

Supporting Information:

In situ generation of $\text{Li}_2\text{FeSiO}_4$ coating on MWNT as a high rate cathode material for lithium ion batteries

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Experimental Details

Synthesis of MWNT@SiO₂ composite: The pristine multi-walled carbon nanotube (MWNT) with diameter of 30-50 nm (purchased from Shenzhen Nanotech Por Co. Ltd) was firstly refluxed in nitric acid (65 wt %) at 140 °C for 6 hours before use. The MWNT@SiO₂ composite was synthesized according to the previously reported method¹. In a typical experiment, 320 mg acid-MWNT was dispersed in 160 mL ethanol and 16 mL de-ionized water and sonicated for 3 hours to form a homogeneous solution. Then, 2 mL NH₃.H₂O (25-28 wt%) and 1.36 mL tetraethoxysilane (TEOS) were added into the above solution under stirring and kept for 24 hours. The final product was filtered and washed with de-ionized water and ethanol for several times, then dried at 80°C overnight.

Synthesis of MWNT@Li₂FeSiO₄ composite: The MWNT@Li₂FeSiO₄ composite was synthesized via a solid-state reaction. Firstly, the stoichiometric amounts of MWNT@SiO₂, lithium acetate dehydrate and ferric oxalate were dissolved in 20 mL ethanol and sonicated for 3 hours. Then the solution was stirred at 60 °C to evaporate the ethanol. Finally, the obtained mixture was ground into power, pressed into plates, and subsequently calcinated at 600 °C for 5 hours under Ar atmosphere.

Synthesis of pure Li₂FeSiO₄: The pure Li₂FeSiO₄ was prepared according to a previous report.² The stoichiometric amounts of lithium acetate dehydrate, ferric oxalate and Si(OC₂H₅)₄ were dissolved in 30 mL ethanol. The mixture was then evaporated at 50 °C under stirring. The resulting powder was pressed into plates and calcinated at 700 °C for 12 hours under Ar atmosphere.

Sample characterization: The morphology and structure characterization of the MWNT, MWNT@SiO₂, and MWNT@Li₂FeSiO₄ samples were performed by transmission electron microscope (TEM, JEM-2010) and X-ray diffraction (XRD, RIGAKU SCXmini). The energy dispersive X-ray spectroscopy (EDS) device was used to identify the element components of the samples. Thermogravimetry analyses (TGA, NETZSCH STA449C) were measured from 30 to 900 °C at a heating rate of 10 K min⁻¹ in air to determine the carbon content in these samples.

Electrochemical measurements: The electrochemical measurements were performed via a CR2025 coin-type test cell. To fabricate the working electrode, 70 wt% active material (MWNT@Li₂FeSiO₄, or pure Li₂FeSiO₄ physically mixed with MWNT in a weight ratio with 80:20), 20 wt% conductivity agent (ketjen black, KB), and 10 wt% polymer binder (polyvinylidene fluoride, PVDF) were mixed with 1-methyl-2-pyrrolidinone (NMP). The resultant slurry was then pasted on stainless steel collector and dried at 80 °C for 12 h under vacuum. Pure lithium foil was used as both counter and reference electrode and the electrolyte was 1 M LiPF₆ in EC: EMC: DMC (1:1:1 in volume). Cells were assembled in an Ar-filled glove box. The galvanostatic charge/discharge test was carried out on a LAND 2001A system over a range of 1.5 V to 4.7 V at room temperature. The specific charge/discharge capacities mentioned in this article were calculated based on the mass of Li₂FeSiO₄.

- [1] K. G. Lee, R. Wi, M. Imran, T. J. Park, J. Lee, S. Y. Lee and D. H. Kim, *Acs Nano*, 2010, **4**, 3933-3942.
- [2] L. M. Li, H. J. Guo, X. H. Li, Z. X. Wang, W. J. Peng, K. X. Xiang and X. Cao, *J. Power Sources*, 2009, **189**, 45-50.

