

Supporting Information

Cactus-like Iron Oxide/Carbon Porous Microspheres Lodged in Nitrogen-Doped Carbon Nanotubes as Anodic Electrode Materials of Lithium Ion Batteries

Ming Chen,^{*a} Feng-Ming Liu,^a Shan-Shuai Chen,^b Rong Wan^a, Xing Qian^c and Zhong-Yong Yuan^d

^a College of Chemistry and Chemical Engineering, Xinyang Normal University, Xinyang 464000, China *E-mail: chenming19830618@126.com

^b Sanya Nanfan Research Institute of Hainan University, Hainan University, Sanya, 572025, China.

^c College of Chemical Engineering, Fuzhou University, Fuzhou 350116, China.

^d School of Materials Science and Engineering, Nankai University, Tianjin 300071, China

Experimental Section

Preparation of Samples.

The synthesis of C₃N₄: 10 g melamine was pressed into a pellet under a pressure of 20 MPa. The pellet was calcined at 600 °C for 1 h in N₂ atmosphere. Then the obtained yellow powder was collected as the carbon and nitrogen precursor for the preparation of Fe₃C@NCNT.

The synthesis of Fe₃C@NCNT: 1.5 g FeCl₃·6H₂O were dissolved in 5 ml deionized water, and a reddish brown solution was obtained after stirring for 15 min.

Then 5 g C_3N_4 powder was added to the above solution under tempestuously stirring to form a brown slurry. Then, the colloidal compounds were milled continually to form a paste, following the evaporation of water. The obtained 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 prepared black powder was treated in 4 M HCl aqueous solution at 80 °C for 12 h, followed by washing in distilled water and dried at 150 °C for 1 h in vacuum. The obtained composite was labeled as $Fe_3C@NCNT$.

The synthesis of cactus-like $Fe_2O_3/C@NCNT$ porous microspheres: The obtained $Fe_3C@NCNT$ powder was calcined in a muffle furnace in air at 450 °C for 0.5 h with a heating rate of 10 °C min^{-1} , and the resultant product was denoted as $Fe_2O_3/C@NCNT$.

The synthesis of cactus-like Fe_2O_3 porous microspheres: The cactus-like Fe_2O_3 was obtained by annealing the $Fe_3C@NCNT$ at 600 °C for 1 h in air.

The synthesis of Fe_2O_3/CB : 3 g $FeC_2O_4 \cdot 2H_2O$ and 0.7 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 450 °C for 1 h in air to form Fe_2O_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 $Cu K_\alpha$ radiation ($\lambda = 1.541 \text{ \AA}$). Thermogravimetric analysis (TGA) was performed on a TA SDT Q600 analyser in air with a heating rate of 10 °C min^{-1} . The morphology of the products was observed by field emission scanning electron microscopy (FE-SEM) on a ZEISS SUPRA 55 microscope and transmission electron microscopy (TEM) on a Tecnai G2

F20 microscope. Raman spectra were collected on a Renishaw-1000 spectrometer by exciting a 514.5 nm Ar ion laser. The carbon content was measured by using Carbon/Sulfur determinator (ELTRA, CS800). N₂ 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

Fe₂O₃/C@NCNT or Fe₂O₃/CB and polyvinylidene fluoride (PVDF) binder in a weight ratio of 90 : 10 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 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 LiPF₆ 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. 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. All of the electrochemical measurements were performed at 25 °C in an ambient atmosphere.

