Supporting Information

In Situ Encapsulation of Iron Oxide Nanoparticles into Nitrogen-doped Carbon Nanotubes as Anodic Electrode Materials of Lithium Ion Batteries

Ming Chen,*a Feng-Ming Liu,a Hui Zhao,b Shan-Shuai Chen,c Xing Qiand, Zhong-Yong Yuane and Rong Wan,*a

aCollege of Chemistry and Chemical Engineering, Xinyang Normal University, Xinyang 464000, China

bSchool of Materials Science and Engineering, Liaocheng University, Liaocheng 252000, Shandong, China

cSanya Nanfan Research Institute of Hainan University, Hainan University, Sanya, 572025, China

dCollege of Chemical Engineering, Fuzhou University, Fuzhou 350116, China

eSchool of Materials Science and Engineering, Nankai University, Tianjin 300071, China

*Corresponding author. E-mail address: chenming19830618@126.com, wanrong1992@163.com
EXPERIMENTAL SECTION

Preparation of Samples.

The synthesis of C$_3$N$_4$: 10 g melamine was pressed into a pellet under a pressure of 20 MPa. The pellet was transferred to a quartz boat covered with a quartz cap and calcined at 600 °C for 0.5 h in N$_2$ atmosphere. Then the obtained yellow powder was collected as the carbon and nitrogen precursor for the preparation of Fe$_3$C@NCNT.

The in situ synthesis of Fe$_3$C@NCNT arrays: 2 g FeC$_2$O$_4$·2H$_2$O and 5 g C$_3$N$_4$ were added to 5 mL aqueous solution under tempestuously stirring to form a yellow slurry. Then, the colloidal compounds were milled continually to form a yellow paste, following the evaporation of water. The obtained yellow paste was dried at 80 °C for 24 h and manually ground into powder. The powder was transferred to a semiclosed quartz boat and heated at 350 °C for 1 h at a heating rate of 2 °C min$^{-1}$ in a tubular furnace under N$_2$ flow, and the temperature was increased to 700 °C at 2 °C min$^{-1}$ and kept at 700 °C for 3 h, followed by cooling to room temperature naturally.

The in situ synthesis of Fe$_2$O$_3$@NCNT arrays: The obtained Fe$_3$C@NCNT powder was calcined in a muffle furnace in air at 300 °C for 0.5 h with a heating rate of 10 °C min$^{-1}$, and the final product was obtained.

The synthesis of Fe$_2$O$_3$/CB: 2 g FeC$_2$O$_4$·2H$_2$O and 0.5 g carbon black was dispersed in 3 mL deionized water and ground by mortar and pestle to form a slurry. Then the slurry was dried at 80 °C in oven overnight. The obtained powder was transferred to a quartz boat and covered by a quartz cap. Then heat treated at 300 °C for 0.5 h in air to form Fe$_2$O$_3$/CB.

Material Characterization

The crystalline structure of the products was characterized by X-ray diffraction (XRD) on a Rigaku SmartLab9 powder diffractometer equipped with Cu $K_a$ radiation (λ =
1.541 Å). Thermogravimetric analysis (TGA) was performed on a TA SDT Q600 analyser in air with a heating rate of 10 K min$^{-1}$. The morphology of the products was observed by field emission scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The SEM was carried out on a ZEISS SUPRA 55 microscope equipped with a secondary electron detector and the applied acceleration voltage was 3 kV. Transmission electron microscope (TEM) images and elemental mapping were taken on a Tecnai G2 F20 microscope with an accelerating voltage of 200 KV. X-ray photoelectron spectroscopy (XPS) was conducted using a Kratos Axis Ultra DLD (delay line detector) spectrometer equipped with a monochromatic Al $K_{\alpha}$ X-ray source (1486.6 eV). Raman spectra were collected on a Renishaw-1000 spectrometer by exciting a 514.5 nm Ar ion laser. $N_2$ adsorption-desorption isotherms were recorded at 77 K on a Quantachrome NOVA 2000e sorption analyzer. Optical absorption spectroscopy was performed in the 300-700 nm range in 1 nm steps on an ultraviolet-visible-near-infrared, double beam spectrophotometer (America PerkinElmer Lambda 950).

