# **Supporting Information**

 $Co_3O_4$  nanoparticles embedded in nitrogen-doped graphitic carbon fibers as free-standing electrode for promotion of lithium ion storage with capacitive contribution  $\dagger$ 

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## **Experimental section:**

Synthesis of nanosized ZIF-67: ZIF-67 was synthesized according to the previous literature. Typically, 2.94 g of cobalt acetate hexahydrate  $(Co(NO_3)_2 \cdot 6H_2O)$ , Sigma Aldrich) and 2.5 g of polyvinylpyrrolidone (PVP, Mw≈290,000, Sigma Aldrich) were dissolved in 250 mL of methanol (CH<sub>3</sub>OH, >99.5%, Sinopharm Chemical Reagent Co., Ltd.) to form solution A. 3.313 g of 2-methylimidazole (>99%, Sigma Aldrich) and 0.2 mL of triethylamine (>99%, Sinopharm Chemical Reagent Co., Ltd.) were dissolved in another 250 mL of methanol to form solution B. Then, solution B was added into solution A under magnetic stirring for 10 min and aged for 24 h at room temperature. The product was collected by centrifugation and washed with methanol for three times, and dried at 100 °C in vacuum for 24 h.

*Synthesis of ZIF-67/PAN:* ZIF-67/PAN fibers were synthesized by a facile electrospinning method. 0.252 g of the as-synthesized ZIF-67 powder was dispersed in 4.725 g of N, N-dimethylformamide (DMF, >99.5%, Sinopharm Chemical Reagent Co., Ltd.) solvent via sonication for 60 min. Then, 0.4 g polyacrylonitrile (PAN,

 $Mw \approx 15,000$ , Sigma Aldrich) was added into the above suspension. The mixture was stirred at 80 °C for 24 h to form a homogeneously dispersed solution. Subsequently, the precursor solution was transferred into a 10 mL syringe and connected to a direct current (DC) high voltage power supplied with a stainless-steel nozzle. The high voltage, feeding rate and rotational speed of metal drum and distance between the needle tip and the collector were fixed at 14 kV, 13  $\mu$ L min<sup>-1</sup>, 300 rpm min<sup>-1</sup> and 13 cm, respectively. Then, the electrospun ZIF-67/PAN was dried at 120 °C overnight in a vacuum.

*Synthesis of Co@NGFs:* To obtain Co@NGFs, the ZIF-67/PAN fibers were first insulated for 5 hours at 600 °C, followed by a further thermal annealing process at 900 °C for 2 h with a ramping rate of 5 °C min<sup>-1</sup> under the protection of  $N_2$  gas.

*Synthesis of*  $Co_3O_4@NGFs$ : The Co@NGFs sample obtained in the previous step was oxidized in air for 2 h at 280 °C at a ramping rate of 5 °C min<sup>-1</sup> to obtain the final electrode material of Co<sub>3</sub>O<sub>4</sub>@NGFs.

*Synthesis of Co*<sub>3</sub>*O*<sub>4</sub>@*NGFs-A:* The prepared Co<sub>3</sub>O<sub>4</sub>@*NGFs* composite was acidified by soaking the material in 1 M hydrochloric acid (HCl, 36%-38%, Sinopharm Chemical Reagent Co., Ltd.) for 24 hours, and the metal oxides were completely removed to obtain the Co<sub>3</sub>O<sub>4</sub>@*NGFs-A* electrode material.

#### Material characterization:

The surface structure and morphology of the synthesized samples were identified by transmission electron microscopy (TEM, JEOL, JEM-2100F) equipped with an energy dispersive spectrometer (EDS, OXFORD) and field-emission scanning electron microscopy (FESEM, JEOL, JSM-7800F). The crystal structure of all samples was tested by X-ray diffractometer (XRD, SmartLab3Kw, Cu K $\alpha$  radiation,  $\lambda$ =1.5418 Å). Thermogravimetric analysis (TGA, METTLERTGA2) was used to test the contents of the samples with a heating rate of 10 °C min<sup>-1</sup> at O<sub>2</sub> atmosphere in the range of 30 °C-800 °C. Raman spectrometer (Horiba-JY-HR800, Japan) was used to identify the carbonization degree of samples. The surface chemical compositions of Co<sub>3</sub>O<sub>4</sub>@NGFs were analyzed by X-ray photoelectron spectroscopy analysis (XPS,

Thermo Scientific Escalab 250XI).