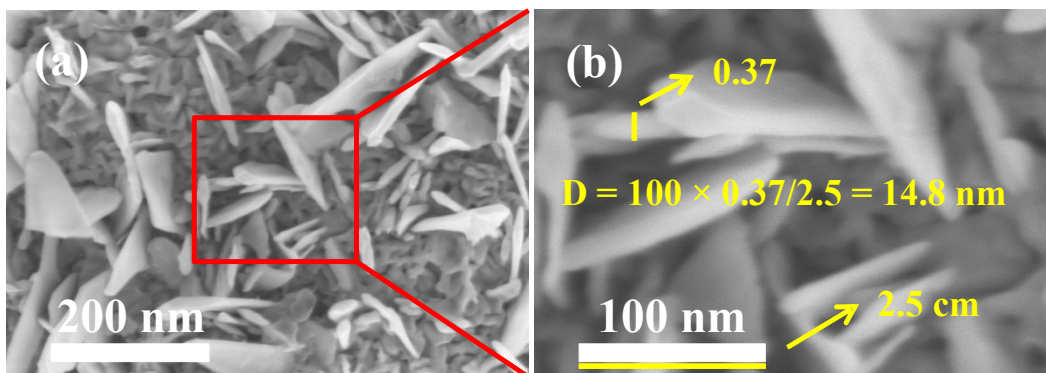


Fig. S1 (a) SEM image of $\text{Fe}_2\text{O}_3/\text{C}@$ NCNT nanocomposite and (b) enlarged SEM image of the selected area in (a).

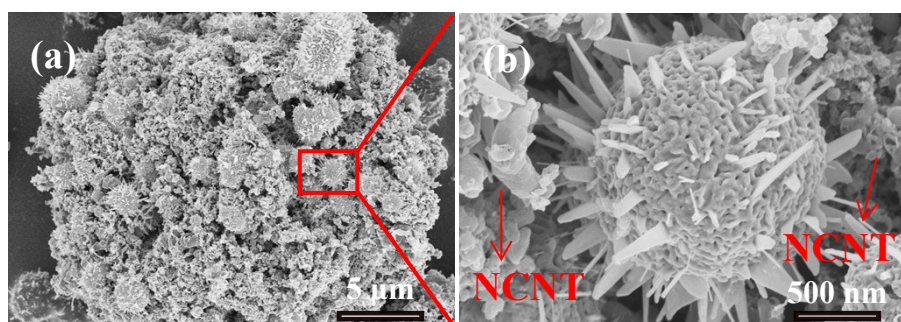


Fig. S2 SEM images of (a) $\text{Fe}_2\text{O}_3/\text{C}@$ NCNT and (b) embedded cactus-like $\text{Fe}_2\text{O}_3/\text{C}$ in wrapped NCNTs of the selected area in (a).

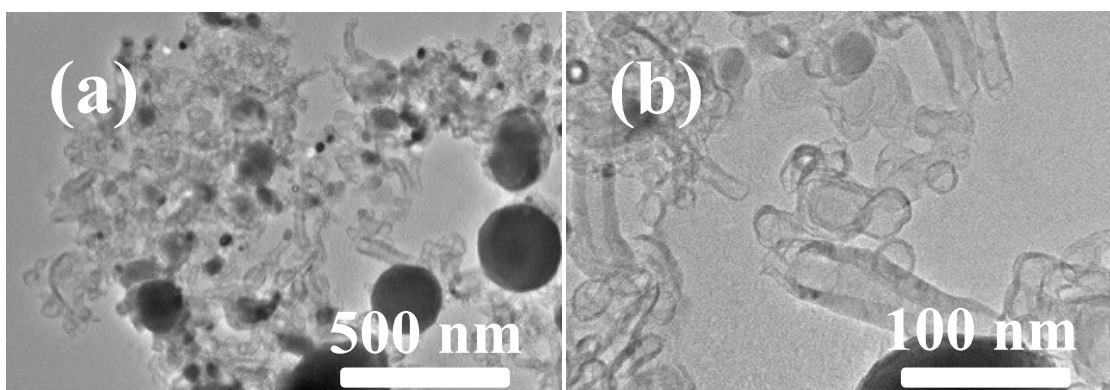


Fig. S3 TEM images of open NCNTs with segregated Fe_3C nanoparticles.