**Electrochemical Characterization**

$Fe_2O_3@NCNT$ or $Fe_2O_3/CB$ and polyvinylidene fluoride (PVDF) binder in a weight ratio of 9 : 1 were mixed in N-methylpyrrolidone (NMP) and stirred for 24 h to make a slurry. The slurry was then spread on a Cu foil (13 mm in diameter, 0.3 mm in thickness) with a surface density of 1.0 mg cm$^{-2}$ (electrode thickness: 9.7 μm, Fig. S4) and dried at 120 °C for 24 h to fabricate the working electrodes in vacuum. Lithium foil was used as both the reference electrode and the counter electrode (13 mm in diameter, 0.5 mm in thickness). 1.0 M LiPF$_6$ in a 1:1 (v/v) mixture of ethylene carbonate (EC) and diethyl carbonate (DEC) was employed as the electrolyte. Celgard 2300 membrane (25 μm-thick polyethylene) was adopted as a separator. The assembly of CR2032-type coin cells was conducted in a high-purity Ar filled glovebox. Three cells were assembled in each batch for every sample and the tested average value was used for plotting the graph. Galvanostatic cycling was performed
between 0.01 and 3 V vs Li⁺/Li at various C rates on a Land Battery Tester (Wuhan, China), where 1 C corresponds to 1000 mA g⁻¹. Cyclic voltammetry (CV) was conducted between 0.01 and 3 V at 0.1 mV s⁻¹ using a CHI660E electrochemical workstation. Electrochemical impedance spectroscopy (EIS) was performed on the same electrochemical system over the frequency range from 100 kHz to 100 mHz with a perturbation voltage of 5 mV. The Nyquist impedance plots were fitted by Zview 2 software based on the equivalent circuit diagram. All of the electrochemical measurements were performed at 25 °C in an ambient atmosphere.

**Fig. S1** XRD pattern of Fe₃C@NCNT

**Fig. S2** XPS survey spectrum of Fe₂O₃@NCNT hybrid.
**Fig. S3** Absorption spectrum of Fe$_2$O$_3$@NCNT hybrid.

**Fig. S4** The cross-sectional SEM image of Fe$_2$O$_3$@NCNT electrode layer on Cu current collector.
Fig. S5 Top-view SEM images of Fe₂O₃@NCNT electrode (a) before and (b) after 800 cycles.

Table S1 Comparison of Li/Fe₂O₃@NCNT half-cell results with literature reports.

<table>
<thead>
<tr>
<th>Reference</th>
<th>Material</th>
<th>Specific capacity (mAh g⁻¹)</th>
<th>Rate-capacity (mAh g⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>This work</td>
<td>Fe₂O₃@NCNT</td>
<td>0.5 C/1075 for 60 cycles</td>
<td>5 C/907</td>
</tr>
<tr>
<td>1</td>
<td>Fe₂O₃/C</td>
<td>0.2 C/790 for 100 cycles</td>
<td>4 C/390</td>
</tr>
<tr>
<td>2</td>
<td>Fe₂O₃/graphene</td>
<td>0.8 C/711 for 50 cycles</td>
<td>1.6 C/660</td>
</tr>
<tr>
<td>3</td>
<td>Fe₂O₃/graphene</td>
<td>0.5 C/780 for 40 cycles</td>
<td>2 C/420</td>
</tr>
<tr>
<td>4</td>
<td>Fe₂O₃/C</td>
<td>0.5 C/734 for 60 cycles</td>
<td>3 C/480</td>
</tr>
<tr>
<td>5</td>
<td>Fe₂O₃/Fe@SWCNT</td>
<td>0.5 C/650 for 25 cycles</td>
<td>1.2 C/550</td>
</tr>
<tr>
<td>6</td>
<td>YS-γ-Fe₂O₃@G-GS</td>
<td>0.5 C/737 for 30 cycles</td>
<td>5 C/443</td>
</tr>
<tr>
<td>7</td>
<td>Fe₂O₃/HCNF</td>
<td>0.2 C/816 for 100 cycles</td>
<td>2 C/602</td>
</tr>
<tr>
<td>8</td>
<td>Fe₂O₃/rGO</td>
<td>0.3 C/881 for 90 cycles</td>
<td>2 C/611</td>
</tr>
<tr>
<td>9</td>
<td>Fe₂O₃@CNFs</td>
<td>0.2 C/612 for 300 cycles</td>
<td>2 C/390</td>
</tr>
<tr>
<td>10</td>
<td>3D graphene/α-Fe₂O₃</td>
<td>1 C/674 for 420 cycles</td>
<td>5 C/336</td>
</tr>
<tr>
<td>11</td>
<td>HI-CNT/Fe₂O₃</td>
<td>0.1 C/651 for 100 cycles</td>
<td>5 C/420</td>
</tr>
<tr>
<td>12</td>
<td>γ-Fe₂O₃/graphene</td>
<td>1 C/833 for 100 cycles</td>
<td>2 C/551</td>
</tr>
</tbody>
</table>

References


7. T. Qing, N. Q. Liu, Y. Z. Jin, G. Chen and D. Min, Helical carbon nanofibers modified with Fe₂O₃ as a high performance anode material for lithium-ion batteries, *Dalton Trans.*, 2021, 50, 5819.