#### **Electrochemical measurements:**

Half-cells (CR2025) were assembled in glovebox by directly using Co<sub>3</sub>O<sub>4</sub>@NGFs as an anode (1.2 cm  $\times$  1.2 cm,  $\sim$  1.36 mg), lithium as a cathode, and polypropylene as a separator (PP, Celgard 2500, Suzhou Zhongyan Chemical Co., Ltd.). LiPF6 (1 M) in a 1:1:1 (v/v/v) dimethyl carbonate (DMC)/ethyl methyl carbonate (EMC)/ethylene carbonate (EC) was used as electrolyte. Galvanostatic charge/discharge performances were tested on a battery tester (LAND, CT-2001A). Cyclic voltammetry (CV) curves were obtained by a multichannel electrochemical workstation (Bio Logic Science Instruments, VMP-300).



Fig. S1. (a-b) TEM and FESEM images of ZIF-67 nanoparticles. (c) XRD pattern of ZIF-67 nanoparticles.



Fig. S2. (a) EDS spectra and (b) XRD pattern of ZIF-67/PAN.



Fig. S3. (a) SEM, (b) TEM and (c) HRTEM images of Co@NGFs.

Combined with previously reported work, during the pyrolysis of ZIF-67/PAN, the Co<sup>2+</sup> will transform to Co atoms and a mass of Co atoms gathered together to form the Co nanoparticles<sup>1</sup>. In addition, the coordination bonds in the ZIF-67 nanoparticles have disappeared and have partly transformed into porous carbon, another part of coordination bonds have been decomposed into active C species for the formation of graphitic carbon on the surface of Co cataylsts due to the catalytic performance of the Co nanoparticles<sup>2-4</sup>.



Fig. S4a. The photographs of Co<sub>3</sub>O<sub>4</sub>@NGFs (a) before, (b) during and (c) after being rolled up.



Fig. S5. The TGA pattern of (a) Co<sub>3</sub>O<sub>4</sub>@NGFs and (b) Co<sub>3</sub>O<sub>4</sub>@NGFs-A.

The thermogravimetric analysis (TGA) was used to confirm the metal contents of  $Co_3O_4$ @ NGFs. In the Fig. S5a, the final metal content was ~40% which exhibit a moderate metal content. The  $Co_3O_4$ @NGFs-A have ~13% mass left (Fig. S5b), this can prove that a small quantity of  $Co_3O_4$  exist in  $Co_3O_4$ @NGFs-A which have not been removed by HCl.





The XRD pattern of the Co@NGFs and Co<sub>3</sub>O<sub>4</sub>@NGFs (Fig. S6a) accorded well with that of Co (JCPDS No. 15-0806) and Co<sub>3</sub>O<sub>4</sub> (JCPDS No. 43-1003), demonstrating the successful oxidization of Co to Co<sub>3</sub>O<sub>4</sub>. The peaks at 31.7°, 36.1°, 45.2°, 59.1° and 65.5° were ascribed to the (220), (311), (400), (511) and (440) planes of the Co<sub>3</sub>O<sub>4</sub>. The broad peaks indicated the Co<sub>3</sub>O<sub>4</sub> inside fibers had a small particle size which was consistent with the TEM results. The broad diffraction peak at ~25° was related to the (002) crystal plane of the graphitic carbon originating from the carbon fibers. Raman spectra (Fig. S6b) were used to confirm the degree of graphitization. The intensive peaks of Co@NGFs and Co<sub>3</sub>O<sub>4</sub>@NGFs at 1,359 and 1,596 cm<sup>-1</sup> corresponded respectively to D band and G band with intensity ratio of I<sub>G</sub>/I<sub>D</sub> = 1.01, indicating the graphitic degree was not influenced by oxidization, which was favorable to enhancing the electrical conductivity of the sample.



Fig. S7. (a) XPS spectrum of Co<sub>3</sub>O<sub>4</sub>@NGFs and high resolution of (b) Co 2p (c) C 1s (d) N 1s.

