## **Supporting Information**

## Oxidizing Solid Co into Hollow Co<sub>3</sub>O<sub>4</sub> within Electrospun (Carbon) Nanofibers towards Enhanced Lithium Storage Performance

Jinkai Wang,<sup>†</sup> Hongkang Wang<sup>†,\*</sup> Fang Li,<sup>†</sup> Sanmu Xie,<sup>†</sup> Guiyin Xu,<sup>§</sup> Yiyi She,<sup>I</sup>Micheal K H Leung,<sup>I</sup> Tianxi Liu<sup>‡</sup>

<sup>†</sup> State Key Lab of Electrical Insulation and Power Equipment, Center of Nanomaterials for Renewable Energy (CNRE), School of Electrical Engineering, Xi'an Jiaotong University, Xi'an 710049, P. R. China. E-mail: <u>hongkang.wang@mail.xjtu.edu.cn</u>

<sup>‡</sup> State Key Laboratory for Modification of Chemical Fibers and Polymer Materials, College of Materials Science and Engineering, Donghua University, Shanghai 201620, P. R. China.

<sup>1</sup>Ability R&D Energy Research Centre (AERC), School of Energy and Environment, City University of Hong Kong, Hong Kong SAR, P. R. China.

<sup>§</sup> Department of Nuclear Science and Engineering and Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, United States

## **Experimental Section**

*Materials Synthesis.* All chemicals including N, N-dimethylformamide (DMF,  $C_3H_7NO$ , J&K Chemical), dicyandiamide ( $C_2H_4N_4$ , denote as DCD, 99%, Alfa Aesar), polyacrylonitrile (PAN, ( $C_3H_3N$ )<sub>x</sub>, average  $M_w$ =150000, Macklin) and cobalt(II) acetate tetrahydrate ( $Co(CH_3COO)_2 \cdot 4H_2O$ , denote as  $Co(Ac)_2$ , 99.5%, Sinopharm Chemical Reagent Co., Ltd) were used as received without further purification.

Synthesis of  $Co(Ac)_2/DCD/PAN$  nanofibers. In a typical synthesis, 0.8 g PAN and 0.2g DCD were dissolved in 8 mL DMF at 60 °C under vigorous stirring overnight. After complete dissolution, 1.0 g  $Co(Ac)_2$  was added into the above solution under continuously stirring until forming a viscous precursor solution. For the electrospinning, a high voltage of 18 kV was applied, and the flow rate

was fixed at 0.6 mL/h. A piece of Al foil was used as a collector, and the distance between the collector and needle was kept at 15 cm. The Co(Ac)<sub>2</sub>/DCD/PAN nanofibers were obtained after electrospinning by drying in an oven at 60 °C overnight.

*Synthesis of Co@C nanofibers*. The Co@C nanofibers were obtained by annealing the as-prepared Co(Ac)<sub>2</sub>/DCD/PAN nanofibers at 700 °C for 2 h with a heating rate of 1 °C/min under Ar atmosphere.

Synthesis of hollow  $Co_3O_4$  nanoparticle self-assembled nanofibers. The porous nanofibers self-assembled from hollow  $Co_3O_4$  nanoparticles were obtained by annealing Co@C nanofibers at 400 °C for 3h in air with a heating rate of 1 °C/min. Besides, the  $Co_3O_4/C$  nanofibers with different carbon content can also be prepared by controlling the annealing temperature as well as the annealing time.

*Materials Characterization.* X-ray diffraction (XRD) patterns were collected on a Bruker D8 ADVANCE X-ray diffractometer with Cu Kα. The morphologies were characterized using the scanning electron microscope (SEM, FEI Quanta 250F) and transmission electron microscope (TEM, JEOL JEM 2100) as well as high-resolution TEM (HRTEM). Raman spectra were measured on a microscope (Renishaw Raman RE01) using a 633 nm excitation Ar laser. Thermogravimetric analysis (TGA) was conducted in air at a heating rate of 10 °C/min from ambient temperature to 800 °C on a Mettler Toledo thermal analysis TGA/DSC system. The specific surface area, as well as the pore features, were investigated by N<sub>2</sub> adsorption-desorption isotherms at 77 K on a Quantachrome Surface Area Analyzer (Autosorb iQ-MP), according to the Brunauere-Emmette-Teller (BET) method. X-ray photoelectron spectroscopy (XPS, Thermo Fisher ESCALAB Xi+) was carried out to analyze the surface elemental composition and chemical states.