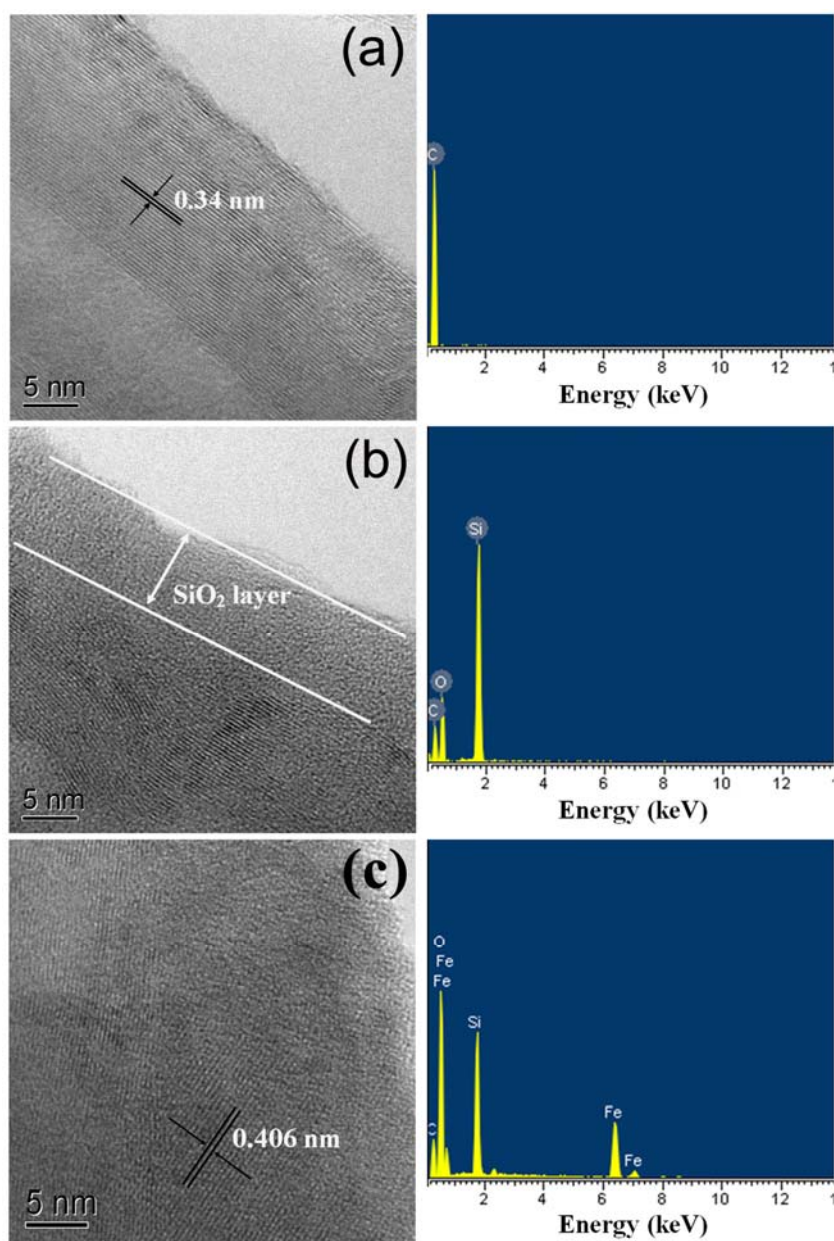


Fig. S1 High resolution TEM and the corresponding energy dispersive spectroscopy (EDS) spectrums of (a) MWNT, (b) MWNT@SiO₂, and (c) MWNT@Li₂FeSiO₄. (a) The HRTEM clearly shows the regular interplanar spacing of 0.34 nm for MWNTs. (b) The amorphous SiO₂ layer with a thickness of 10 nm was uniformly coated on the surface of MWNT. The regular interlayer spacing of 0.406 nm is ascribed to the (002) planes of monoclinic Li₂FeSiO₄, as shown in (c). The EDX spectrum indicates the presence of MWNT along with the prepared Li₂FeSiO₄.

