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Supplementary information

Hierarchically structured Co_3O_4@carbon porous fibers derived from electrospun ZIF-67/PAN nanofibers as anode of lithium ion batteries

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Experimental section

Materials.

All chemicals are analytical grade and are used without further purification.

Synthesis of ZIF-67 NPs and the electrospun solution.

A reported typical procedure was used with some modifications to synthesize ZIF-67 NPs.[1] Firstly, 1.456 g of $Co(NO_3)_2 \cdot 6H_2O$ and 3.28 g of 2-methylimidazole were respectively dissolved in 50 mL of N, N-dimethylformamide (DMF) and the two solutions were quickly mixed together and were then magnetically stirred for 2 h at room temperature. After the reaction, the product was centrifuged and washed with DMF, and was redispersed in 5mL of DMF by sonication. Finally, 0.35 g of PAN was added to the ZIF-67 DMF solution and was dissolved completely by stirring. The obtained homogeneous purple solution was used as the electrospun solution.

Preparation of ZIF-67/PAN nanofibers by electrospinning

The electrospun solution was loaded into a 10 mL syringe that was connected to an 11.0 kV voltage (EST705, High voltage generator) and the nanofibers were connected by a copper net, the distance between needle and collector was about 10 cm, a syringe pump (PHD 2000 infusion，HARVARD APPARATUS) was used to control the flow rate at about 0.2 mL h^{-1}. After electrospinning, ZIF-67/PAN nanofibers were obtained.

Preparation of ES-CNCo_3O_4 fibers

ZIF-67/PAN nanofibers were heated to 200 ^oC for 2 h with a heating rate of 1 ^oC min^{-1} and were further carbonized at 800 ^oC for 4 h with a heating rate of 2 ^oC min^{-1} under the H_2/Ar atmosphere to obtain ES-CNCo. ES-CNCo was pyrolyzed in air at 360 ^oC for 10 min with a heating rate of 5 ^oC min^{-1} to oxidize Co into Co_3O_4, and ES-CNCo_3O_4 were obtained. The two comparative samples were prepared by the same procedures with ES-CNCo_3O_4 but different precursors. CNCo_3O_4 was prepared by directly carbonizing ZIF-67 NPs, while CS-CNCo_3O_4 was prepared from the casting film of electrospun solution that was vacuum dried at 80 ^oC.

Characterizations.

Transmission electron microscope (TEM) images were obtained on a Hitachi H-7650 with a voltage of 100 kV. High resolution TEM (HRTEM), EDS and element mapping were obtained on a JEM- ARM 200F with an acceleration voltage of 200 kV. Scanning electron microscopy (SEM) images were obtained on a Zeiss Supra 40 with an acceleration energy of 5 kV. X-ray photoelectron spectrometer (XPS) spectra were obtained using an ESCALAB250Xi equipped with an excitation source of Al Kα radiation. X-Ray diffraction (XRD) spectra were obtained on an X, Pert PRO MPD using Cu Kα radiation as the excitation source. Pore volume and size analysis were performed by Brunaure-Emmett-Teller (BET) and Barrett-Joyner-Halenda (BJH). N_2 sorption analysis was conducted using an ASAP 2020 accelerated surface area and porosimetry instrument (Micromeritics), equipped with the automated surface area. Raman spectra were examined on an LABRAM-HR confocal laser micro Raman spectrometer. TGA was obtained on a Perkin Elmer Diamond thermal analyzer with a heating rate of 10 $^{o}C\ min^{-1}$ in air.

Electrochemical measurements.

The working electrode material was prepared by mixing the materials of ES-CNCo_3O_4, Ketjen black, and poly-(vinyl difluoride) (PVDF) on a copper foil with a weight ratio of 8:1:1, and the composite were vacuum dried at 80 ^{o}C for overnight. The copper foil was cut into disks with a diameter of 12 mm. The loading of active materials was about 1 mg cm^{-1}. Lithium tablets were used as the counter electrode. The electrolyte was composed of 1 M LiPF6 in ethylene carbonate/dimethyl carbonate (50: 50 wt %). The glass fiber (GF/D, Whatman) was used as a separator. Cells assembly was conducted in a glove box filled with argon gas. The charging-discharge test was performed at an Arbin BT-1 system with the potential among 0.01-3 V at several different current densities. The CV tests were carried on an electrochemical workstation (Autolab PG302N) with the voltage range of 0.01-3 V and a scan rate of 0.1 mV s^{-1}.