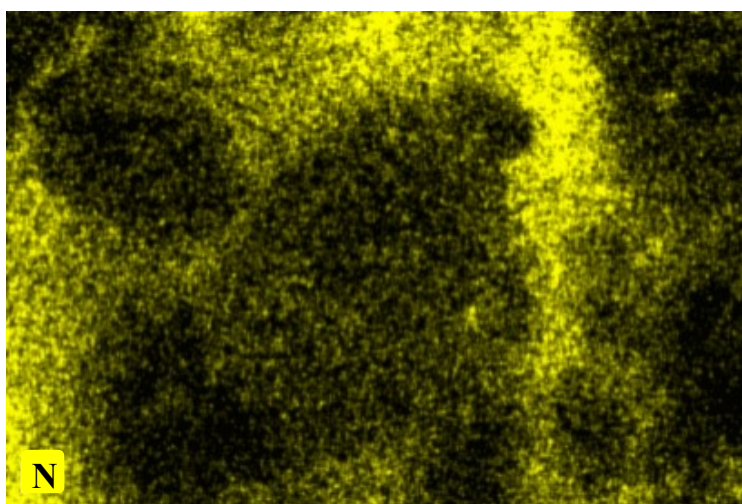


Fig. S4 The EDS mapping for N element in cactus-like $\text{Fe}_2\text{O}_3/\text{C}$ porous microspheres in Fig. 3f.

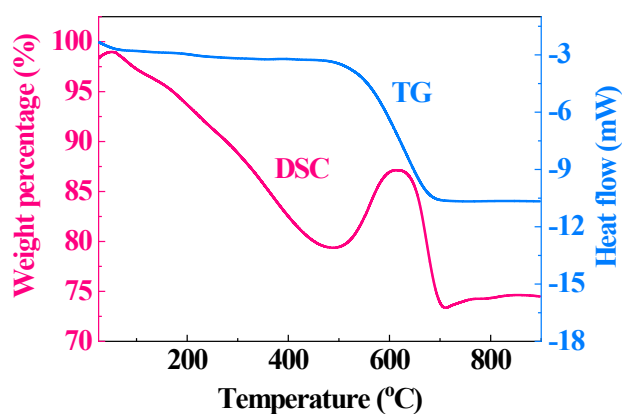


Fig. S5 TG/DSC curves of $\text{Fe}_2\text{O}_3/\text{C}@\text{NCNT}$ measured in air.

The detailed chemical compositions in $\text{Fe}_2\text{O}_3/\text{C}@\text{NCNT}$ composite were further quantified by thermogravimetric curve, which was recorded under air at a heating rate of $10\text{ }^\circ\text{C min}^{-1}$. As presented in Fig. S3, the TG curve of $\text{Fe}_2\text{O}_3/\text{C}@\text{NCNT}$ composite exhibited a main mass loss of 14.59 wt % in the temperature range of 450-600 $^\circ\text{C}$, which was attributed to oxidation of carbon nanotubes and amorphous carbon. The mass percentage of residual Fe_2O_3 were examined to about 85.41 wt %. Finally, the TG-DSC curve combined with result of carbon/sulfur determinator further identified that the weight percentages of Fe_2O_3 and C in $\text{Fe}_2\text{O}_3/\text{C}@\text{NCNT}$ were ca. 14.59, and 85.41 wt. %, respectively.

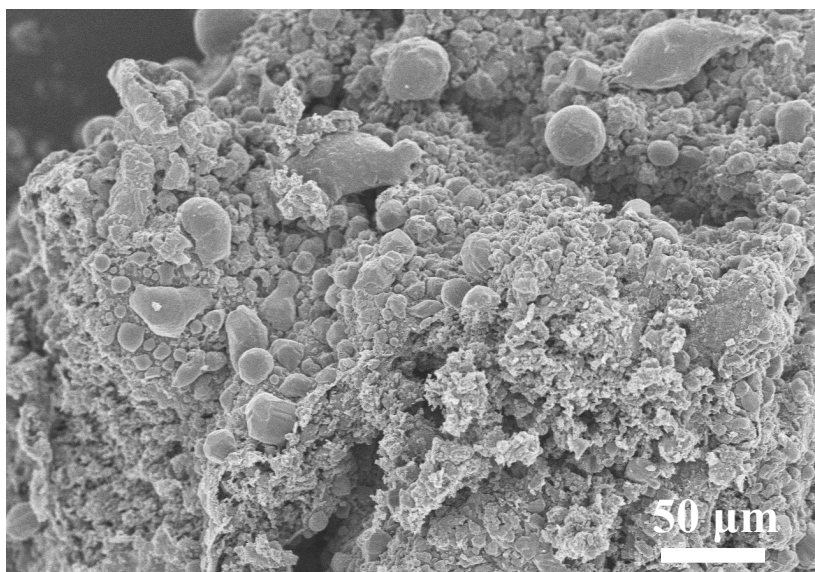


Fig. S6 The SEM image of Fe₂O₃/CB.