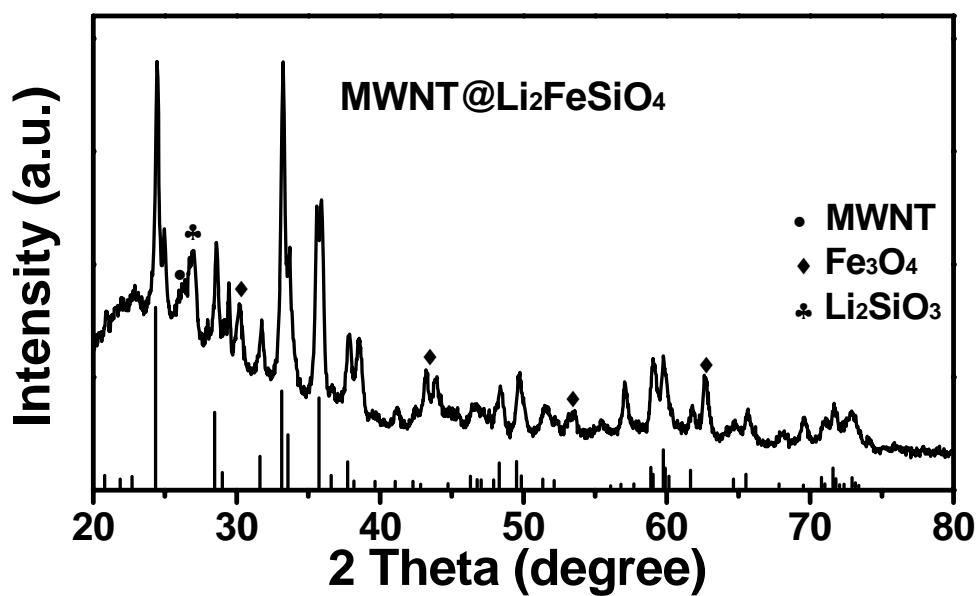


Fig. S2 XRD pattern of the MWNT@Li₂FeSiO₄ coaxial nanocable. The main diffraction peaks of the MWNT@Li₂FeSiO₄ composite could be indexed to the monoclinic Li₂FeSiO₄ with P2₁/n space group. A small amount of Fe₃O₄ and Li₂SiO₃ can also be detected in this composite. The diffraction peak near 26° was resulted from the MWNT.

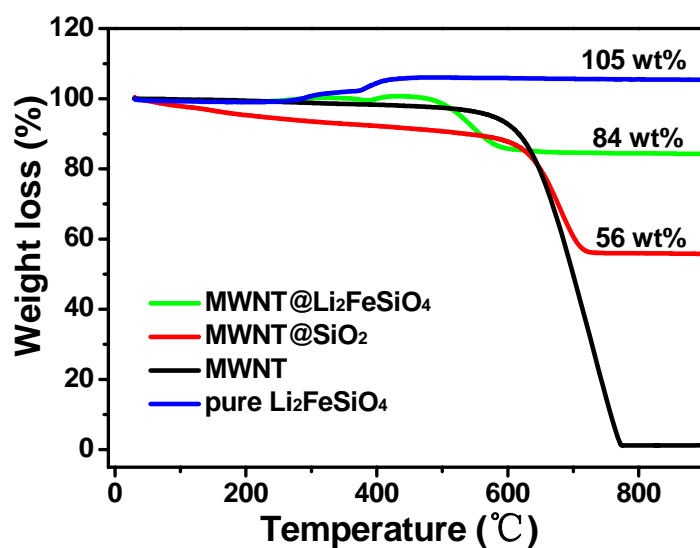


Fig. S3 Thermal gravimetric analysis (TGA) curves of the MWNT, MWNT@SiO₂, MWNT@Li₂FeSiO₄, and pure Li₂FeSiO₄ samples. The decomposition of MWNT takes place between 500 and 770 °C. The content of SiO₂ in the MWNT@SiO₂ composite is about 56 wt%. The pure Li₂FeSiO₄ suffered from a weight increase from 100 wt% to 105 wt%. For MWNT@Li₂FeSiO₄ composite, the final residues have the same composition with the pure Li₂FeSiO₄ sample after 900 °C. So the weight content of Li₂FeSiO₄ in the MWNT@Li₂FeSiO₄ composite = 84 wt% / 105 % = 80 wt%.

