

Electronic Supplementary Information for

Direct Scattered Growth of MWNT on Si for High Performance Anode Material in Li-ion Batteries†

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Experimental details

Preparation of Si-MWNT nanocomposite:

Nano-size silicon was supported by Nanjing Emperor Nano Material Co., Ltd. (Nanjing, China). In a typical experiment, Si powder was subsequently modified with iron colloid by surface adsorption and separated via centrifuge at a speed of 6000 rpm. Then the obtained powder was dried in a vacuum oven at 100°C for half an hour and ready for MWNT deposition. Chemical vapor deposition of MWNTs was carried out using a commercially available Thermal CVD System (Atomate, USA), which allowed software control of the gas flow rates, individual furnace temperatures, and deposition time. The iron modified Si powder was put into the furnace and first flushed with argon gas (200 ml per min) for 30 min to flush away any oxygen in the reactor (quartz tube). Then the temperature of the furnace was increased up to 550°C under a mixed gas flow of argon (200 ml per min) and hydrogen (20 ml per min) and held for 25 min for the reduction of the iron(III) to iron nanoparticles by hydrogen gas. The temperature was further increased to 750 °C, whereupon acetylene (C₂H₂) was introduced for 20 min, under H₂/C₂H₂/Ar (5/30/200 ml/min) mix-gas flow. After MWNT deposition, the furnace was turned off, while the argon gas (200 ml per min) was continuously flushed through the quartz tube until the temperature was less than 120°C.

Structural and morphological characterization:

Raman spectroscopy was used to identify the characteristics of Si-MWNT composite using a JOBIN YVON HR800 Confocal Raman spectrometer (HORIBA, Ltd., France) with 632.8 nm diode laser excitation on a 900 lines/mm grating at room temperature.

Thermogravimetric analysis (TGA) was performed using a Q500 TGA analyzer (TA Instruments, UK) to evaluate the residual level of Si-MWNT composite after MWNT deposition.

The morphology and microstructure of the Si-MWNT composite were monitored using a JSM-7500F Cold Field Emission Gun Scanning Electron Microscopy (FEGSEM) and a JEM-2100 Transmission Electron Microscopy (TEM) (JEOL Ltd., Japan) with an attachment of the energy dispersive X-ray Spectrometer (EDX). For SEM observation, the cycled electrode (in fully de-lithiated state) was taken out of the cell in an argon-filled glove box and immersed in acetone for days to remove the binder. Then the electrode material was centrifuged several times for complete purification.

Electrochemical characterization:

Electrode preparation:

Si-MWNT working electrodes were prepared by slurring 80 wt.% active material, 10 wt.% acetylene black, and 10 wt.% polyvinylidene fluoride (PVDF) in a volatile solvent, and then casting the mixture onto a copper foil. After vacuum drying at 120°C for about 8 h, the electrode disks (1 cm²) were punched and weighed to monitor the active material loaded on the electrode disks.

Cell assemble:

Commercial available CR 2032 type coin cells were assembled in an Ar gas filled glove box (MBraun, Unilab, Germany) by staking a porous polypropylene membrane as the separator between the Si-MWNT electrode and a lithium foil counter electrode. The electrolyte filled in the coin cell was 1M LiPF₆ electrolyte in a mixture of dimethyl carbonate (DMC) and ethylene carbonate (EC) (1:1 by volume, provided by MERCK LagA, Germany). The testing cell were galvanostatically charged/discharged at room temperature between 0.01 V and 2.00 V using a commercially available battery test system (LAND CT2001A model, Wuhan Jinnuo Electronics., Ltd.) under constant current condition.

EIS test:

A.C. electrochemical impedance spectroscopy (EIS) measurements of the testing coin cells were performed at room temperature to study the interface property. Impedance was measured at open circuit potential (OCP) over the frequency range 100 KHz to 10 MHz with an AC amplitude of 10 mV using a Gamry EIS 3000™ system.

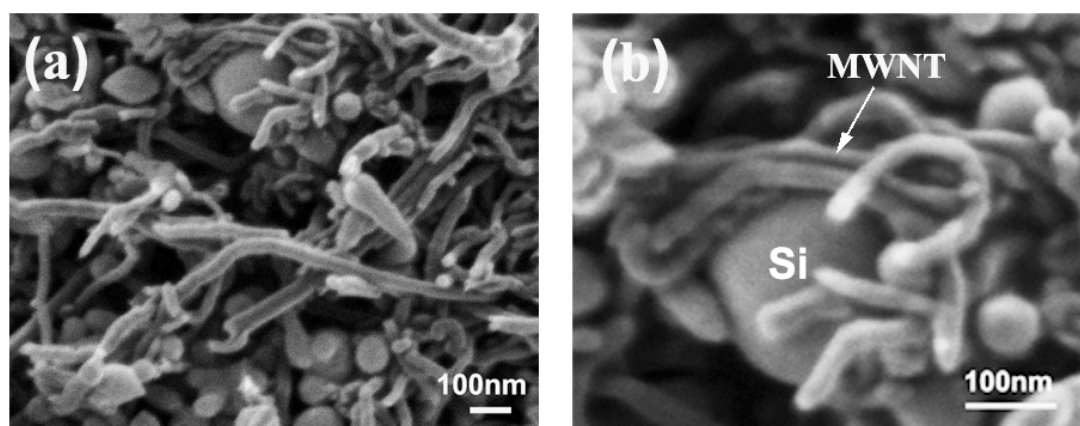


Fig. S1 SEM micrographs of the Si/MWNT mixture (a, b).

