Electronic Supplementary Information

Assembling carbon-coated hollow α-Fe_2O_3 nanohorns on the CNT backbone for superior lithium storage capability

Corresponding author: Xiong Wen (David) Lou*

School of Chemical and Biomedical Engineering, Nanyang Technological University, 70 Nanyang Drive, Singapore, 637457. Email: xwlou@ntu.edu.sg; Tel: +65 63168879

Experimental Details

Pre-treatment of carbon nanotubes

Carbon nanotubes (CNTs) used in this work are provided by X2 Labwares Pte. Ltd., of which the diameter is in a range of 20 – 60 nm and the length is around several micrometers. 3 g of the CNTs is refluxed in 90 mL of HNO_3 (65 wt.%) at 120 ^oC for 6 h. After that, the acid treated CNTs are rinsed with DI water until a neutral pH value is reached. Then they are collected by filtration and dried at 60 ^oC for further use.

Synthesis of the CNT@FeOOH hierarchical structure

For the growth of β-FeOOH nanospindles on CNT backbones, 5 mg of the CNTs is dispersed in 10 mL of aqueous solution of $FeCl_3$ (0.12 M) by ultra-sonication for 30 – 60 min in a capped bottle. After thorough mixing, the suspension is kept in an oil bath under stirring at 75 ^oC for 5 h. The final products are collected by several rinse-centrifugation (2000 rpm) cycles before drying at 60 ^oC.

Synthesis of the CNT@Fe_2O_3 hierarchical structure

For the formation of hollow α-Fe_2O_3 nanohorns on CNT backbones, certain amount of CNT@FeOOH hierarchical structures is annealed in air at 400 ^oC for 4 h with a slow ramp rate of 0.5 $^oC\ min^{-1}$.

Carbon coating of CNT@Fe_2O_3 hierarchical structures

For the carbon coating of CNT@Fe_2O_3 hierarchical structures, 20 mg of the CNT@Fe_2O_3 samples is dispersed in 40 mL of aqueous solution of glucose (0.06 M). After thorough mixing, the suspension is transferred into a 50 mL Teflon-lined stainless steel autoclave and kept in an oven at 180 ^oC for 6 h. The obtained products are collected by several rinse-centrifugation (2000 rpm) cycles before drying at 60 ^oC.

Materials characterization

All samples were characterized by field-emission scanning electron microscope (FESEM, JEOL, JSM-7600F), transmission electron microscope (TEM, JEOL, JEM-2010 and JEM-2100F), powder X-ray diffraction (XRD, Bruker, D8-Advance X-ray Diffractometer, Cu Kα, λ = 1.5406 Å), nitrogen adsorption/desorption (Quantachrome Instruments, Autosorb AS-6B) and thermogravimetric analysis (TGA, Shimadzu, DRG-60).

The electrochemical measurements were conducted using two-electrode Swagelok cells with pure lithium foil as the counter and reference electrode at room temperature. The

working electrode consists of a test material (*e.g.*, CNT@Fe_2O_3 with or without carbon coating), carbon black (Super-P-Li) and polyvinylidene difluoride (PVDF) in a weight ratio of 7:2:1. The electrolyte used is 1.0 M $LiPF_6$ in a 50:50 (w/w) mixture of ethylene carbonate and diethyl carbonate. Cell assembly is carried out in an Ar-filled glovebox with concentrations of moisture and oxygen below 1.0 ppm. The galvanostatic charge/discharge tests were performed using a Neware battery tester at different current densities with a cut-off voltage window of 0.01 – 3.0 V. The calculation of the specific capacity is based on the overall mass of the composite material synthesized, for example, carbon coated CNT@Fe_2O_3 structures. Electrochemical impedance spectroscopy (EIS) was performed using an CHI660C electrochemistry workstation by applying an ac amplitude of 5 mV over the frequency range from 0.1 to 10^5 Hz.

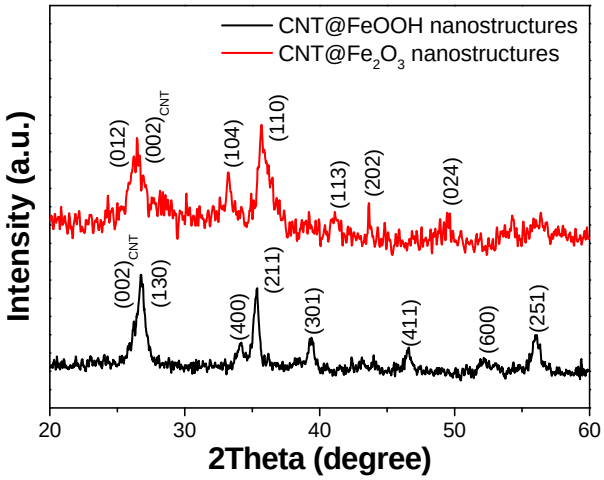

Figure S1 XRD profiles of CNT@FeOOH and CNT@Fe_2O_3 hierarchical structures.