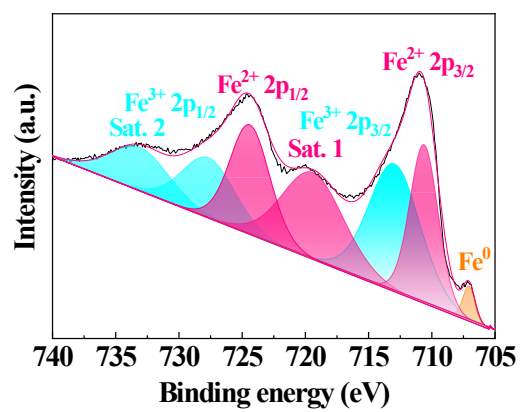


Fig. S7 High-resolution XPS spectrum of Fe 2p of Fe₃C@NCNT hybrid.

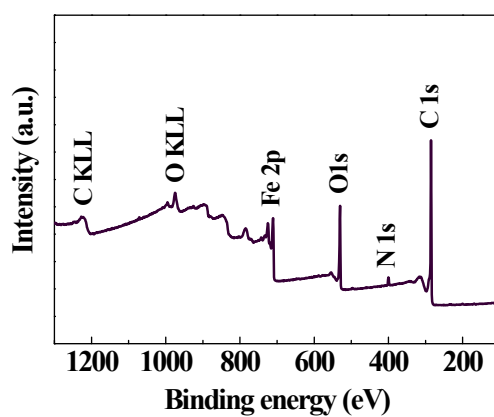


Fig. S8 XPS survey spectrum of Fe₂O₃/C@NCNT hybrid.

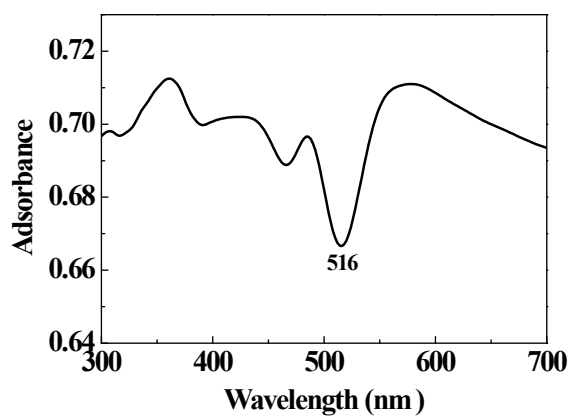


Fig. S9 Absorption spectrum of Fe₂O₃/C@NCNT hybrid.

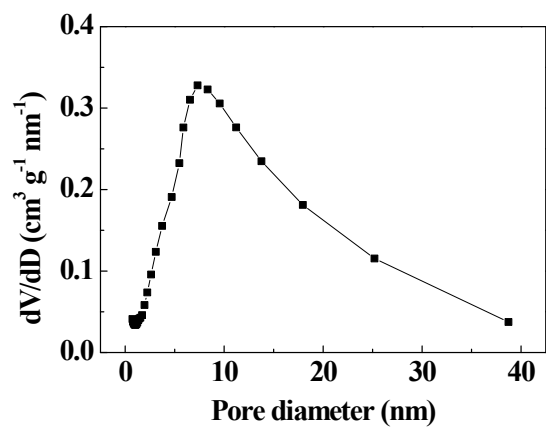


Fig. S10 The BJH pore size distribution curve of Fe₂O₃/C@NCNT..

