Supporting Online Materials for

In-situ Self-catalyzed Formation of Core-shell LiFePO$_4$@CNTs Nanowire for High Rate Performance Lithium-ion Batteries

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Experimental part

Synthesis of LFP@CNTs composites
The following describes a typical synthesis for LFP@CNTs composites. First: 100 mg PMMA was dissolved in 30 mL of water via strong ultrasonic agitation. Next, 1.039 lithium dihydrogen phosphate (LiH₂PO₄, Sigma) was dissolved in 100 mL of water and stirred at 70 °C for 1 h. Separately, 1.739 M iron (II) acetate (Fe(AC)₂, Sigma) dissolved in 80 ml of water by stirring at 60 °C for 1 h. The three solutions were mixed together and dried at 70 °C for 24 h. After thorough grinding of the xerogel followed by annealing in a furnace filled with an argon atmosphere at 700 °C for 5 h, 10 h and 20 h with a heating rate of 10 °C min⁻¹, the core shell LFP@CNTs composites were obtained.

Characterization
The synthesized material was then characterized by various methods. Powder X-ray diffraction (XRD, Rigaku, Japan) using a Co Ka radiation source was used to identify the crystalline phase. FE-SEM (S-4800, Hitachi) with an operating voltage of 5 kV, TEM (H-7000, Hitachi) and HRTEM (JEOL 2010F) was used to determine the morphology and microstructure of the samples. A Raman scattering spectroscopy apparatus (HORIBA) equipped with a 532.4 nm laser was performed to study the phonon modes of Fe, P, O and C. N₂ adsorption/desorption isotherms were performed using a Folio Micromeritics TriStar II Surface Area Analyser. The Fe K-edge XANES spectra were obtained on the Soft X-ray Microcharacterization Beamline (SXRMNB, ΔE/E: 10⁻⁴), and C K-edge were conducted on the undulator Spherical Grating Monochromator (SGM) beamline at the Canadian Light Source (CLS) located at the University of Saskatchewan in Saskatoon.

Electrochemical Measurements
The electrochemical cell used in our study was a CR2032 coin cell. The electrolyte used in our experiment was 1 M LiPF₆ in a mixture of ethylene carbonate/dimethyl carbonate (1: 1 v/v) solvents. All electrochemical tests were performed in an Arbin BT-2000 Battery Test Station within a voltage range of 2.5-4.2 V (versus Li⁺/Li). The composites were mixed with acetylene black and poly-(vinylidene fluoride) (PVDF)
binder with a weight ratio of 75:15:10, using N-methyl-2-pyrolidene (NMP) as the solvent, and then the mixture was ground in a mortar and pestle and pasted onto pure Al foils. The coin cells were assembled in a high-purity argon filled glove box, and all of the electrochemical measurements were conducted at room temperature.

Figure S1. TEM image (a), (b) and HRTEM image (c) of LFP@CNTs nanowires.

Figure S2. Selected-area electron diffraction of core shell LFP@CNTs-10h nanowire.
**Figure S3.** SEM images of (a) LiFePO₄ precursor and (b) LFP@CNTs-10h nanowire.

**Figure S4.** SEM image (a) and TEM image (b) of core-shell LFP@CNTs-5h; SEM image (c) and TEM image (d) of LFP@CNTs-20h nanorod.
Figure S5. Raman spectrum of LFP@CNTs composites annealed at different time.

Figure S6. Charge-discharge galvanostatic curves for different cycles (1st, 10th, 50th and 100th).