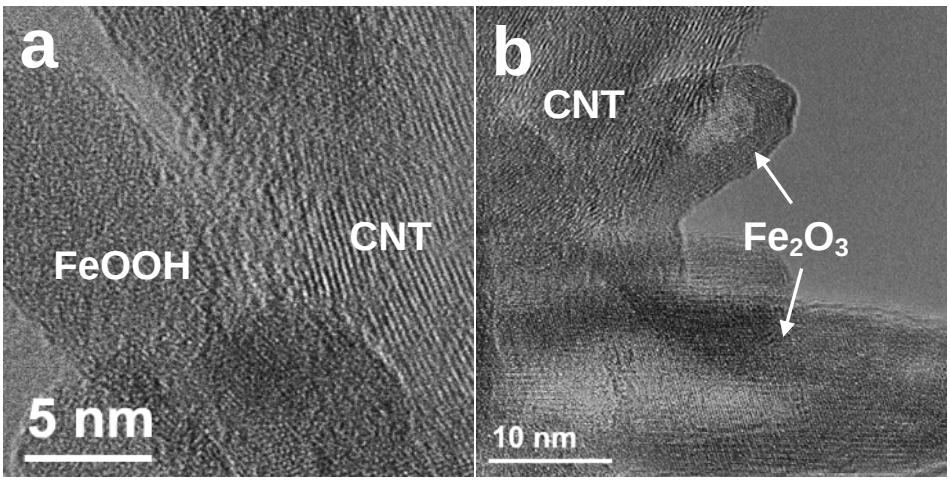

Figure S2 HRTEM images of CNT@FeOOH and CNT@Fe_2O_3 hierarchical structures.

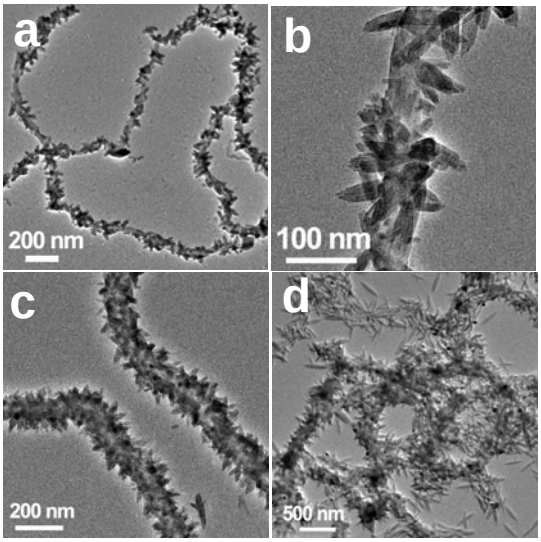

Figure S3 TEM images of the samples obtained by the hydrolysis of $FeCl_3$ with various initial concentration: (a, b) 0.03 M, (c) 0.06 M, (d) 0.36 M.

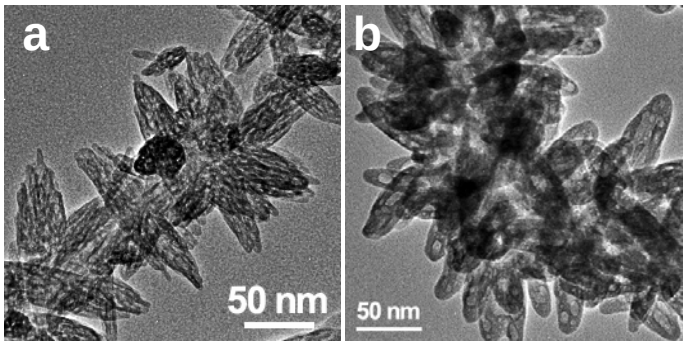

Figure S4 TEM images of CNT@Fe_2O_3 structures obtained by annealing at different temperature: (a) 250 ^oC, (b) 300 ^oC.

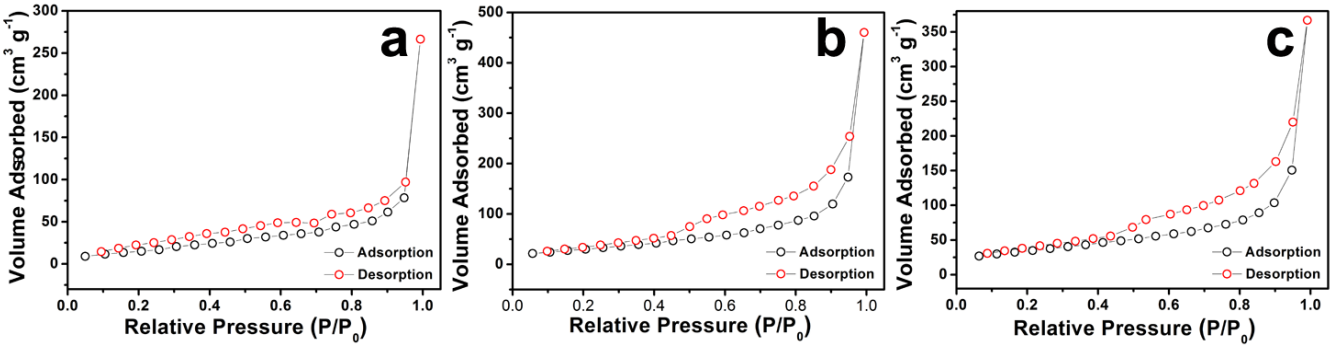

Figure S5 N_2 adsorption/desorption isotherms of (a) CNT@FeOOH, (b) CNT@Fe_2O_3 and (c) carbon coated CNT@Fe_2O_3 hierarchical structures.