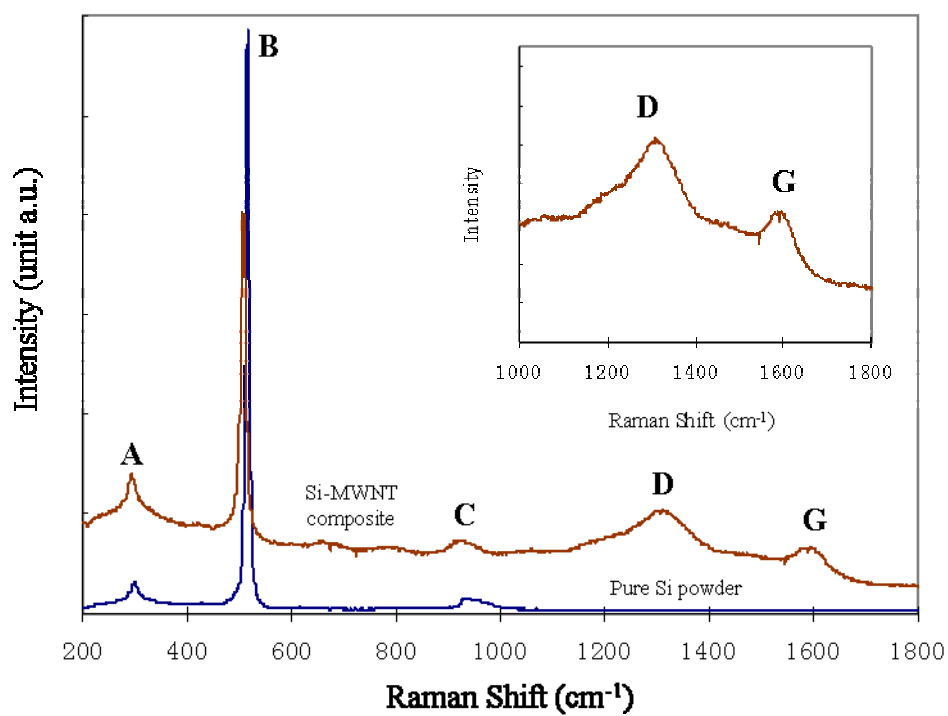


Fig. S2 Raman spectra of Si-MWNT composite and pure Si powder.

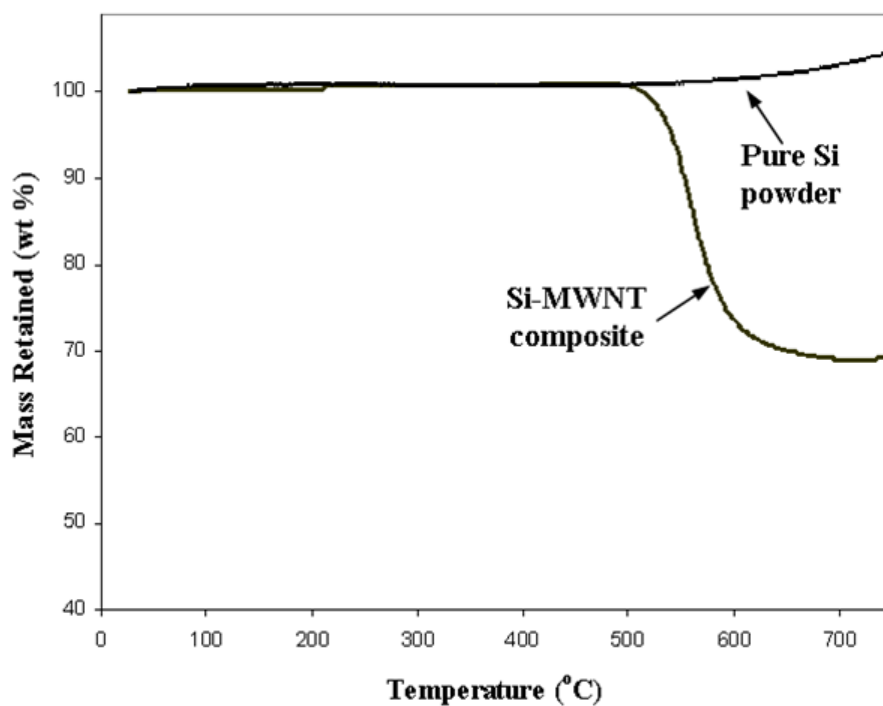


Fig. S3 Thermogravimetry results of Si-MWNT composite and pure Si powder.