*Electrochemical Measurements.* The working electrodes were prepared by casting slurry, which contained active materials (Co@C, or Co<sub>3</sub>O<sub>4</sub>), conductive agent (Ketjenblack, Carbon ECP-600JD) and polyacrylic acid (PAA,  $M_w$ =100000, Sigma-Aldrich) in a weight ratio of 7:2:1 using deionized water as solvent, on the current collector of copper foil. After drying in a vacuum oven at 120 °C overnight, the electrodes with circular disk-shape and a diameter of 14 mm was obtained, and the loading amount of the active materials was kept in the range of 1.0 ± 0.2 mg. CR2025 coin-type cells were assembled in an Ar-filled glove-box (both H<sub>2</sub>O and O<sub>2</sub> content less than 1.0 ppm). The lithium metal was used as the counter electrode and the Celgard 2400 microporous membrane as a

separator. An electrolyte containing 1M LiPF<sub>6</sub> in ethylene carbonate/dimethyl carbonate (1:1 in volume) was used. Cyclic voltammetry was recorded on an Autolab PGSTAT 302N electrochemical workstation at a scan rate of 0.2 mV/s in the range of 0.01-3.0 V. Galvanostatic discharge-charge cycling tests of the cells were carried out on a battery test system (Neware BTS, Neware Technology Co., Ltd., China) at 25 °C. The electrochemical impedance spectroscopy (EIS) was recorded in the frequency range of 10 MHz to 0.01 Hz with a voltage amplitude of 5 mV.



Figure S1. SEM images of the precursor Co(Ac)<sub>2</sub>/DCD/PAN nanofibers.



**Figure S2.** Survey XPS spectra of the  $Co_{\alpha}C$  and  $Co_{3}O_{4}$  nanofibers.



**Figure S3**. Comparison of (a) the TGA curves for the different samples and (b) their lithium storage performance at different current densities.



Figure S4. Comparison of the CV curves of (a) Co@C and (b) Co<sub>3</sub>O<sub>4</sub> electrodes at 0.2 mV/s.

As shown in Figure S4, the Co@C electrode showed similar CV profiles with that of  $Co_3O_4$ , which indicates that the oxidation of Co nanoparticles happened when exposing in air. Besides, the broad cathodic/anodic peaks below 1.0 V in the Co@C electrode can be attributed the reversible lithium insertion/extraction in the carbon nanofiber matrices.



**Figure S5**. Comparison of the Nyquist plots of (a) Co@C and (b) Co<sub>3</sub>O<sub>4</sub> electrodes before and after cycling.



**Figure S6.** Comparison of the (a) TGA, (b)  $N_2$  sorption isotherms, and (c) pore size distribution plots for the Co@C nanofibers obtained with or without DCD introduction.

In order to further reveal the importance of the DCD introduction during synthesis, the TGA curves, surface area and pore size distribution plots for the Co@C nanofibers obtained with or without DCD were provided, as shown in Figure S6. From the TGA curves, the Co content in the Co@C obtained without DCD can be calculated to be ~38 wt.%, while the Co content in the Co@C obtained with DCD is ~36 wt.%, indicating that DCD did not greatly affect the relative contents of Co and C in the composites. As revealed by the BET results, the Co@C obtained without DCD showed a specific surface area of 342.2 m<sup>2</sup>/g with an average pore size of 4.3 nm. In contrast, the Co@C obtained with DCD possessed a higher specific surface area of 420.5 m<sup>2</sup>/g with an average pore size of 5.6 nm. These demonstrated that the introduction of the DCD can largely affect the microstructures of the Co@C nanofibers and thus resulting in the different structure of its derived



Figure S7. (a, b) TEM, (c) HRTEM images, and (d) XRD pattern of the as-prepared  $Co_3O_4$  nanofibers obtined without the introduction of DCD during the synthesis all with all the parameters constant.



Figure S8. (a) Cycle performance at 200 mA/g and (b) rate performance at different current densities for  $Co_3O_4$  nanofibers without DCD.



**Figure S9**. (a, b) TEM, (c) HRTEM images, and (d) XRD pattern of the as-prepared NiO nanofibers, which were prepared by replacing cobalt (II) acetate with nickel (II) acetate with all the other parameters constant.



