A Long-Life Li-CO_2 Battery Employing a Cathode Catalyst of Cobalt-Embedded Nitrogen-Doped Carbon Nanotubes Derived from a Prussian Blue Analogue

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Experimental details

1. Catalyst synthesis

The cobaltic precursor Prussian blue analogue $Co_3[Co(CN)_3]_2$ was prepared through a precipitation reaction. The typical procedure was described as follows: 1.428 g of $CoCl_2 \cdot 6H_2O$ and 1.329 g of $K_3Co(CN)_6$ were dissolved in 50 mL deioinized water, respectively. Then 0.6 g of polyvinylpyrrolidone (K30) was added into the $K_3Co(CN)_6$ solution. Afterwards the two solutions were mixed together with 30 min stirring. After being kept in dark for 6h, the pink precipitates were collected by centrifugation and repeating washing with distilled water and ethanol. After drying at 60 °C for 8h and grinding, we obtained the $Co_3[Co(CN)_6]_2$ powers. For synthesizing the Co-N-CNTs, the pink powders were carbonized at 800 °C for 2h with a ramping rate of 4 °C min^{-1} under Ar protection. Subsequently the carbonization products were soaked in 2 M HCl acid for 2 days, followed with water washing and drying in vacuum overnight. At last the acid-soaked powders were annealed for another 2 h at 800 °C to remove the residues (noted as Co-N-CNTs). In order to

remove the Co nanoparticles in the tips of the CNTs, the carbonization products were treated with an oxidizing acid mixture of hydrochloric acid solution (9 M) and nitric acid (3 M) at 60 ^{o}C for 4 days. Thereafter, the sample was obtained by repeatedly washing with deionized water and drying in vacuum. Finally the acid mixture-treated powders were annealed for another 2 h at 800 °C to remove the residues (noted as N-CNTs).

2. Physical characterization

The crystallization structures were characterized by powder X-ray diffraction (XRD) with a Miniflex II diffractometer with the scan rate of 1^{o} min^{-1}. Scanning electron microscopy (SEM, Hitachi S-4800) and transmission electron microscopy (TEM, FEI Tecnai G2 F20) were performed to observe the structures and morphologies. X-ray photoelectron spectroscopy (XPS) analysis was performed to reveal the element state of the catalyst through PHI Versaprobe 5000 electron spectrometer. Characteristic structure of carbon nanotube was analyzed by Raman spectroscopy (Renishaw) with a 514 nm laser. The N_2 adsorption/desorption isotherms were obtained at 77 K using a Micromeritics ASAP 2050 system.

3. Battery assembly and electrochemical measurements

The Li-CO_2 battery was assembled in the form of 2032-type coin cell, which consists of a Li foil, a carbon paper supported with the catalysts, 50 ul dimethyl sulfoxide solution containing 1 M LiTFSI and 0.3 M $LiNO_3$ and a glass-fiber film, employed as the anode, cathode, electrolyte and separator, respectively. For catalyst ink preparation, 5 mg of Co-N-CNTs or commercial carbon nanotubes were dispersed in 1 mL of ethanol containing 50 ul of 5 wt.% Nafion solution. Afterwards the ink was pipetted to the carbon paper with a loading of 0.2 mg as the cathode. For the performance measurement, the battery was sealed in a bottle filled with CO_2 and tested through a Land battery testing system (Wuhan). EIS measurements were conducted on a CHI 760E electrochemical

workstation at the open circuit potential with the frequency of 10^5 to 10^{-2} Hz. The cathodes for the batteries at different states were obtained from the disassembled batteries to conduct the XRD, SEM and Raman measurements.

