Supporting Information for

Novel anode of C&N co-doped Co_3O_4 nanofibers with

excellent performance for lithium-ion batteries

Chunshuang Yan, Gang chen,* Jingxue Sun,* Xin Zhou, Chade Lv

2 Experimental Section

2.1 Synthesis of PAN nanofiber:

Poly(acrylonitrile) (PAN) (Mw~89000, 99%), N,N-dimethylformamide (DMF, 99%), and $Co(NO_3)_2 \cdot 6H_2O$ (97%) were purchased. In a typical process, PAN were dissolved in DMF to harvest homogeneous dispersion at 80 °C for 5 h under magnetic stirring. PAN nanofibers were collected on the alumina foil 10 cm away from a syringe needle linked to a variable high voltage power supply of 12 kV with a feeding rate of 0.3 mL/h.

2.2 Typical synthesis of C&N co-doped Co_3O_4 hollow nanofibers:

In a typical synthesis, first, PAN nanofibers was obtained similar to previous reports.[1] Then, 0.291 g of $Co(NO_3)_2$ was dissolved in alcoholic solution (35 mL) under magnetic stirring for 30 min. The resulting solution was transferred into a 50 mL Teflon-lined autoclave with electrospun PAN nanofibers. The autoclave was sealed and heated at 180°C for 12 h, and cooled naturally to room temperature. The obtained membrane was washed with ethanol, and dried at 80 °C. The dry membrane was first stabilized in an ambient atmosphere at 300 °C for 2 h and then carbonized under ammonia protection at 600 °C.

2.3 Materials Characterizations.

XRD patterns were recorded over a 2θ range from 10° to 90° at a speed of 10° min^{-1} using a Rigaku D/max-2000 diffractometer with Cu-Kα radiation. The morphology of the samples was assessed by the scanning electron microscopy (SEM). Transmission electron microscopy (TEM) images of the as-prepared samples were collected by employing an FEI Quanta 200F field emission scanning electron microscope and an FEI Tecnai G2 S-Twin transmission electron microscope, respectively. Raman spectra were recorded on a Renishaw *via* micro-Raman spectroscopy system in the backscattering geometry with a 458 nm argonion laser as the excitation source. The surface analysis was conducted using X-ray photoelectron spectroscopy with an Al Ka chromatic X-ray source (1486.60 eV, PHI 5700 ESCA System, USA). The thermal stability

was determined by a SETARAM DSC-141 under a stream of air and a heating rate of 10 K min^{-1}.

2.4 Electrochemical Measurements.

The electrodes were prepared with C&N co-doped Co_3O_4 nanofibers, carbon black, and poly(vinyl difluoride) (PVDF) at a weight ratio of 80:10:10. The slurry was cast on Cu foil and dried at 120 °C in vacuum for 12 h. The cells were assembled with pure lithium foil (99.9%, Aldrich) as the counter electrode, Celgard 2400 film as the separator, and 1 M $LiPF_6$ EC:DMC (1:1) electrolyte in an argon-filled glove box. The discharge and charge measurements were carried out on a NEWARE BTS-610 (Neware Co., Ltd, China) battery tester. All the tests were performed in the range between 0.01 V and 3 V.

2.5 Computational Details

The calculations were performed using the Vienna Ab Initio Simulation Package (VASP).[1] All our calculations are based on DFT within spin-unrestricted PBE approximation to the exchange-correlation energy.[2] Both atomic positions and cell parameters were optimized with the conjugate gradient algorithm until the residual forces were converged to less than 0.03 eV/Å and 1×10^{-5} eV. A $10\times10\times10$ k-point for optimization and $25\times25\times25$ k-point for the subsequent electronic properties sampling in reciprocal space and a plane-wave basis set with an energy cutoff of 500 eV were used.

