

Electronic supplementary information for:

Template-free construction of hollow ZnFe₂O₄ nanotubes coated with nano-carbon layer as a competitive anode for Li-ion batteries

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Experimental section

Synthesis of the ZFO NTs

Typically, the electrospinning process was performed to synthesize the precursor. Specifically, 2 g of polyvinyl pyrrolidone (PVP, Mw: 360,000) was well dissolved in 20 mL of absolute ethanol under vigorously stirring for 5 h, and the solution A is obtained. Meanwhile, 0.22 g of zinc acetate dihydrate and 0.808 g of ferric sulfate nonahydrate were dissolved in 10 mL of N, N-dimethylformamide, and the solution B is obtained. Then, the two solutions were mixed well, and loaded into a syringe of 10 mL in volume. The distance of the needle to the collection board is 15 cm, and the applied voltage is 15 kV. The constant flow rate was set as 1 mL h⁻¹. And the temperature in the electrospinning box is maintained as 25 °C. The resulted NFs are marked as ZnFe-PVP, and further calcinated at 500 °C for 5h. Thus, the ZFO NTs were fabricated.

Synthesis of the ZFO@C NTs

130 mg of the resulting ZFO NTs were added into the tris solution with a pH value of 8.5. After vigorously stirred for 6 h, 30 mg of dopamine was added into the mixture under ultrasonication. After further stirring for 24 h, the product was collected, dried, and annealed at 500 °C in pure N₂ atmosphere. Accordingly, the ZFO@C NTs were finally prepared.

Materials characterization

Typical X-ray diffraction (XRD) patterns of obtained products were collected by a BREKER-D8ADVANCE type X-ray diffractometer with Cu K α . X-ray

photoelectron spectroscopy (XPS) analysis was carried out by an X-ray photoelectron spectrometer (thermo ESCALAB 250XI). Raman analysis (514 nm excitation) was recorded by laser Raman spectrometer (T6400, Jobinyzon Corp., France). Morphologies and microstructures of resulted samples were investigated by field-emission scanning electron microscopy (FESEM, JEOL-6300F), transmission electron microscopy (TEM), high-resolution TEM (HRTEM), scanning TEM (STEM), and selected area electron diffraction (SAED) (JEOL JEM-2100) coupled with energy dispersive X-ray (EDX) spectroscopy. N₂ adsorption-desorption measurements were conducted to obtain Brunauer-Emmett-Teller (BET) specific surface area (SSA) and pore size distribution (PSD) on an Autosorb-IQ/MP surface area analyzer (Quantachrome, America).

Electrochemical evaluation

The working electrode in half cells was composed of electroactive ZFO@C NTs (or ZFO NTs), acetylene black and carboxymethylcellulose sodium with a mass ratio of 7 : 2 : 1, and the deionized water was applied as the dispersant. The obtained slurry was then coated on fresh copper foil and dried at 100 °C for 12 under vacuum. Typical mass loading was ~1.2 mg cm⁻² per cell. The electrolyte in our work is 1 M LiPF₆ in ethylene carbonate and diethylene carbonate (1 : 1 in volume). The micro-porous Celgard 2400 film was used a separator for assembling coin cells (CR2032) in a glove box filled with high-purity argon (both water and O₂ concentration < 0.1 ppm). The charge-discharge tests were performed on an 8-channel Land Test System (CT2001A). Cyclic voltammetry (CV) and electrochemical impedance spectroscopy

(EIS) were performed on an electrochemical workstation (IviumStat. h, the Netherlands) at 25 °C.

