Electronic Supplementary Material (ESI) for Energy & Environmental Science


# Supplementary Information

## A multilayer Si/CNT coaxial nanofiber LIB anode with a high areal capacity

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### Experimental Section

Fabrication of the Si/CNT multilayer was performed using layer-by-layer assembly method. Firstly, a copper foils substrate was washed with acetone and isopropanol, and then thin buffer layers of 20 nm Ti and 50 nm TiN were deposited using a RF magnetron sputtering system (ELITE RF/ DC magnetron sputtering). A 10 nm nickel film used as the catalyst was then deposited using electronic beam evaporation technique (HHV, auto 306). The prepared substrates were loaded into a thermal chemical vapor deposition reactor (Atomate inc.) and annealed at 650 $^{o}$C with argon and hydrogen flow for 10 min for nucleation of nickel nanoparticles. A 5μm high CNT film was then grown at 650 $^{o}$C for about 10 min from the nickel nanoparticles using ethanol as carbon source fed together with a mixture of argon (50 sccm), hydrogen (200 sccm) passing through an ethanol bubbler. Secondly, silicon was coated into the CNTs film using a PECVD system. To prepare Si/CNT multilayer, nickel nitrate ($Ni(NO_3)_2 \cdot 6H_2O$) solution(0.1 mmol/L in ethanol) was dropped onto the CNT thin film at 70 $^{o}$C. The second round of CNTs growth and silicon coating were performed using the conditions and processes described above. The masses of CNTs and deposited silicon were determined by weighing a sample before and after CNTs growth and silicon deposition using an analytical balance (Mettler Toledo XP 26, 0.01 mg).

Morphological characterization of Si/CNT coaxial nanlfiber films was investigated by field-emission scan electron microscopy (SEM, LEO 1550 Gemini), and the nanostructures were characterized using a transmission electron microscopy(JEOL, Model JEM-2100) operating at 200 kV. The suspension of the prepared Si/CNT network in ethanol was dropped onto carbon coated copper grids and tried under ambient

condition before TEM testing. Raman spectra were obtained with a laser wavelength of 532 nm using a WITec Raman system.

Electrochemical performance was evaluated by assembling two electrode CR 2032 type half cells in a glove box filled with pure Ar. The cells consisted of Si/CNT multilayer on a copper substrate as the working electrode, pure Li metal as reference and counter electrodes and $LiPF_6$ (1.0 M) dissolved in ethylene carbonate and diethyl carbonate (EC/ DEC, 1:1 by volume) as electrolyte. The cyclic voltammetry (CV) measurements were performed using a multi-channel electrochemical station (AUTOLAB, M 101). Discharge/charge capacities were measured using galvanostatic cycling from 1.2 V to 0.05 V (NEWARE BTS-5 V, Neware Technology Co., Ltd.)

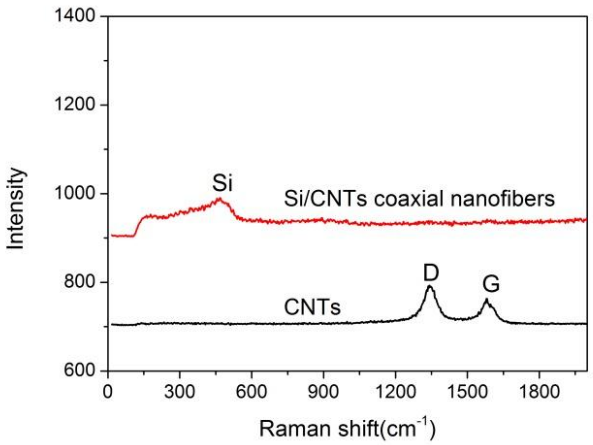


**Figure S1** The Raman spectra of an as-prepared CNT network and a silicon coated CNT network.

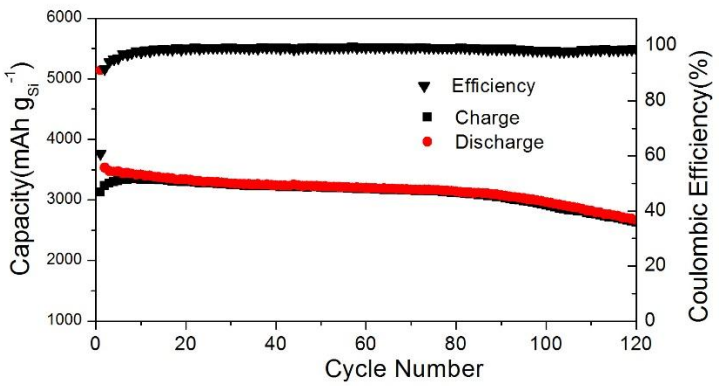


**Figure S2** The cycle performance of the 4-layer Si/CNT anode with 120 cycles

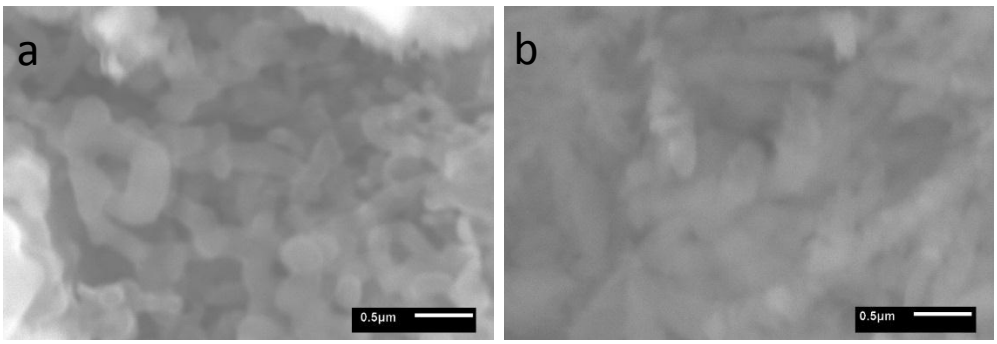


**Figure S2** The SEM images of the 4-layer Si/CNT anode with diffirent cycles (a) 25 cycles and (b) 75 cycles