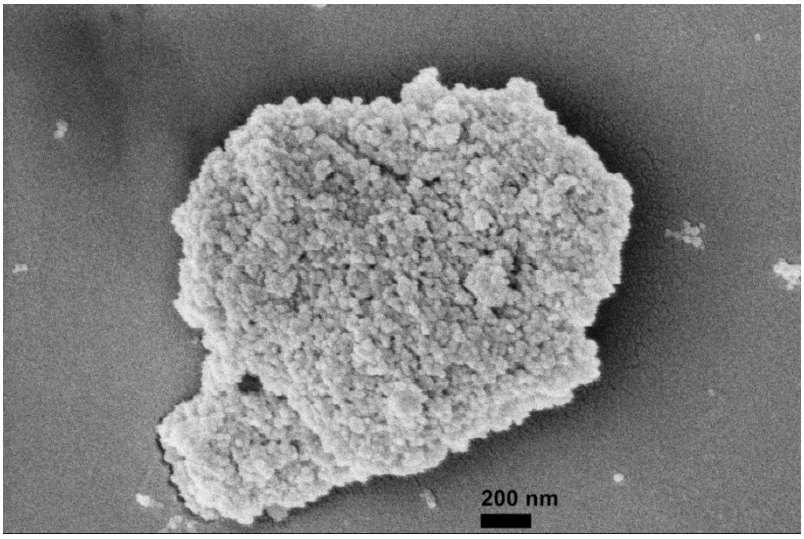

Fig. S1 SEM image of the precursor cobaltic Prussian blue analogue $Co_3[Co(CN)_6]_2$.

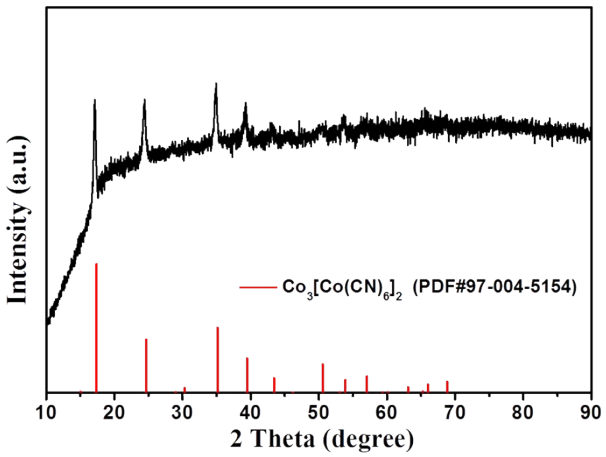

Fig. S2 XRD pattern of the precursor cobaltic Prussian blue analogue $Co_3[Co(CN)_6]_2$.

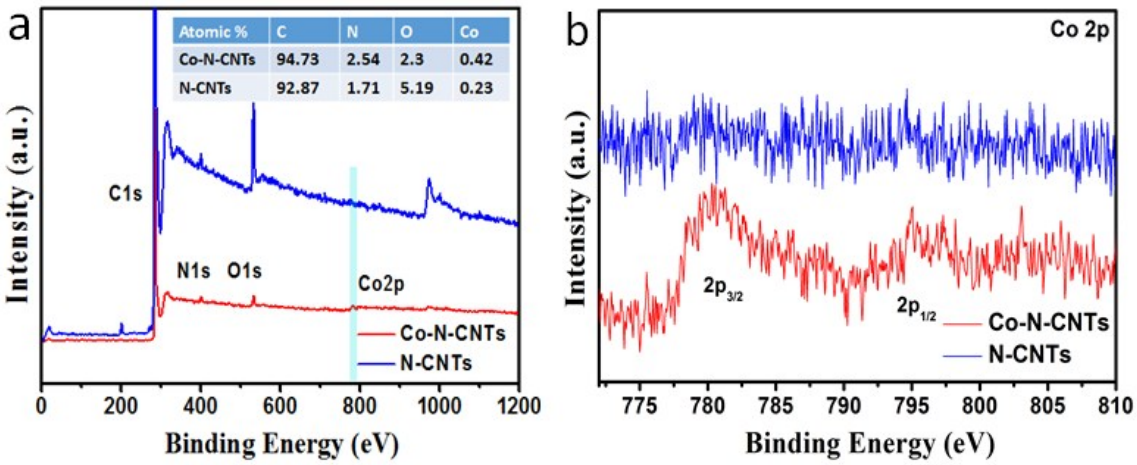

Fig. S3 (a) XPS survey spectrum and (b) Co 2p spectrum of the Co-N-CNTs and N-CNTs.