Comparison lithium ion chemical diffusion coefficients through a galvanostatic intermittent titration technique (GITT).

From the measurements of GITT, the cells were discharged at 0.5 A g^{-1} for 20 min, and then relaxed under open circuit for 10 h.

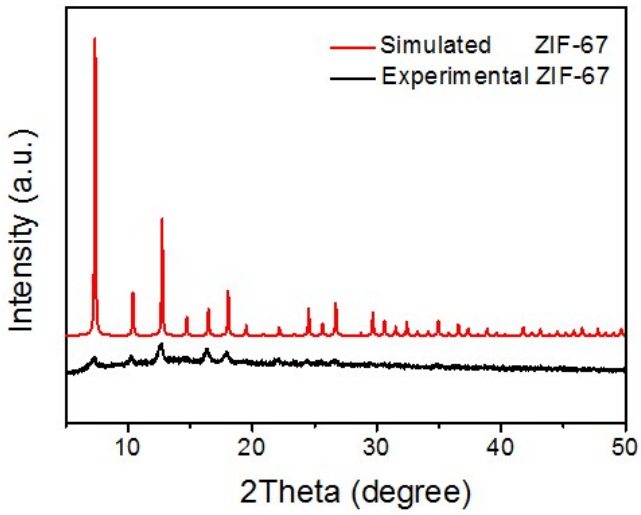

Fig. S1. Powder XRD pattern of ZIF-67 NPs.

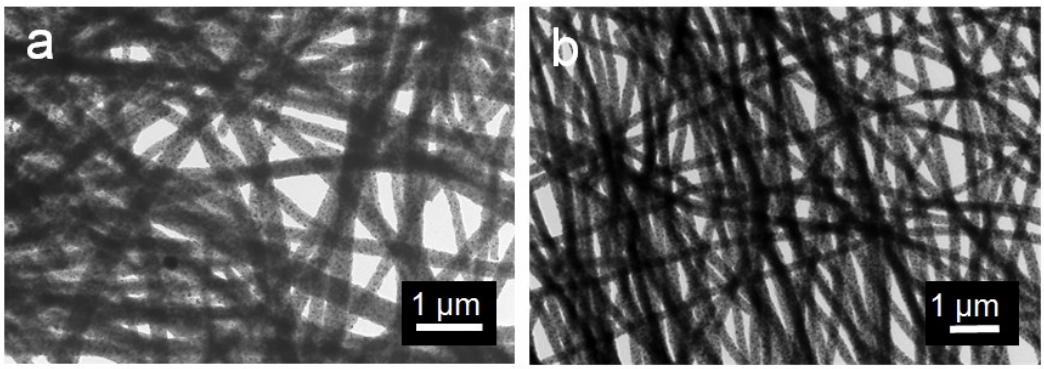

Fig. S2. TEM images of (a) ES-CNCo and (b) ES-CNCo_3O_4.

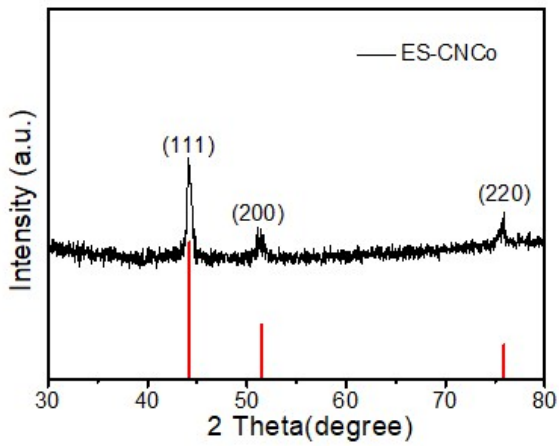

Fig. S3. Powder XRD pattern of ES-CNCo.