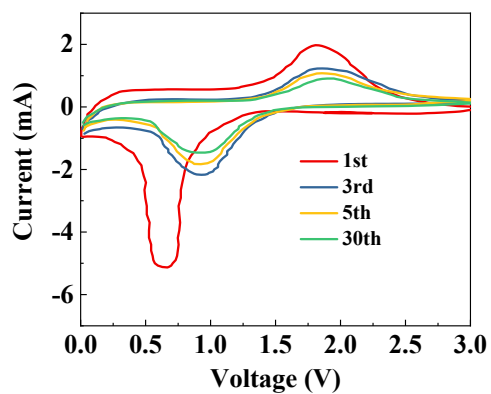


Fig. S11 CV of cactus-like Fe₂O₃ || Li half-cells at 0.1 mV s⁻¹ for the 1st cycle.

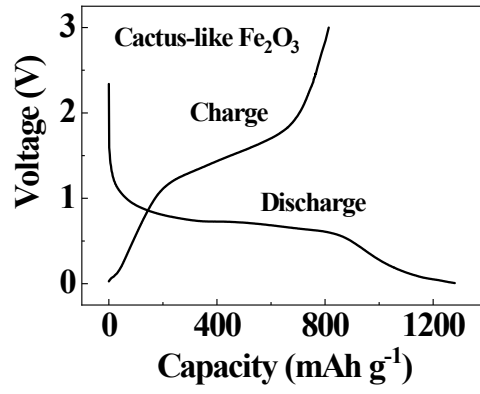


Fig. S12 The charge and discharge curve of cactus-like Fe_2O_3 based half-cell at 0.1 C (100 mA g^{-1}).

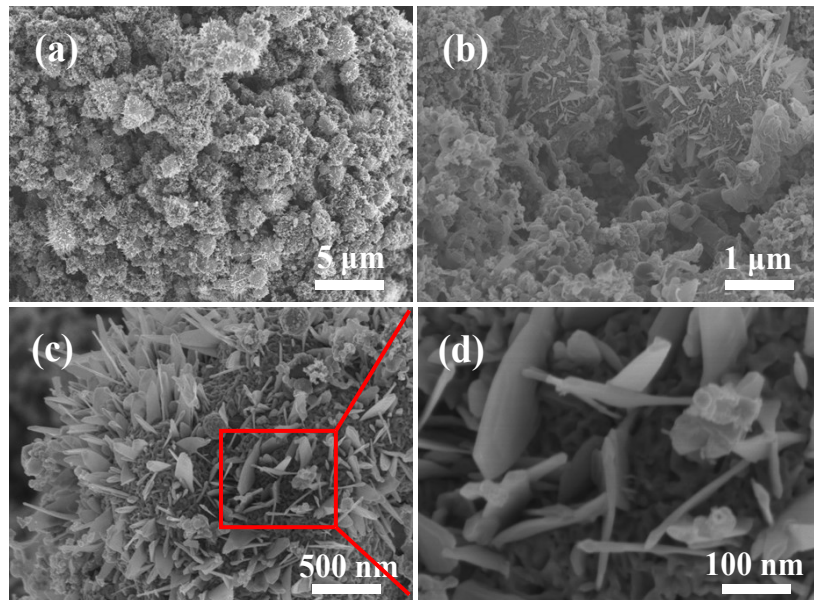


Fig. S13 Top-view SEM images of $\text{Fe}_2\text{O}_3/\text{C}@\text{NCNT}$ electrode after 600 cycles.

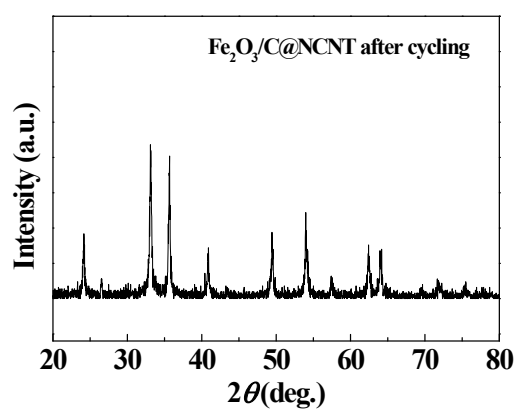


Fig. S14 XRD pattern of Fe₂O₃/C@NCNT electrode after 600 cycles.