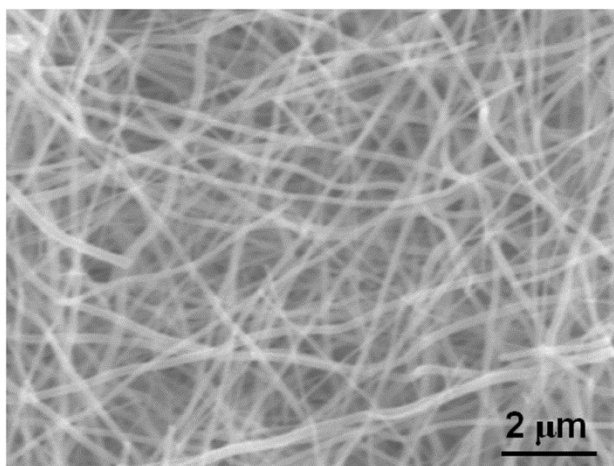


Fig. S1 FESEM image of the electrospun ZnFe-PVP fibers

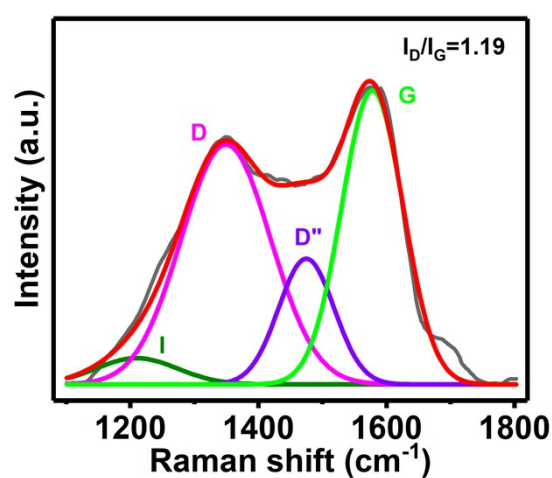


Fig. S2 Raman spectrum for the ZFO@C NTs

As seen in **Fig. S2**, the fitted peak at $\sim 1578\text{ cm}^{-1}$ (G-band) is corresponding to the E_{2g} phonon of sp^2 carbon atoms, indicative of the tangential vibration of carbon atoms and characteristic feature of ordered graphitic layers. And the peak located at $\sim 1349.3\text{ cm}^{-1}$ (D-band) is related to the disordered graphitic structure.

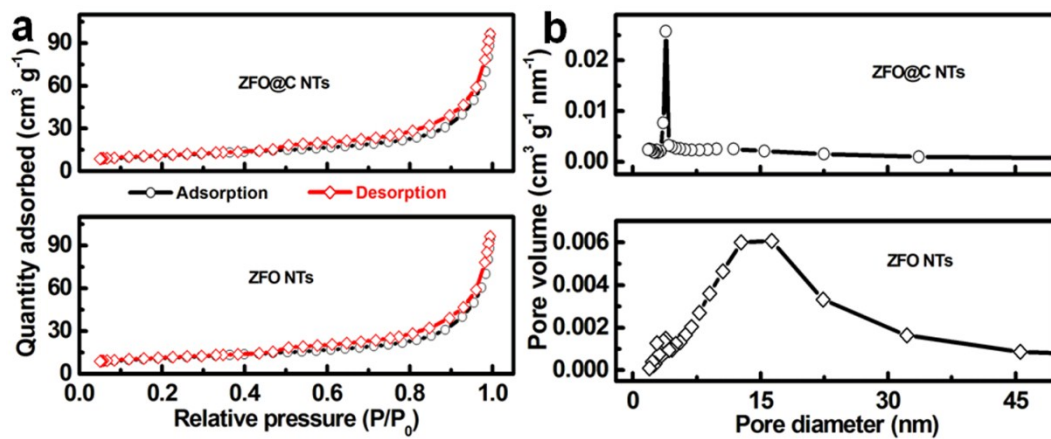


Fig. S3 (a) N₂ sorption thermals and (b) pore size distribution plots of the ZFO and ZFO@C NTs

Table S1 Specific surface area, pore volume and average pore size of the ZFO@C NTs and ZFO NTs

Samples	Specific surface area ($\text{m}^2 \text{g}^{-1}$)	Pore volume ($\text{cm}^3 \text{g}^{-1}$)	Average pore size (nm)
ZFO NTs	~34.9	~0.18	~20.3
ZFO@C NTs	~38.5	~0.15	~15.2