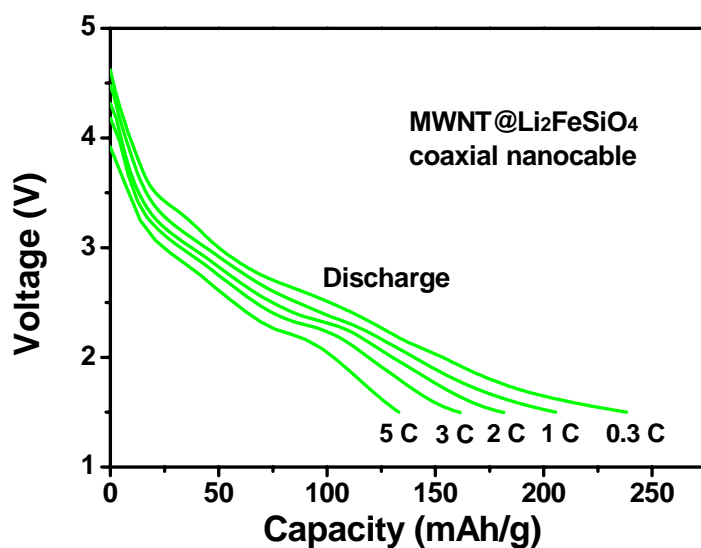


Fig. S4 The representative discharge curves of the MWNT@Li₂FeSiO₄ composite under various current densities from 0.3 C to 5 C. At a low current density of 50 mA g⁻¹ (0.3 C), the Li₂FeSiO₄ shell exhibited a stable discharge capacity of ~240 mAh g⁻¹, corresponding to 1.44 Li⁺ ion per formula insertion into the host matrix. More surprising, even at a high current density of 2C, this Li₂FeSiO₄ could still delivered more than one lithium insertion with capacities around 180 mAh g⁻¹.

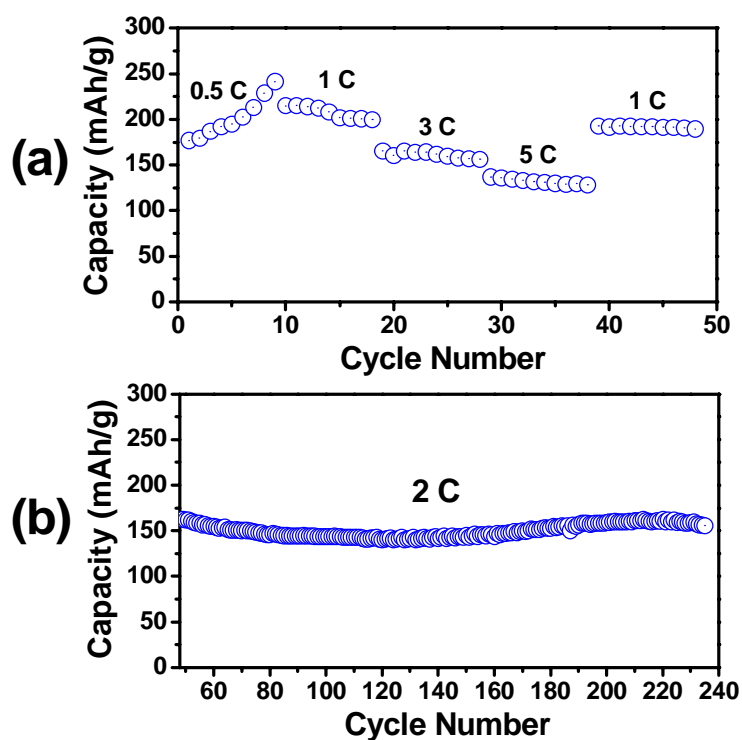


Fig. S5 Electrochemical performance of another cell made with MWNT@Li₂FeSiO₄ coaxial nanocable. Though there were variations from cell to cell, the excellent rate performance of this composite shown in Figure 3b could be repeatable. Furthermore, the specific capacity of this composite still kept around 160 mAh g⁻¹ after 230 cycles at a high current density of 2C, demonstrating the excellent cycling performance of our MWNT@Li₂FeSiO₄ composite.