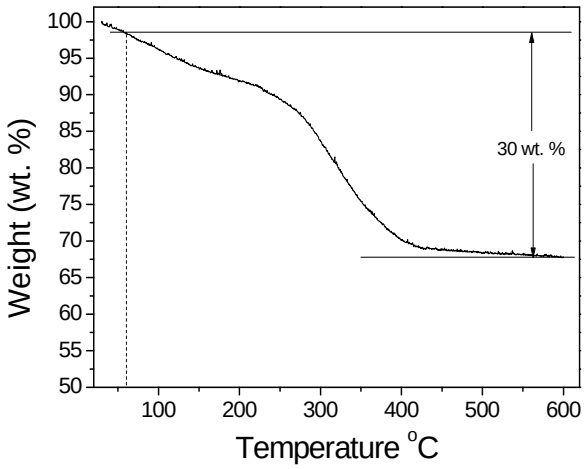

Figure S6 Thermogravimetric analysis of carbon coated CNT@Fe_2O_3 structures. The test was conducted in air with a rampe rate of 10 ^oC min^{-1}.

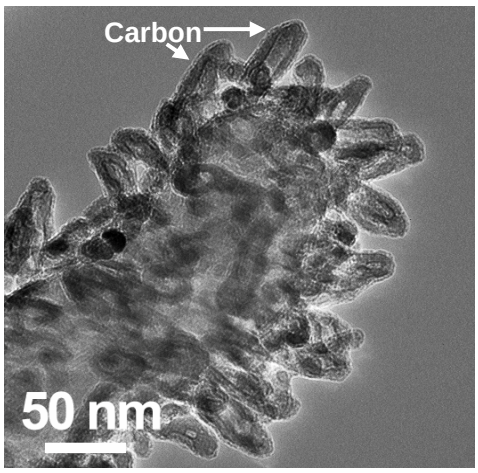

Figure S7 TEM image showing the presence of uniform carbon nanocoating around the scaffold of CNT@Fe_2O_3 hierarchical structures.

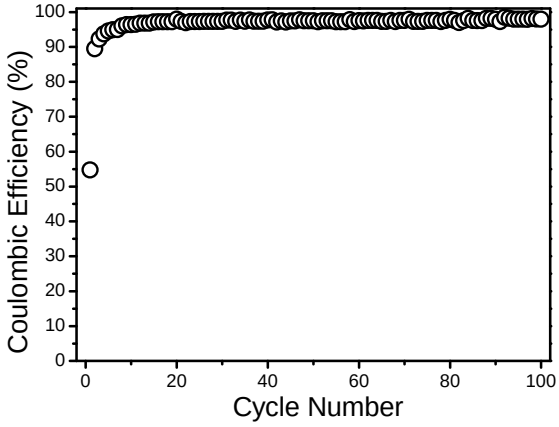

Figure S8 Coulombic efficiency of carbon coated CNT@Fe_2O_3 structures cycled between 0.01 – 3V at a current density of 500 mA g^{-1}.

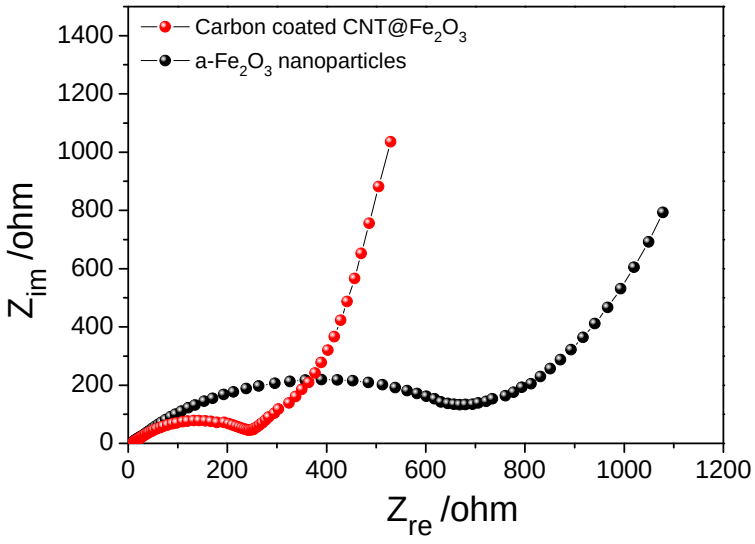

Figure S9 Nyquist plots of the electrodes composed of the hierarchical structures of carbon coated CNT@Fe_2O_3 or α-Fe_2O_3 nanoparticles.