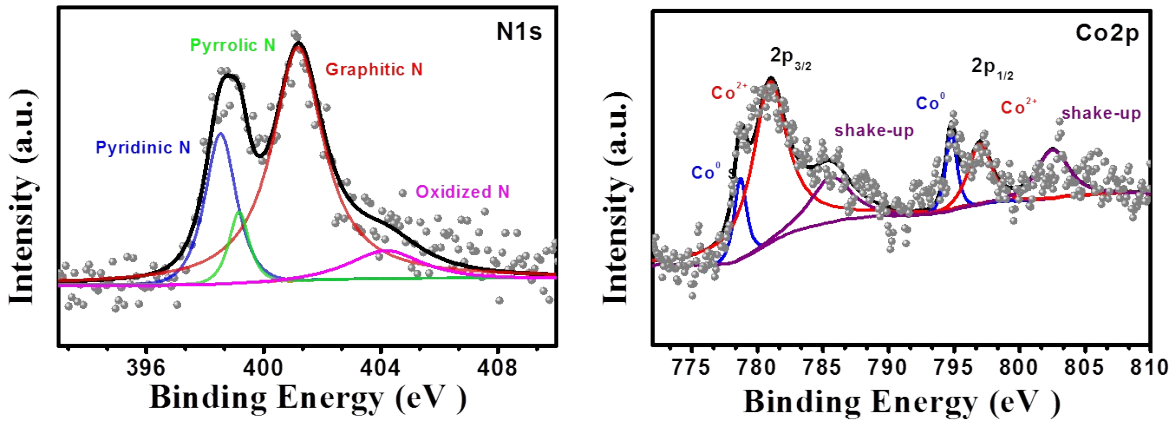

Fig. S4 High resolution XPS spectra of (a) N 1s and (b) Co 2p of Co-N-CNTs.

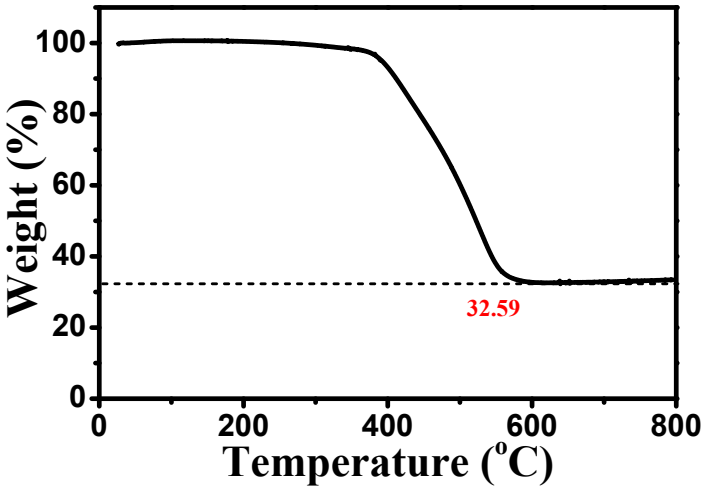

Fig. S5 The TG curve of Co-N-CNTs obtained at air atmosphere.