Co_3O_4 is a highly correlated insulator, an obvious underestimated band gap was obtained because the conventional PBE functional failed to describe the strong correlation effects between the d electrons, thus GGA+U method was imperative. In the PBE+U_{eff} calculation, the effective on-site Coulomb interaction U_{eff}=2 for the Co^{2+} ions and Co^{3+} ions was used to obtain the correct band gap, in which U_{eff}=U-J, U=2.2 and J=0.2. Similar dispersion trend in conduction and valence bands to those calculated by HSE06 method[3] guaranteed the rationality of our results.
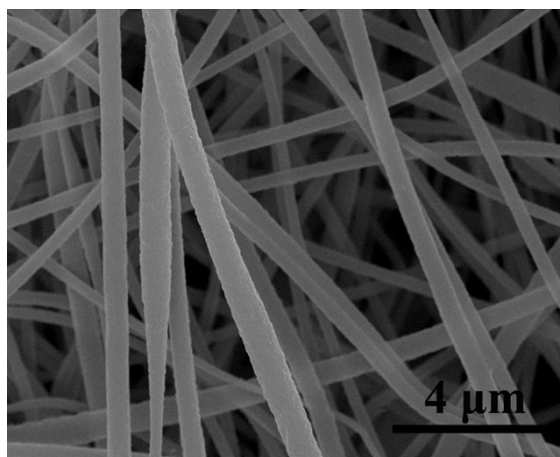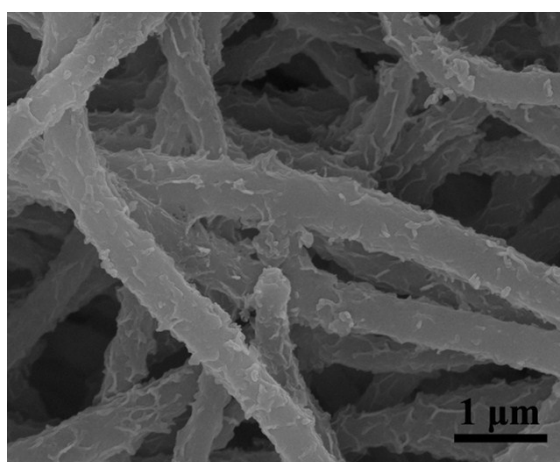
Fig. S1 SEM images of the bare PAN NFs.

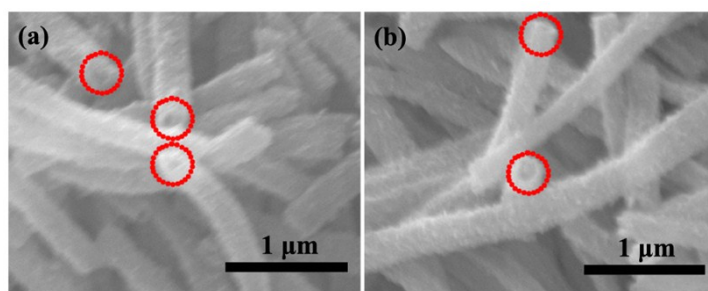Fig. S2 SEM images of the prepared precursor in alcoholic $Co(NO_3)_2$ solution.

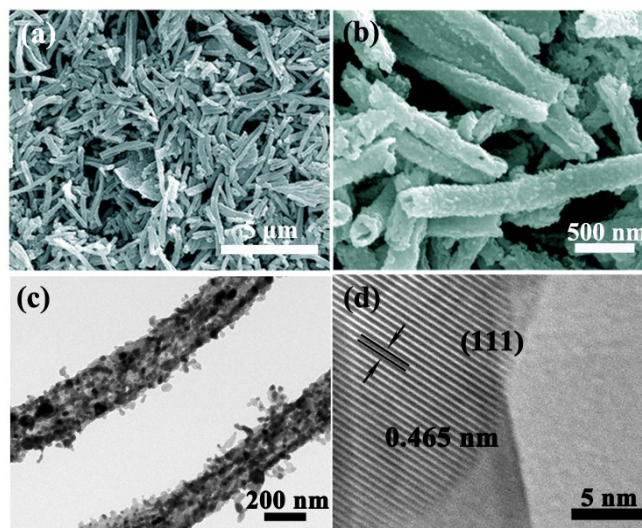Fig. S3 SEM images of the obtained Co_3O_4 NFs by calcinating in air at 300 °C.

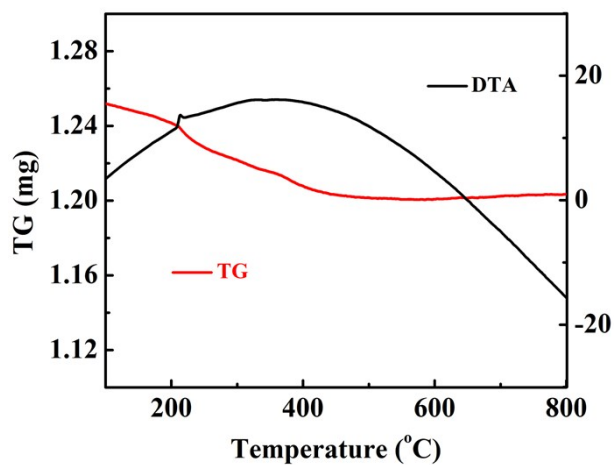Fig. S4 Microstructure analysis of the as-prepared un-HNFs (a, b) SEM and (c, d) TEM and HRTEM images.