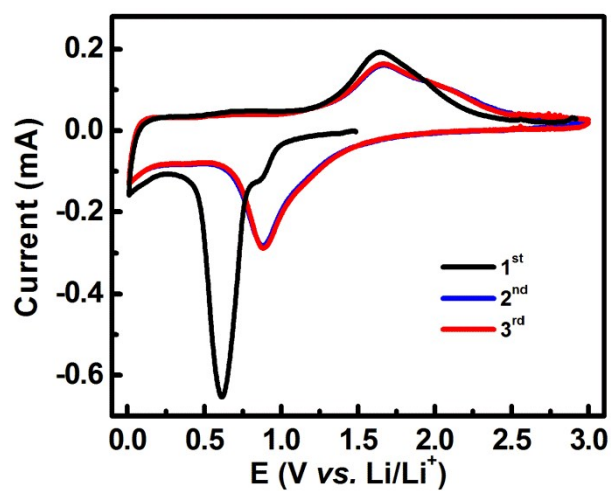


Fig. S4 Initial three CV cycles for the ZFO@C NTs at a sweep rate of 0.1 mV s^{-1}

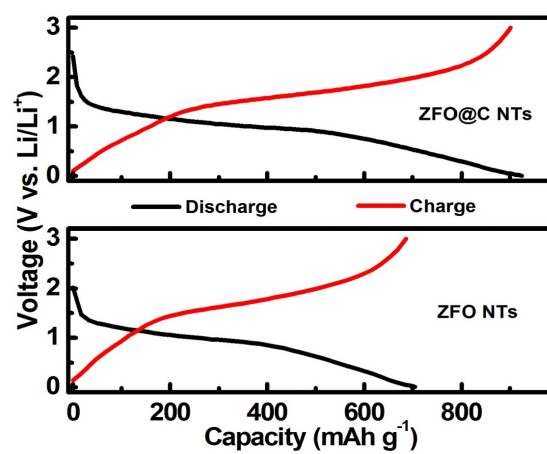


Fig. S5 The 2nd discharge-charge plots for the ZFO and ZFO@C NTs at 300 mA g⁻¹

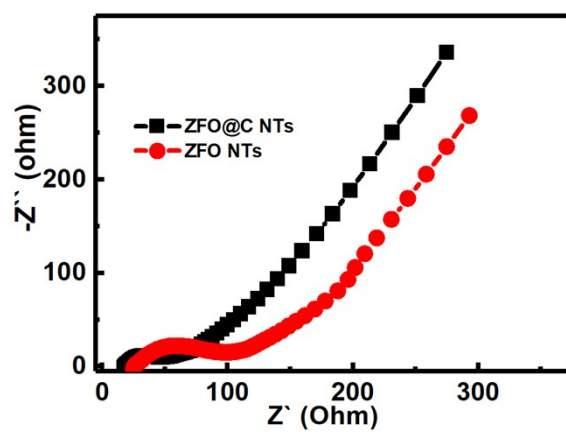


Fig. S6 EIS spectra of the ZFO and ZFO@C NTs electrodes

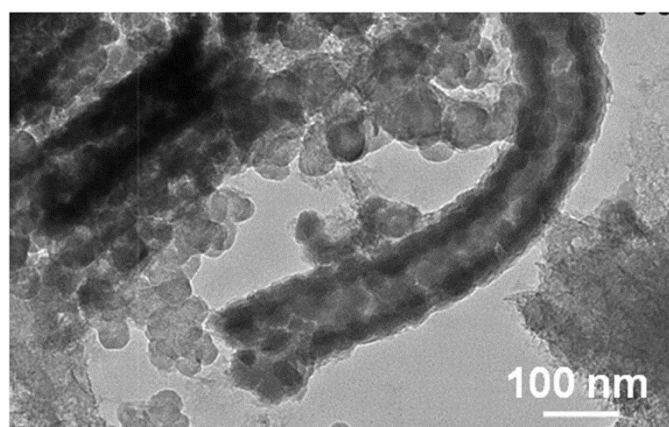


Fig. S7 TEM image for the ZFO@C NTs electrode after 500 cycles at 500 mA g⁻¹