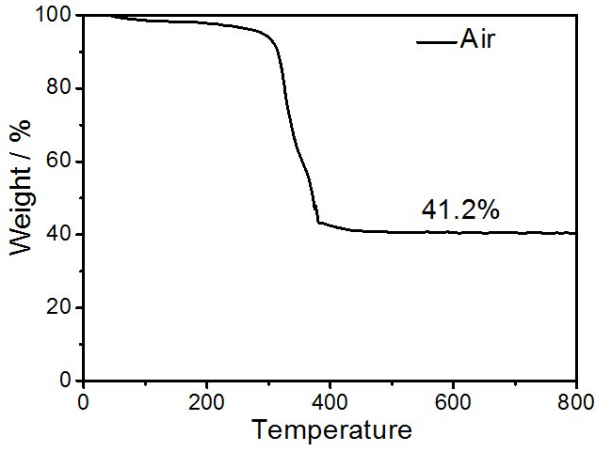

Fig. S4. TG curve of ES-CNCo.

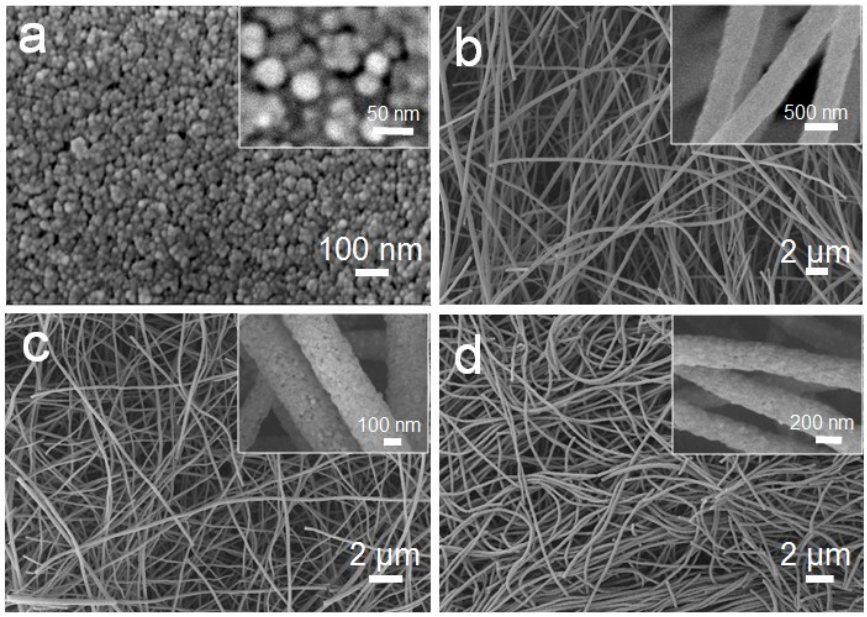

Fig. S5. SEM images of (a) ZIF-67 NPs, (b) ZIF-67/PAN, (c) ES-CNCo, and (d) ES-CNCo_3O_4.

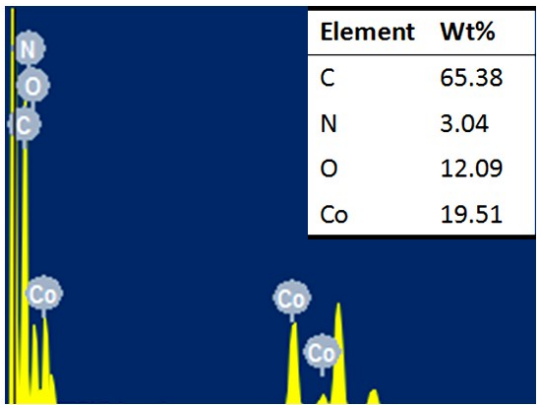

Fig. S6. EDS spectrum of ES-CNCo_3O_4, which shows the existence of C, N, O, and Co.