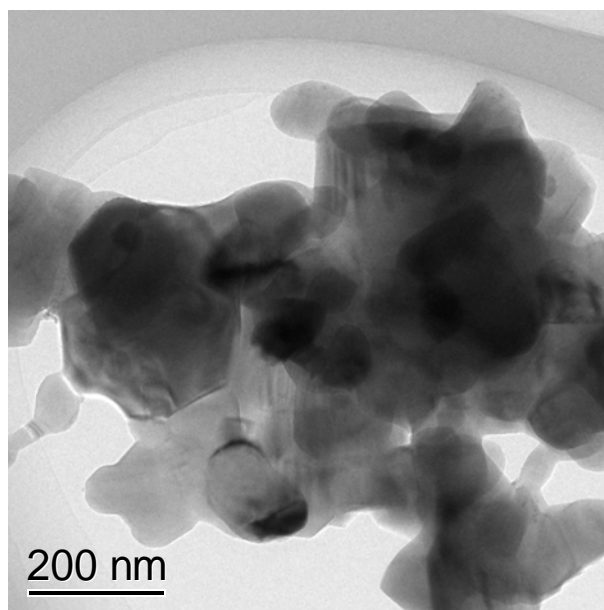


Fig. S6 TEM image of the pure Li₂FeSiO₄. As can be seen, the pure Li₂FeSiO₄ presented an irregular and agglomerated morphology with particles size from 60-300 nm.

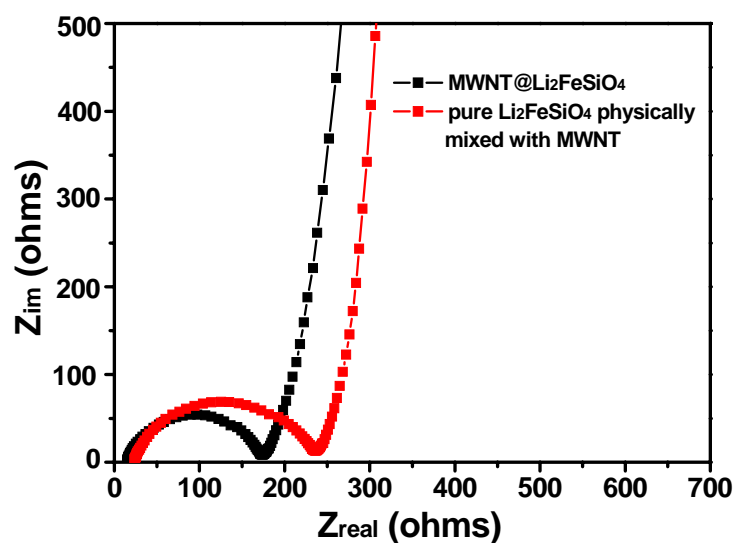


Fig. S7 Electrochemical impedance spectra for MWNT@Li₂FeSiO₄ coaxial nanocable and pure Li₂FeSiO₄ physically mixed with MWNT. As can be seen, the MWNT@Li₂FeSiO₄ composite showed better electron conductivity than pure Li₂FeSiO₄ physically mixed with MWNT.

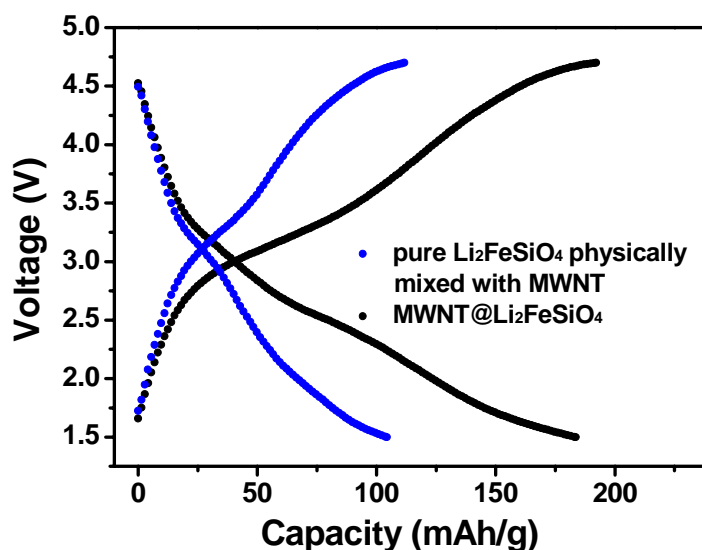


Fig. S8 The 10th charge/discharge curves of the MWNT@Li₂FeSiO₄ coaxial nanocable and pure Li₂FeSiO₄ physically mixed with MWNT at a current density of 1C between 1.5 V and 4.7 V.

