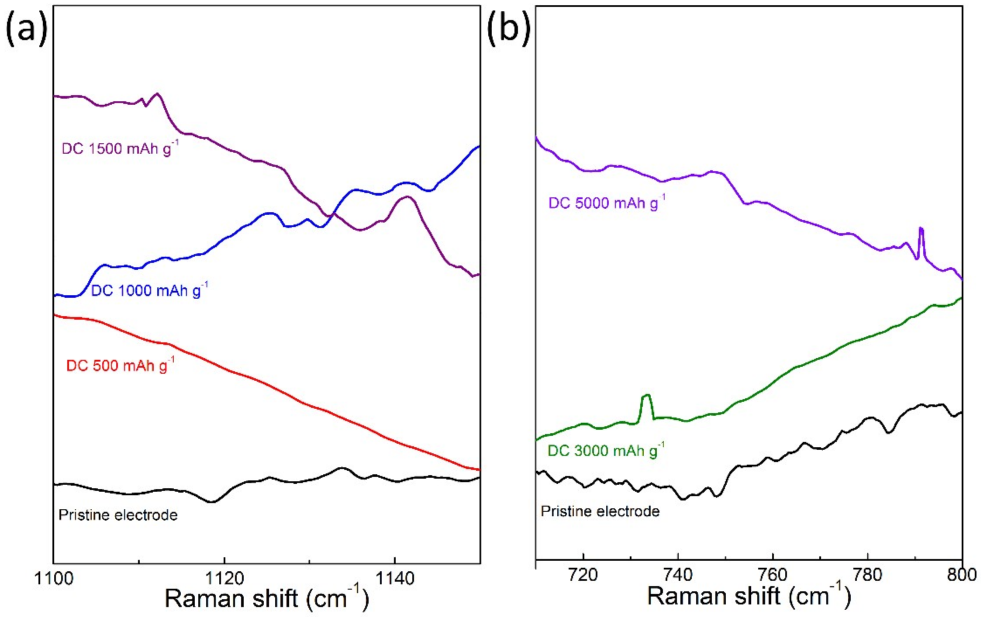

Fig. S10 Raman spectrum CoO$_x$@NCF based cathode for Li-O_2 cells under different discharge states at 50 mA g^{-1} (a) and (b).