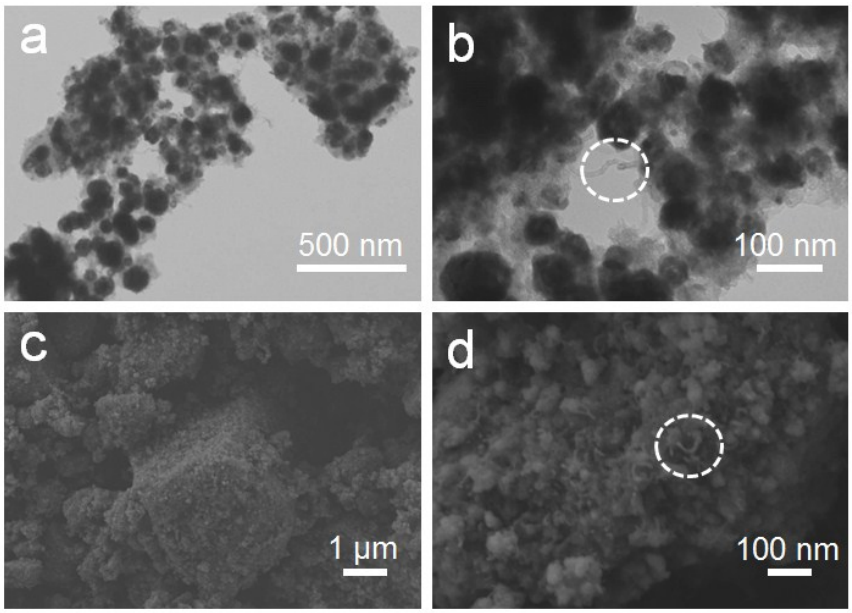

Fig. S7. TEM (a, b) and SEM images (c, d) of $CNCo_3O_4$ with different magnifications.

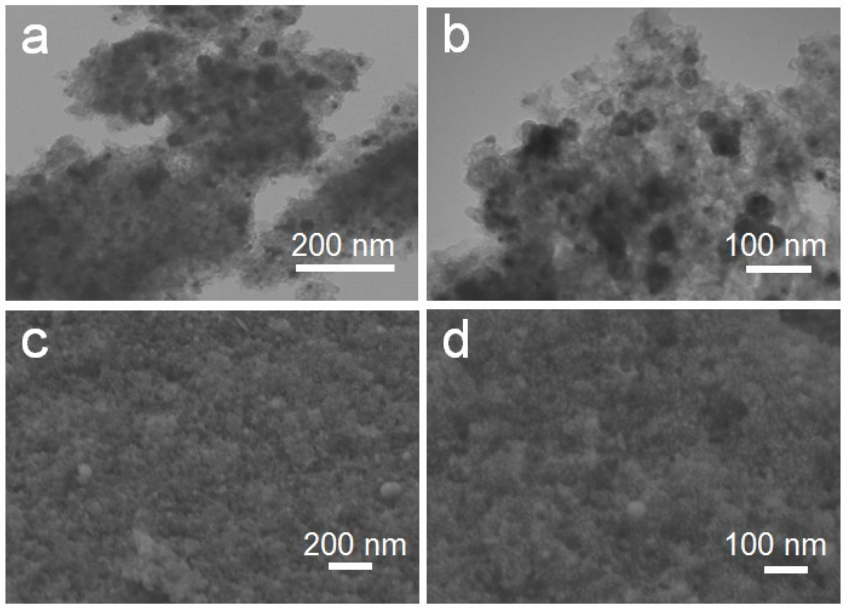

Fig. S8. TEM (a, b) and SEM images (c, d) of CS-$CNCo_3O_4$ with different magnifications.