The X-ray photoelectron spectroscopy (XPS) measurement was used to obtain the near-surface composition and element bonding of the as-prepared Co<sub>3</sub>O<sub>4</sub>@NGFs sample. The presence of Co, C, O, and N in Co<sub>3</sub>O<sub>4</sub>@NGFs was once again confirmed as reflected in Fig. S7a. The Co 2p high resolution peaks in Fig. S7b showed two major peaks located at 795.2 and 779.6 eV relating to Co  $2p_{1/2}$  and Co  $2p_{3/2}$  in Co<sub>3</sub>O<sub>4</sub>, which was consistent with the reported data<sup>5, 6</sup>. The peaks at 784.7 and 801.9 eV were considered to be satellite peaks<sup>7</sup>. The C 1s spectrum of Co<sub>3</sub>O<sub>4</sub>@NGFs was fitted to four peaks as shown in Fig. S7c. The strong peak at 284.8 eV corresponded to graphitic carbon (C–C sp<sup>2</sup> bonds), and the other three weaker peaks were associated with C–C sp<sup>3</sup> (285.5 eV), C=O/C=N (288.0 eV), and COOR (290.9 eV), respectively<sup>5, 8</sup>. The N 1s spectrum in Fig. S7d was deconvoluted into four component peaks of pyridinic N (397.7 eV), pyrrolic N (399.8 eV), graphitic N (401.5 eV), and oxidized N (402.8 eV)<sup>6, 8</sup>. These N-containing species could create massive defects on 3D carbon fibers that would provide more active sites for lithium storage properties, especially pyridinic N and pyrrolic N in nitrogen-doped carbon materials. The redox reactions between Co<sub>3</sub>O<sub>4</sub> and lithium:

$$Co_{3}O_{4} + 8Li^{+} + 8e^{-} \leftrightarrow 4Li_{2}O + 3Co \qquad (1)$$
  
8Li \leftarrow 8Li^{+} + 8e^{-} \qquad (2)

$$Co_3O_4 + 8Li \leftrightarrow 3Co + 4Li_2O \tag{3}$$



**Fig. S8.** (a) CV curves and (b) Galvanostatic discharge/charge voltage profiles of Co<sub>3</sub>O<sub>4</sub>@NGFs-A electrode.

The capacity contribution of  $Co_3O_4$  in the  $Co_3O_4$ @NGFs electrodes can also be calculated, at 0.1 A g<sup>-1</sup>, after 100 cycles, the capacity of  $Co_3O_4$ @NGFs and  $Co_3O_4$ @NGFs-A were about 739 mA h g<sup>-1</sup> and 408 mA h g<sup>-1</sup>, we assume that the capacity contribution of  $Co_3O_4$  is x, from the TGA data we know the mass percentage of  $Co_3O_4$  in  $Co_3O_4$ @NGFs is about 40%, so we can get the following equation:

$$0.4 \text{ x} + 0.6 \cdot 408 = 739 \text{ x} = 1235.5$$

So, the capacity contribution of  $Co_3O_4$  in the  $Co_3O_4$ @NGFs is about 1235.5 mA h g<sup>-1</sup>, this value is higher than theoretical capacity of  $Co_3O_4$  (890 mA h g<sup>-1</sup>), the excess capacity should be provided by capacitors which is consistent with our calculation of DCP and SCP.

According to previous studies, the relationship between the sweep rate (v) and the peak current (i) can be defined as: <sup>9</sup>

$$i = a v^b$$
 (1)

in which both a and b are adjustable parameters. The value of b is in the range of  $0.5\sim1$ ; when b is close to 0.5, it represents DCP dominance; when b approaches 1, it

reflected SCP dominance.10

The SCP contribution could be quantified by using the following equation:<sup>11</sup>

$$i(V) = k_1 v + k_2 v^{1/2}$$
 (2)

in which  $k_1 v$  and  $k_2 v^{1/2}$  represent the current generated by the DCPs and SCPs, respectively



**Fig. S9.** (a-d) The calculated total current and capacitive current from the CVs at different scan rates  $(0.5 \text{ mV s}^{-1}, 2 \text{ mV s}^{-1}, 6 \text{ mV s}^{-1}, \text{ and } 10 \text{ mV s}^{-1})$ .

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