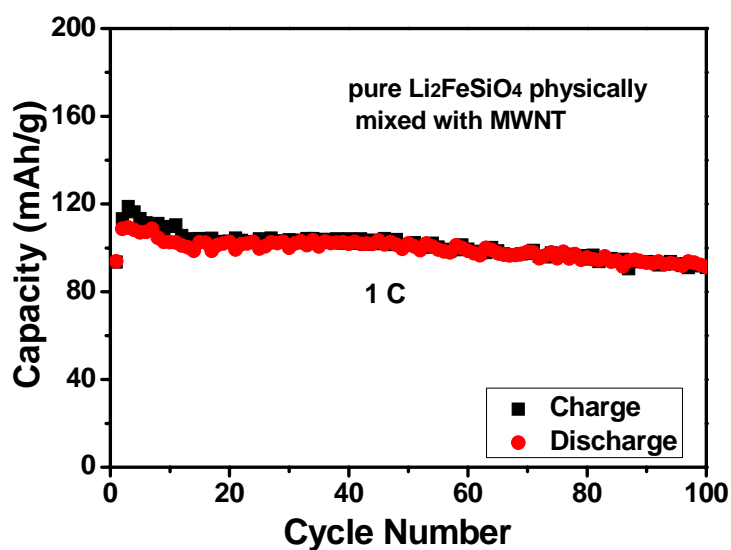


Fig. S9 Cycling performance of pure $\text{Li}_2\text{FeSiO}_4$ physically mixed with MWNT at a current density of 1C between 1.5 V and 4.7 V. The pure $\text{Li}_2\text{FeSiO}_4$ physically mixed with MWNT showed a worse electrochemical performance than MWNT@ $\text{Li}_2\text{FeSiO}_4$ coaxial nanocable. It delivered capacities of 110 mAh g^{-1} in the initial cycles and finally decreased to 90 mAh g^{-1} after 100 cycles at 1C.

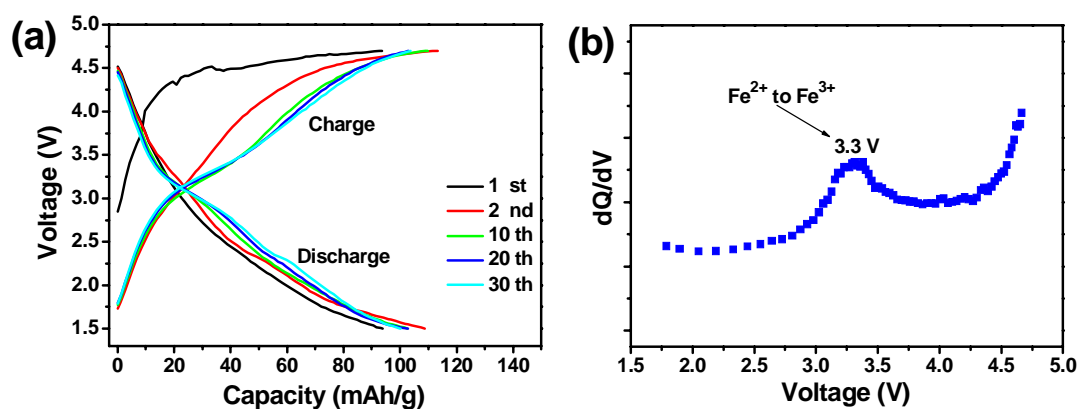


Fig. S10 (a) typical charge/discharge curves, (b) dQ/dV vs voltage plot of the 30th charge curve of the pure $\text{Li}_2\text{FeSiO}_4$ physically mixed with MWNT at a current density of 1C between 1.5 V and 4.7 V. Compared with the MWNT@ $\text{Li}_2\text{FeSiO}_4$ coaxial nanocable, the pure $\text{Li}_2\text{FeSiO}_4$ only showed one oxidation peak, corresponding to the $\text{Fe}^{2+}/\text{Fe}^{3+}$ redox couple, in the 30th charge curve.