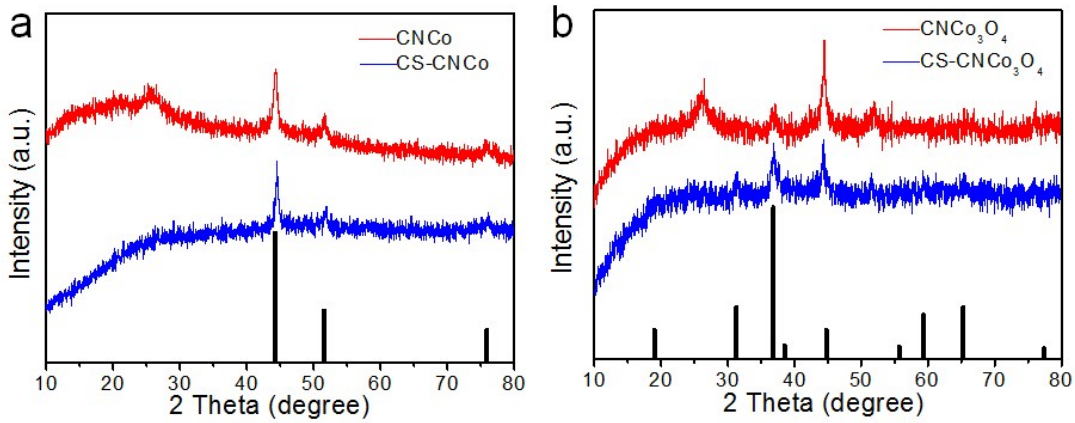

Fig. S9. Powder XRD patterns of the two comparative samples before (a) and after (b) oxidation.

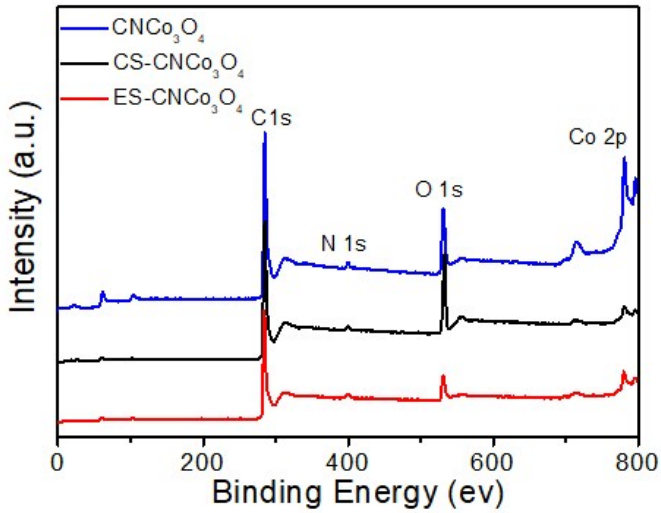

Fig. S10. XPS survey spectra of $CNCo_3O_4$, CS-$CNCo_3O_4$, and ES-$CNCo_3O_4$.

