Supplementary Information

**High performance carbon nanotube-Si core-shell wires with a rationally structured core for lithium ion battery anodes**

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**Experimental section**

**CNT growth:** A piece of stainless steel (SS) foil is used as the substrate. After sequentially cleaned in acetone, IPA and DI water by ultrasonic, the SS foil was loaded into an electron beam evaporator (Auto 306, HHV) to deposit a thin layer of nickel as the catalyst. After that, CNTs were produced using a PECVD system. In a typical growth process, the chamber was firstly evacuated and the temperature was fast ramped up to 800°C upon which NH$_3$ is introduced into the chamber at a flow rate of 240 sccm. Plasma was then initiated in the chamber and C$_2$H$_2$ was introduced at a flow rate of 60 sccm to start the growth of CNTs. The power was maintained at 120 W.

**Si coating:** After the growth of CNTs, a Si shell was coated onto the CNTs in a PECVD system with SiH$_4$ balanced with N$_2$ (SiH$_4$/N$_2$ 50/160 sccm) as the precursor. During growth, the temperature was maintained at 200°C and the deposition rate calculated on a Si wafer was 1 nm/sec. The Si mass loading was determined by weighing the SS foil before and immediately after Si coating using an analytical balance (Mettler Toledo XP 26, 0.002 mg). As we find that the high CNT growth temperature changes the weight of the SS current collector, the mass ratio between the CNT core and the Si shell is therefore calculated according to their diameter ratio, as shown in the TEM image in Fig. 1c. It is seen that the outer diameter of the CNT is ~150nm, diameter of the hollow inner is ~50nm and the CNT-Si after Si coating is ~270nm. The density of the solid graphitic wall
of the CNT is assumed to be the same as graphite (2.2 g cm\(^{-3}\)) and the density of the amorphous Si prepared with our recipe is \(\sim 2\) g cm\(^{-3}\), the mass ratio is calculated according to the formula:

\[
\text{Si:CNT} = \frac{\rho_{\text{Si}}(\pi r_3^2 - \pi r_2^2)}{\rho_{\text{C}}(\pi r_2^2 - \pi r_1^2)} = 2.3:1,
\]

where \(r_1\), \(r_2\) and \(r_3\) stand for the radius of the hollow inner, the CNT and the Si shell, respectively. \(\rho_{\text{Si}}\) and \(\rho_{\text{C}}\) represent the densities of amorphous Si and graphite, respectively.

**Electrochemical characterization:** To perform electrochemical characterization, the CNT-Si core-shell wires directly rooted on SS was assembled into CR 2032 type half cells with pure Li metal as the counter electrode in a glove box filled with pure Ar (Innovative Technology, Inc.). No binders or conductive additives were needed. The electrolyte used was LiPF\(_6\) (1.0 M) dissolved in ethylene carbonate and diethyl carbonate (EC/DEC, 1:1 by volume). The CV curves were obtained using a multi-channel electrochemical workstation (Multi Autolab/ M 101, Metrohm) at a scan rate of 0.1 mV/sec. Discharge/charge capacities were determined by galvanostatic cycling the half cells over the potential range of 0.01-1.2 V vs. Li/Li\(^+\) in a battery tester. (NEWARE BTS-5 V, Neware Technology Co., Ltd.)

**Structural characterization:** SEM characterization was carried out in a field-emission SEM (LEO 1550 Gemini). TEM was performed using JEOL 2010. Raman spectrum was obtained using a WITec Raman system with a laser operating at \(\lambda=633\) nm as excitation source. To inspect morphology of the electrode after cycling, the half cell was disassembled in the fully de-lithiated state in the glove box, the CNT-Si electrode was immediately immersed in propylene carbonate (PC) for at least 24 hrs to completely remove the residual electrolyte. After that, the sample was baked in a vacuum oven at \(\sim 100^\circ\text{C}\) to remove the PC.
Fig. S1 Raman spectrum of the CNT-Si composite, the absence of crystalline Si peak at 520 cm\(^{-1}\) confirms amorphous structure of the Si coating, a small peak at \(~900\) cm\(^{-1}\) indicates the presence of SiO\(_2\). The oxide is likely to be developed during sample transfer process.

Fig. S2 Overall charge/ discharge capacities of the CNT electrode in comparison with that of the CNT-Si electrode. The charge/ discharge currents for both types of electrodes are the same at the various rates (C refers to \(C_{\text{Si}}\)). It is found that the CNTs only contribute to less than 10\% of total capacities of the CNT-Si electrodes.
**Fig. S3** CV curves of the electrode for the first 4 cycles. As battery cycles, the currents gradually increase. In addition, the cathodic peaks slightly shift to more positive values and the anodic peaks to less positive values, indicating reduced polarization. All the phenomena could be related to the activation process in the electrode.

**Fig. S4** TEM image of the CNT-Si core-shell wire after 50 galvanostatic cycles at 0.2 C.
Fig. S5 (a) SEM image of the CNT array using thinner Ni catalyst film and, (b) TEM image of a single CNT-Si core-shell wire.

Fig. S6 De-lithiation capacities of the CNT-Si anode with the thin CNT core in comparison with that with the thick CNT core. Both samples are cycled at 0.2 C over the same potential range of 0.01-1.2 V.