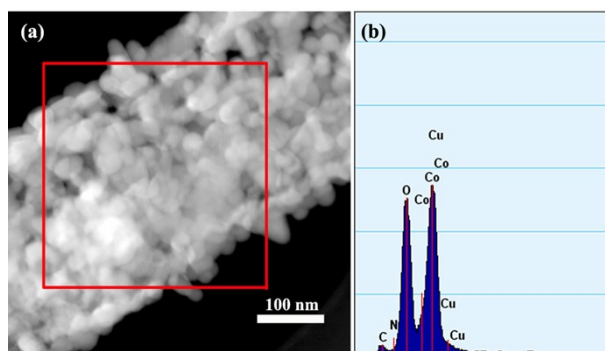Fig. S5 TG-DTA analysis of the undoped Co_3O_4 HNFs.

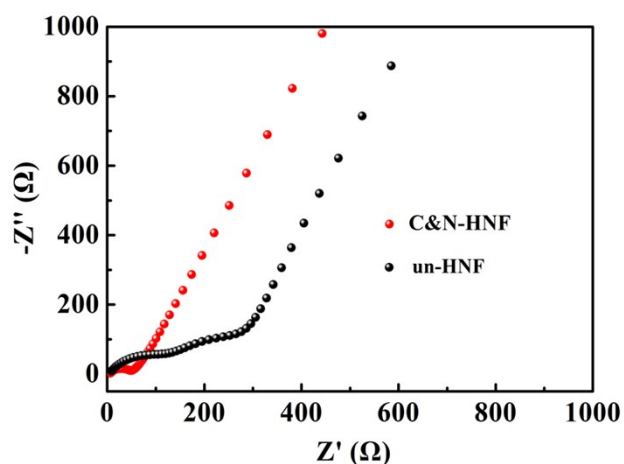Fig. S6 The energy-dispersive X-ray spectroscopy (EDS) spectrum of C&N-HNFs.

Fig. S7 The electrochemical impedance spectroscopy (EIS) of the un-HNFs and C&N-HNFs electrodes before cycling measurements.
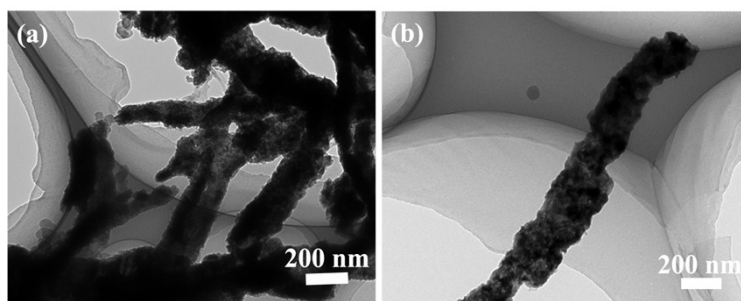

Fig. S8 (a, b) The TEM images of C&N co-doped Co_3O_4 HNFs after 60 cycles.
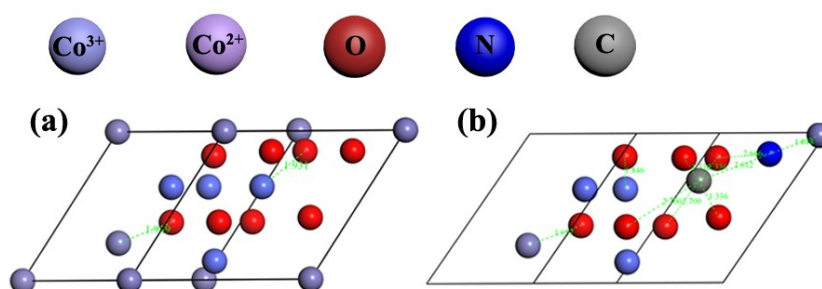

Fig. S9 Optimized structures (a, b) of Co_3O_4 and C&N co-doped Co_3O_4.

The Face-centered-cubic (FCC) primitive cell of Co_3O_4 is shown in Fig. S6, where Co^{3+} ions, Co^{2+} ions, O^{2-} ions, C and N are indicated by blueviolet, violet, red, gray and navy balls, respectively. The bond distances of Co^{2+}-O^{2-} (1.95Å) and Co^{3+}-O^{2-} (1.93 Å) by PBE+U are overestimated by about 1% compared with experiment and as also found in other GGA+U studies.[4] Based on our Raman spectra and XPS results, one Co^{3+} and O^{2-} ions can be displaced by carbon and nitrogen. The optimized C&N co-doped Co_3O_4 structure is shown in Fig. S6b.

1. (a) G. Kresse, J. Hafner, Phys. Rev. B 1993, 47, 558−561, (b) G. Kresse, J. Furthmüller, Phys. Rev. B 1996, 54, 11169−11186.

2. J. P. Perdew, K. Burke, M. Ernzerhof, Phys. Rev. Lett. 1996, 77, 3865−3868.

3. V. Singh, M. Kosa, K. Majhi, D. Thomas Major, J. Chem. Theory Comput. 2015, 11, 64−72.

4. J. Chen, X. F. Wu, A. Selloni, Phys. Rev. B 2011, 83, 245204.