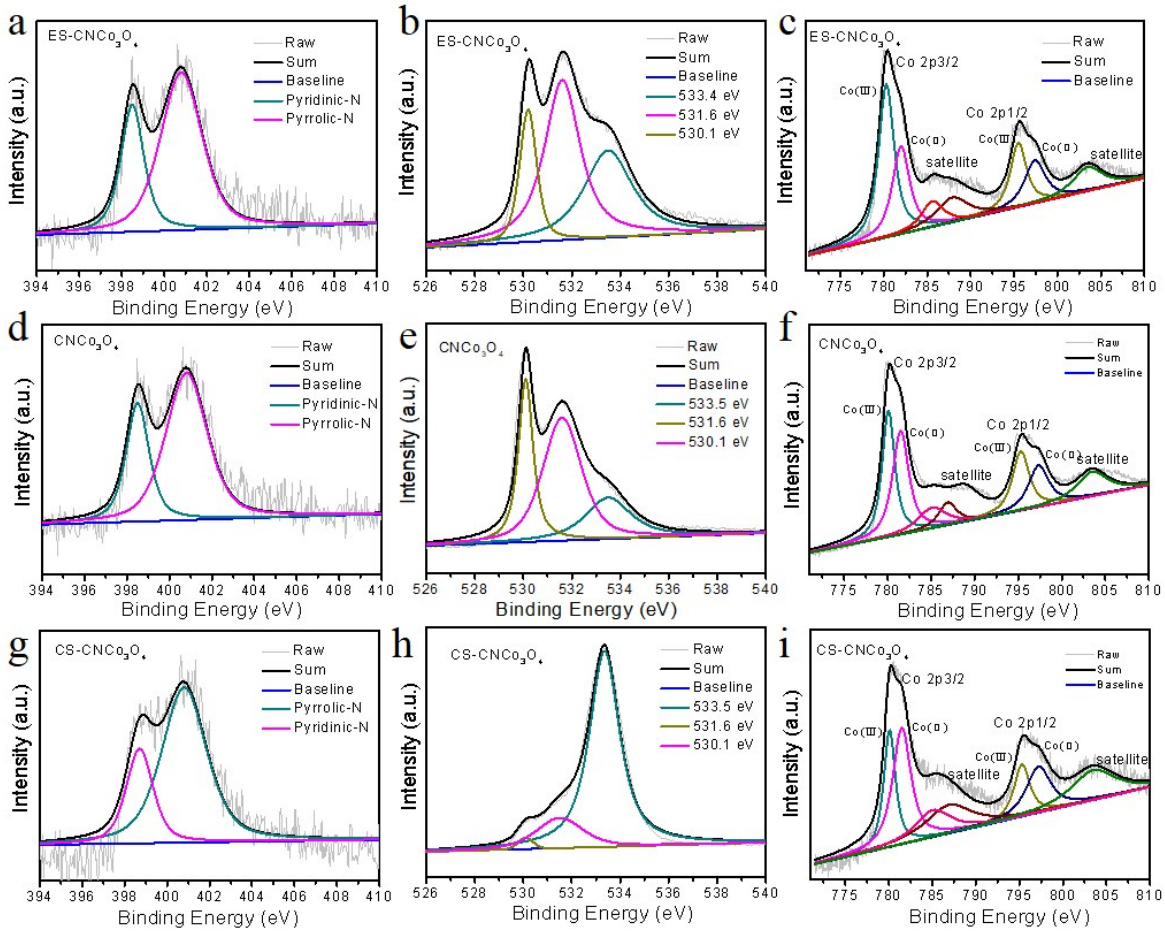

Fig. S11. N1s XPS spectra of (a) ES-$CNCo_3O_4$, (d) $CNCo_3O_4$, and (g) CS-$CNCo_3O_4$. O1s XPS spectra of (b) ES-$CNCo_3O_4$, (e) $CNCo_3O_4$, and (h) CS-$CNCo_3O_4$. Co2p XPS spectra of (c) ES-$CNCo_3O_4$, (f) $CNCo_3O_4$, and (i) CS-$CNCo_3O_4$.

