Supporting Information

General strategy of decorating 3D carbon nanofiber aerogel derived from bacterial cellulose with nano-Fe₃O₄ for high-performance flexible and binder-free lithium-ion battery anodes

Yizao Wan, Zhiwei Yang, Guangyao Xiong,* and Honglin Luo* b

a School of Mechanical and Electrical Engineering, East China Jiaotong University, Nanchang 330013, China

b School of Materials Science and Engineering, Tianjin Key Laboratory of Composite and Functional Materials, Key Laboratory of Advanced Ceramics and Machining Technology, Ministry of Education, Tianjin University, Tianjin 300072, China

Corresponding authors.

E-mail addresses: xiongguangyao@163.com (G. Xiong), hlluotju@126.com (H. Luo)
Experimental section

Preparation of nano-Fe$_2$O$_3$-decorated BC aerogels

The preparation and cleaning procedures of BC pellicles were identical to those described in our previous work. The resulting BC pellicles were freeze-dried in liquid nitrogen (-196 °C) to obtain BC aerogels. The nano-Fe$_2$O$_3$-decorated BC aerogels were synthesized by the hydrothermal method. Typically, a BC aerogel (25 × 25 × 1 mm$^3$) was immersed in 50 mL of 0.05 M Fe(NO$_3$)$_3$•9H$_2$O aqueous solution for 48 h at room temperature. Next, the BC aerogel was immersed in 40 mL of 0.5 M urea aqueous solution under agitation, and subsequently transferred to a closed container at 120 °C for 10 h. The product was taken out and freeze-dried, resulting in a nano-Fe$_2$O$_3$-decorated BC aerogel, which was named as Fe$_2$O$_3$-BC-05. Other nano-Fe$_2$O$_3$-decorated BC aerogels were synthesized with the same procedure except that the concentration of Fe(NO$_3$)$_3$•9H$_2$O was different, namely 0.1 and 0.2 M. The resultant samples are denoted as Fe$_2$O$_3$-BC-10 and Fe$_2$O$_3$-BC-20, respectively.

Preparation of Fe$_3$O$_4$-BC-CNFs

The as-obtained Fe$_2$O$_3$-BC aerogels were carbonized in a tube furnace under nitrogen atmosphere. The samples were heated from room temperature to 300 °C at a heating rate of 1 °C min$^{-1}$, held for 1 h and then heated to 600 °C at 2 °C min$^{-1}$. The carbonization lasted for 2 h to yield Fe$_3$O$_4$-BC-CNFs (named as Fe$_3$O$_4$-BC-CNFs-x, corresponding to Fe$_2$O$_3$-BC-x, x=05, 10, 20).
**Preparation of coin cells**

To prepare working electrodes, BC-CNFs and Fe$_3$O$_4$-BC-CNFs were punched into circular samples with a diameter of 13 mm and vacuum dried at 100 ºC for 12 h. The dried samples were directly used to assemble into cells without any additives or binders. For comparison, Fe$_3$O$_4$ nanoparticles (around 10 nm in size) obtained from Sinopharm Chemical Reagent Co., Ltd., Beijing, China, were used to prepare coin cells. Fe$_3$O$_4$ nanoparticles, carbon black, and polyvinylidene fluoride (PVDF) with a mass ratio of 80 : 10 : 10 were mixed into a homogeneous slurry using N-methyl-2-pyrrolidone (NMP) as the solvent. The slurry mixture was coated onto Cu foil followed by vacuum drying at 100 ºC for 12 h. The coin cells (CR2032) were fabricated using metallic lithium as the counter electrode, porous polypropylene film (Celgard 2400) as the separator, and 1 M LiPF$_6$ in ethylene carbonate (EC)–dimethyl carbonate (DMC)–ethylmethyl carbonate (EMC) (1 : 1 : 1 by volume) as the electrolyte. The cell assembly was carried out in an Ar-filled glovebox. Before all electrochemical measurements, cells were aged for 12 h.

**Electrochemical measurements**

Charge–discharge experiments were performed at a constant current density between 0.005 and 3 V (vs Li$^+$/Li) using a BTS-5V10mA battery tester. Cyclic voltammetry (CV) measurement was performed using a CHI 660B electrochemical workstation at 0.5 mV/s within the range of 0.0-3.0 V (vs Li$^+$/Li). For the electrochemical impedance spectroscopy (EIS) measurements, the excitation voltage applied to the cell was 5 mV and the frequency ranges from 0.01 Hz to 100 kHz.
Characterization

Samples were characterized by scanning electron microscopy (SEM, Nova Nanosem 430), transmission electron microscopy (TEM, Tecnai G2F-20), and X-ray diffraction (XRD, Rigaku D/Max 2500 v/pc) with Cu Kα radiation. Thermogravimetric analysis (TGA) was performed on a simultaneous TGA/DSC analyzer (STA449F3) from 30 to 800 °C at a heating rate of 10 °C/min in air. Fourier transformed infrared spectroscopy (FTIR) analysis was conducted by Shimadzu IRPrestige-21 (Japan) and FTIR spectra were recorded in a spectral range of 4000-400 cm⁻¹ with a resolution of 4 cm⁻¹. Raman spectra were recorded by an RM2000 spectrometer (Renishaw Co.). XPS analysis was performed by an X-ray photoelectron spectrometer (Thermo ESCALAB 250Xi, Thermo Fisher Scientific Inc., Waltham, MA, USA). Conductivity measurements were carried out on a Keithley 2635 sourcemeter unit as previously reported.¹ Nitrogen adsorption isotherms and the Brunauer–Emett–Teller (BET) surface area of Fe₃O₄-BC-CNFs were measured at 77 K with a surface area analyzer (W-BK132F, Beijing JWGB Sci. & Tech., China).