Figure S10. TEM image of the as-prepared Ni-Co-O nanofibers with inset showing its XRD pattern.



**Figure S11**. (a) Cycle performance at 200 mA/g and (b) rate performance at different current densities for NiO nanofibers and Ni-Co-O nanofibers.

**Table S1.** Structures, syntheses and electrochemical performances of various Co<sub>3</sub>O<sub>4</sub>-based composites as anode materials for lithium-ion batteries (LIBs).

Structures	Specific capacity (mA h/g)	Current density (mA/g)	Synthetic method	Ref.
Uniform multishelled Co <sub>3</sub> O <sub>4</sub> hollow	1615.8/30th	50	A hard-template method	1
microspheres				
Graphene anchored with Co <sub>3</sub> O <sub>4</sub>	935/30th	50	Solution-phase dispersion and subsequent	2
nanoparticles			transformation by calcination	
Co <sub>3</sub> O <sub>4</sub> Nanocages	970/30th	50	A simple thermal decomposition of	3
			Co <sub>3</sub> [Co(CN) <sub>6</sub> ] <sub>2</sub> ·nH <sub>2</sub> O nanoparticles	
Co <sub>3</sub> O <sub>4</sub> -graphene sheet-on-sheet	1065/30th	89	A microwave-assisted method	4
nanocomposites				
Co <sub>3</sub> O <sub>4</sub> /carbon nanotube anodes	910/50th	89	A pyrolysis method with $\text{Co}(\text{NO}_3)_2$ as a	5
			precursor	
Co <sub>3</sub> O <sub>4</sub> /nitrogen modified graphene	910/100th	100	Microwave exfoliated graphite oxide and	6
electrode			refluxed under 90 °C	
Mesoporous Peapod-like Co <sub>3</sub> O <sub>4</sub>	781/60th	100	A controllable nanocasting method	7
@Carbon Nanotube Arrays				
MOF-derived porous hollow Co <sub>3</sub> O <sub>4</sub>	1115/50th	100	A facile one-step calcination of a novel	8
parallelepipeds			cobalt-based metal-organic framework	
			template	
Hollow Co <sub>3</sub> O <sub>4</sub> nanoparticle	1491.5/180th	200	A electrospun method and two-step	
assembled nanofibers			annealing	This
Hollow Co <sub>3</sub> O <sub>4</sub> /C nanofibers	871.5/500th	200	A electrospun method and two-step	paper
			annealing at lower temperature	

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## **References.**

- Wang, J.; Yang, N.; Tang, H.; Dong, Z.; Jin, Q.; Yang, M.; Kisailus, D.; Zhao, H.; Tang, Z.; Wang,
  D. Angewandte Chemie 2013, 52, (25), 6417-20.
- Wu, Z.-S.; Ren, W.; Wen, L.; Gao, L.; Zhao, J.; Chen, Z.; Zhou, G.; Li, F.; Cheng, H.-M. ACS nano
  2010, 4, (6), 3187-3194.
- 3. Yan, N.; Hu, L.; Li, Y.; Wang, Y.; Zhong, H.; Hu, X.; Kong, X.; Chen, Q. *The Journal of Physical Chemistry C* 2012, 116, (12), 7227-7235.
- 4. Chen, S. Q.; Wang, Y. Journal of Materials Chemistry 2010, 20, (43), 9735.
- He, X.; Wu, Y.; Zhao, F.; Wang, J.; Jiang, K.; Fan, S. *Journal of Materials Chemistry A* 2013, 1, (37), 11121.
- Lai, L.; Zhu, J.; Li, Z.; Yu, D. Y. W.; Jiang, S.; Cai, X.; Yan, Q.; Lam, Y. M.; Shen, Z.; Lin, J. Nano Energy 2014, 3, 134-143.
- Gu, D.; Li, W.; Wang, F.; Bongard, H.; Spliethoff, B.; Schmidt, W.; Weidenthaler, C.; Xia, Y.; Zhao,
  D.; Schuth, F. *Angewandte Chemie* 2015, 54, (24), 7060-4.
- Han, Y.; Zhao, M.; Dong, L.; Feng, J.; Wang, Y.; Li, D.; Li, X. *Journal of Materials Chemistry A* 2015, 3, (45), 22542-22546.