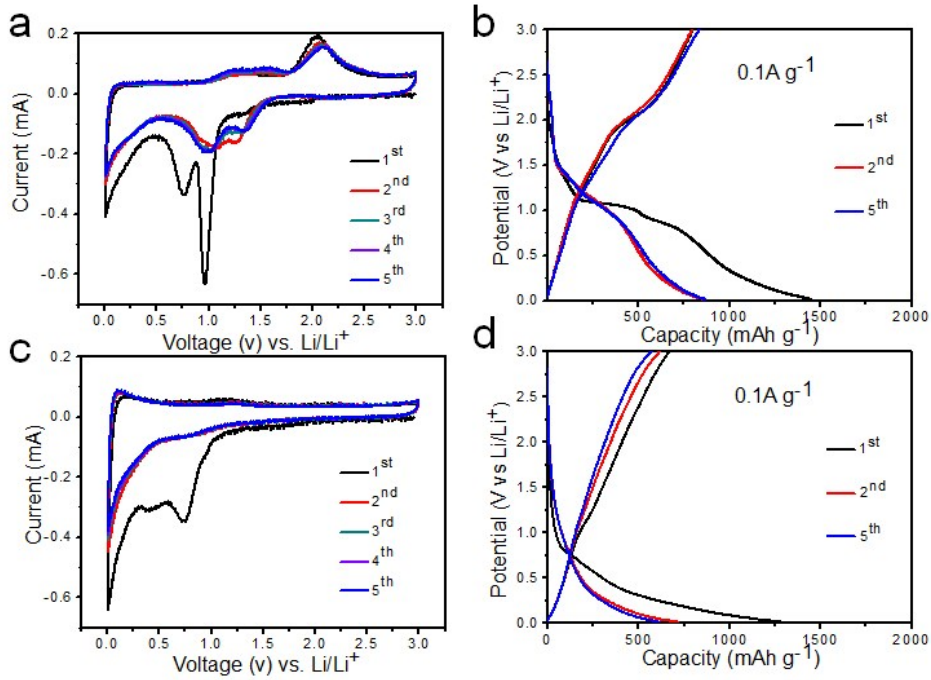

Fig. S12. CV profiles of $CNCo_3O_4$ (a) and CS-$CNCo_3O_4$ (c). GDC profiles of $CNCo_3O_4$ (b) and CS-$CNCo_3O_4$ (d) at 0.1 A g^{-1}.

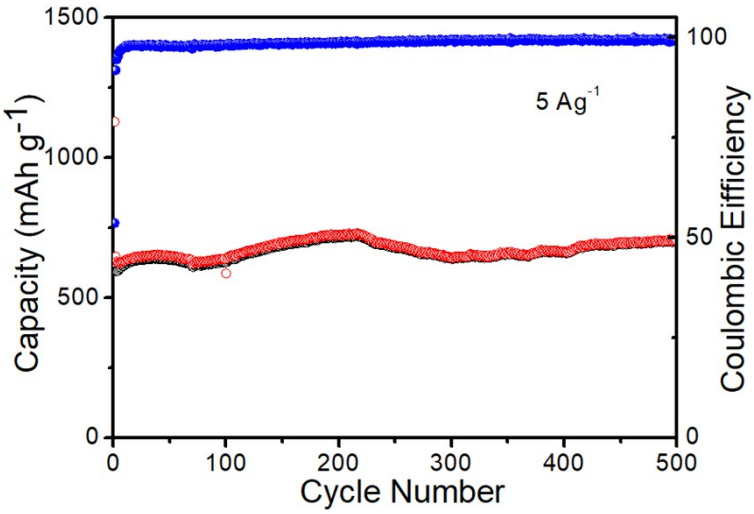

Fig. S13. Cycling performance of ES-$CNCo_3O_4$ at 2 A g^{-1}.

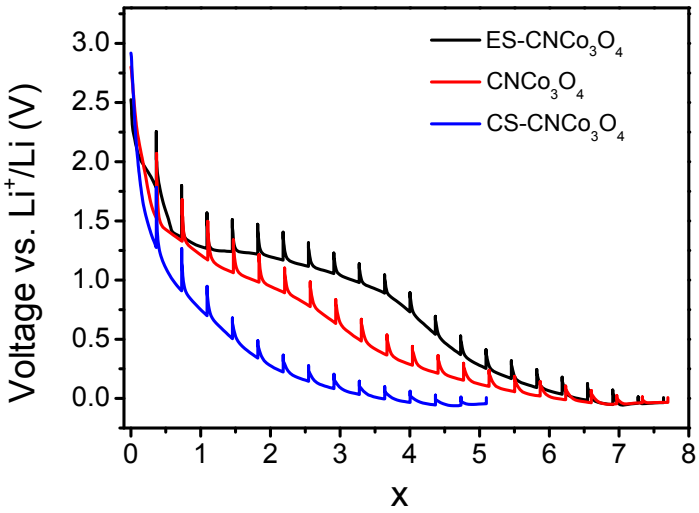

Fig. S14. GITT curves ("x" represents the stoichiometry of intercalated lithium ion per mole of samples) of the three samples.