Notes and references


Fig. S1 The XRD patterns of α-Fe$_2$O$_3$, BC, and Fe$_2$O$_3$-BC-10.

Fig. S2 XRD patterns of BC-CNFs (a), Fe$_3$O$_4$-BC-CNFs-05 (b), Fe$_3$O$_4$-BC-CNFs-10 (c), and Fe$_3$O$_4$-BC-CNFs-20 (d).
Fig. S3 Particle size distribution of Fe$_3$O$_4$ nanoparticles on the surface of Fe$_3$O$_4$-BC-CNFs-05 (a), Fe$_3$O$_4$-BC-CNFs-10 (b), and Fe$_3$O$_4$-BC-CNFs-20 (c) ($p > 0.05$ when any two materials are compared).
**Fig. S4** HRTEM images of Fe₃O₄-BC-CNFS-05 (a), Fe₃O₄-BC-CNFS-10 (b), and Fe₃O₄-BC-CNFS-20, showing lattice fringe with a spacing of 0.253 nm.
Fig. S5 EDX pattern of Fe₃O₄-BC-CNFs.
Fig. S6 X-ray photoelectron spectroscopy (XPS) spectra of wide scan (a), Fe 2p peaks (b), and C 1s peaks of Fe$_3$O$_4$-BC-CNFs.
**Fig. S7** TG curves of Fe₃O₄-BC-CNFs-05 (a), Fe₃O₄-BC-CNFs-10 (b), and Fe₃O₄-BC-CNFs-20 (c).

**Fig. S8** Raman spectra of BC-CNFs (a), Fe₃O₄-BC-CNFs-05 (b), Fe₃O₄-BC-CNFs-10 (c), and Fe₃O₄-BC-CNFs-20 (d).
Fig. S9 Nitrogen adsorption and desorption isotherm (a) and pore-size distribution (b) of Fe$_3$O$_4$-BC-CNFs-10 (the Brunauer-Emmett-Teller specific surface area was calculated to be 322 m$^2$ g$^{-1}$).
**Fig. S10** Cyclic voltammetry (CV) curves of Fe$_3$O$_4$-BC-CNFs during the first three cycles.

**Fig. S11** Discharge/charge profiles of bare Fe$_3$O$_4$ nanoparticles.
Fig. S12 Charge and discharge capacities with Coulombic efficiency as a function of cycle number of bare Fe$_3$O$_4$ nanoparticles at a current density 100 mA g$^{-1}$. 

![Graph showing charge and discharge capacities with Coulombic efficiency as a function of cycle number. The graph indicates a specific capacity of 297 mAh g$^{-1}$.](image)
Table S1 $R$ values of bare BC-CNFs and Fe$_3$O$_4$-BC-CNFs.

<table>
<thead>
<tr>
<th>Samples</th>
<th>D peak (cm$^{-1}$)</th>
<th>G peak (cm$^{-1}$)</th>
<th>$R$</th>
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<tbody>
<tr>
<td>Bare BC-CNFs</td>
<td>1342</td>
<td>1590</td>
<td>0.80</td>
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<tr>
<td>Fe$_3$O$_4$-BC-CNFs-05</td>
<td>1339</td>
<td>1589</td>
<td>0.81</td>
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<td>Fe$_3$O$_4$-BC-CNFs-10</td>
<td>1338</td>
<td>1588</td>
<td>0.85</td>
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<td>Fe$_3$O$_4$-BC-CNFs-20</td>
<td>1329</td>
<td>1587</td>
<td>0.88</td>
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Table S2 Relevant parameters of Fe$_3$O$_4$-BC-CNFs-10 and bare Fe$_3$O$_4$ under different conditions.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Conditions</th>
<th>$R_f$ (Ω)</th>
<th>$R_{ct}$ (Ω)</th>
</tr>
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<tbody>
<tr>
<td>Fe$_3$O$_4$-BC-CNFs-10</td>
<td>Before rate performance tests</td>
<td>23.0</td>
<td>136.2</td>
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<tr>
<td></td>
<td>After rate performance tests</td>
<td>8.6</td>
<td>106.3</td>
</tr>
<tr>
<td>Bare Fe$_3$O$_4$</td>
<td>Before rate performance tests</td>
<td>39.8</td>
<td>361.9</td>
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</table>