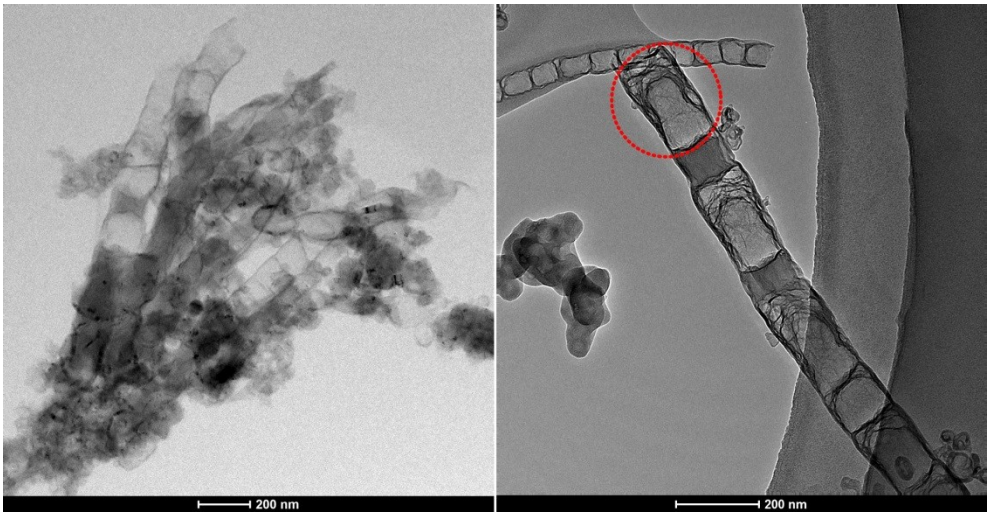

Fig. S6 TEM images of N-CNTs.

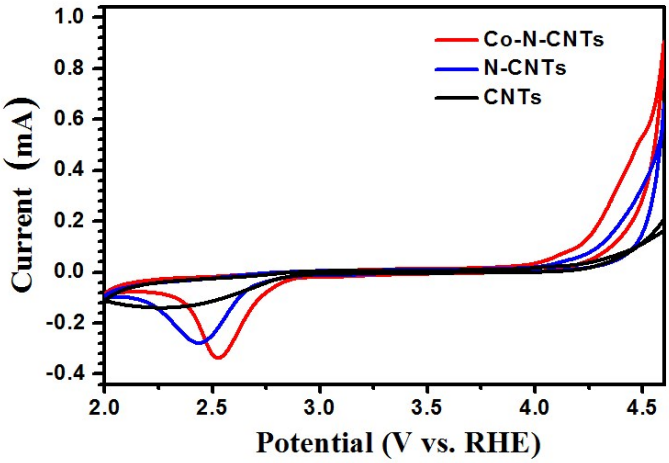

Fig. S7 CV curves of the Li-CO_2 batteries using the Co-N-CNTs, N-CNTs and commercial CNTs catalysts at a scanning rate of 0.2 mV s^{-1}.

Table S1. The comparison of this work compared with the reported works.

Cathode Catalyst	Electrolyte	Capacity (mAh g^{-1})	Cyclic life (cycles)	Reference
Co-N-CNTs	Liquid	6042 (0.2 A g^{-1})	92 (0.4 A g^{-1})	This work
N-CNTs	Liquid	7116 (0.2 A g^{-1})		This work
CNTs	quasi-solidus gel	5139 (100 mA g^{-1})	60	[S1]
Mo_2C/CNT cloth	quasi-solidus gel	3415 μAh cm^{-2} (50 μA cm^{-2})	40	[S2]
Wrinkled N-CNTs	quasi-solidus gel	9292.3 (50 mA g^{-1})	25 (50 mA g^{-1}) 45 (250 mA g^{-1})	[S3]
Conjugated cobalt polyphthalocyanine	Liquid	13.6 mAh cm^{-2} (0.1 mA cm^{-2})	50 (0.05 mA cm^{-2})	[S4]
graphene	Liquid	14722 (50 mA g^{-1}) 6600 (100 mA g^{-1})	20 10	[S5]
CNTs	Liquid	8379 (50 mA g^{-1}) 5786 (100 mA g^{-1})	29 22	[S6]
CNTs	Liquid	5139 (100 mA g^{-1})	60	[S7]
NiO–CNT	Liquid	9000 (0.1 A g^{-1})	25	[S8]
MFCN	Liquid	8827 (0.1 A g^{-1})	90	[S9]
Mn_2(dobdc)	Liquid	18022 (50 mA g^{-1})	50 (0.2 A g^{-1})	[S10]
Cu-NG	Liquid	14864 (0.1 A g^{-1})	50	[S11]
Ru@Super P	Liquid	8299 (0.1 A g^{-1})	80	[S12]
RuO_2/LDO	Liquid	5455 (0.1 A g^{-1})	60 (166 mA g^{-1})	[S13]
Ir/C Nanofiber	Liquid	18 813 (0.1 Ag^{-1})	120 (20 uA)	[S14]
Crumpled Ir Nanosheets/CNF	Liquid	8466.7 (166.7 mA g^{-1})	400 (500 mA g^{-1})	[S15]

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