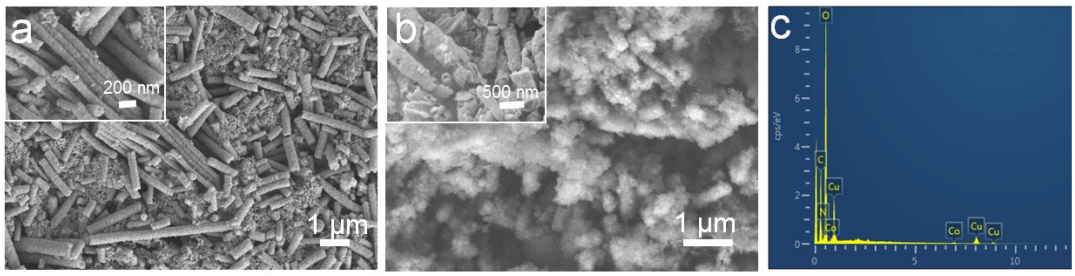

Fig. S15. SEM images of ES-$CNCo_3O_4$ before (a) and after (b) 500 cycles at 1 A g^{-1}. (c) The corresponding EDS spectrum of ES-$CNCo_3O_4$. Insets in (a) and (b) are their corresponding magnified SEM images.

Table S1. XPS element contents of C, N, O, and Co in ES-$CNCo_3O_4$, CS-$CNCo_3O_4$, and $CNCo_3O_4$, respectively.

	Weight (%)		
Element	ES-$CNCo_3O_4$	CS-$CNCo_3O_4$	$CNCo_3O_4$
C	66.70	72.00	63.48
N	2.92	2.40	2.67
O	13.85	20.14	14.30
Co	16.53	5.46	19.54

Table S2. BET data and BJH summary of ES-$CNCo_3O_4$, CS-$CNCo_3O_4$, and $CNCo_3O_4$.

Samples	BET surface area ($m^2 g^{-1}$)	Total pore volume ($cm^3 g^{-1}$)
ES-$CNCo_3O_4$	338.439	0.353
$CNCo_3O_4$	81.620	0.303
CS-$CNCo_3O_4$	267.361	0.356

Table S3. Comparison of electrochemical performances of ES-CNCo_3O_4 and Co_3O_4 based materials in previous reports.

Materials	Current density (mA/g)	Initial Discharge Capacity (mAh/g)	Initial Charge Capacity (mAh/g)	Reversible Capacity (mAh/g) after (Cycle number) at current density(mA/g)	reference
ES-CNCo_3O_4	**100**	**1824**	**1003**	**1100(200)(100)**	**This Work**
Co_3O_4@CNT	100			700(100)(100)	*Angew. Chem. Inter. Edi.***2015**, 54, 7060
Co_3O_4/PCNF	100	1187	1006	952(100)(100)	*J. Mater. Chem. A*. **2014**, 2, 16939
70%Co_3O_4/NMEG	100	1037	799	910(100)(100)	*Nano Energy*. **2014**, 3, 134
C-doped Co_3O_4 HNFs	200	1385	972	1125(200)(100)	*Adv. Funct. Mater*. **2016**, 26, 1428
Hollow Co_3O_4 nanoparticles	50	1107	880	880(50)(50)	ACS Nano. **2015**, 9, 1775
MWCNTs/ Co_3O_4	100	1171	812	813(100)(100)	ACS Nano. **2015**, 9, 1592
C@Co_3O_4@COAl	200	1377	767	755(100)(200)	Carbon. **2016**, 104, 1
Co_3O_4 parallelepiped	100	1608	1080	1100(50)(100)	J. Mater. Chem. A. **2015**, 3, 22542
Co_3O_4/EG	30	1000	713	722(50)(100)	Carbon. **2015**, 95, 494
Co_3O_4 hollow dodecahedra	100	1317	921	780(100)(100)	Small, **2014**, 10, 1932
CNT/Co_3O_4	100	1840	1281	1256(200)(100)	Angew. Chem. Int. Ed. **2016,** 55, 5990
G-Co_3O_4	90	1635.1	1112.1	(990.8)(100)(90)	*Acs Applied Materials & Interfaces*. **2017**, 9, 9662
Co_3O_4@Co@GO	100	1550	843	(686)(60)(200)	*Chem. Eng. J*. **2017**, 321, 495
CF@Co_3O_4	100	630	392	(420)(150)(100)	*J. Electroanal. Chem*. **2017**, 807, 196

References

1 Y.-Z. Chen, C. Wang, Z.-Y. Wu, Y. Xiong, Q. Xu, S.-H. Yu, H.-L. Jiang, *Adv. Mater.,* 2015, **27**, 5010-5016.