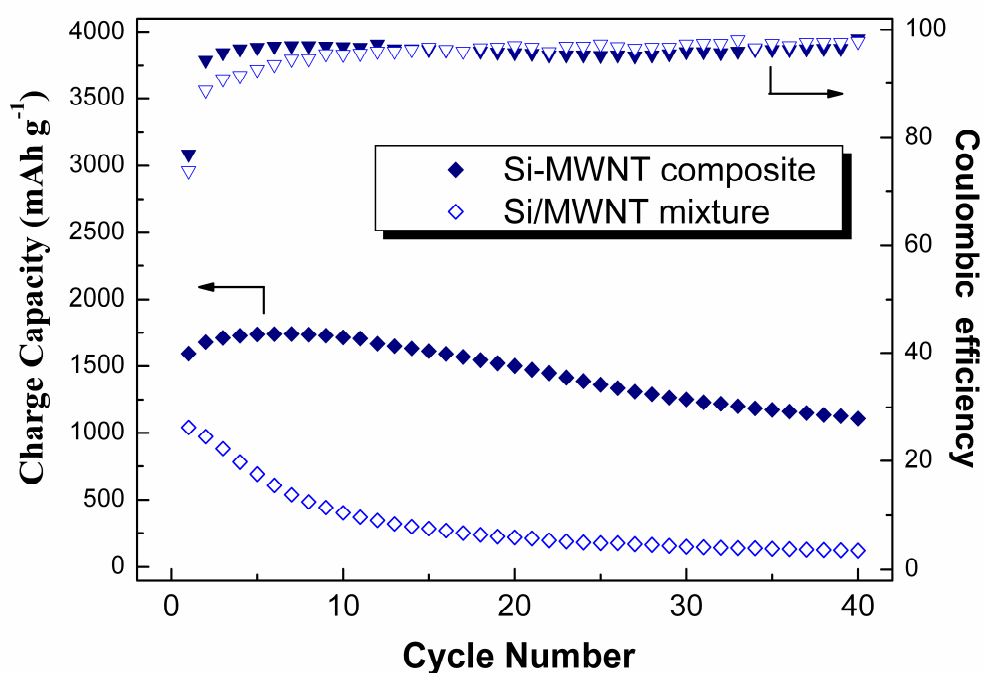
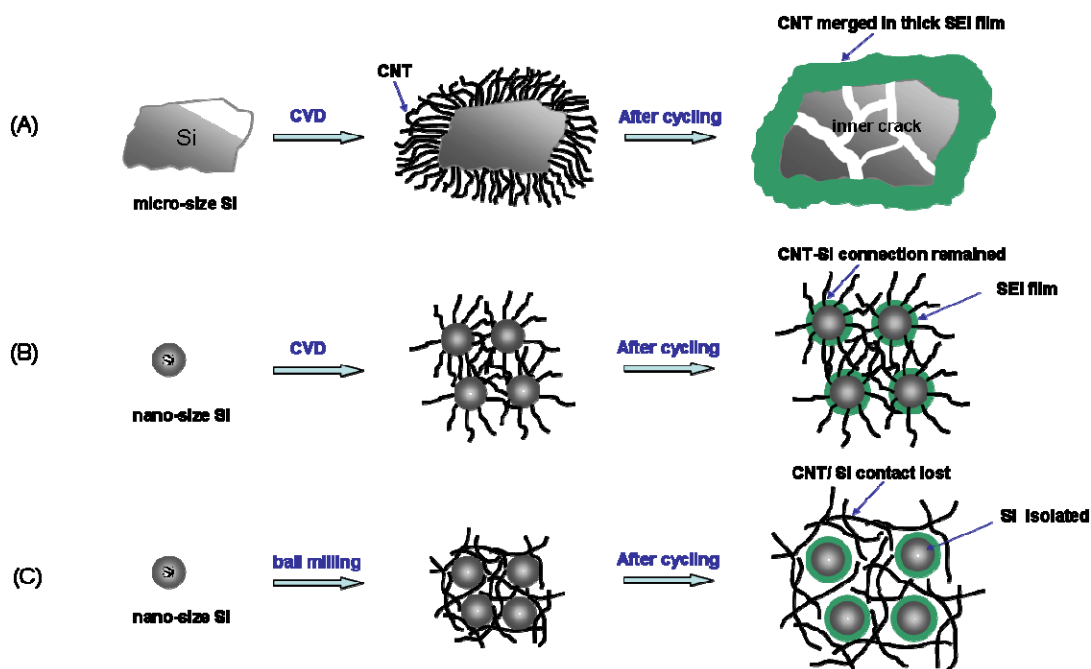


Fig. S4 Reversible capacities of Si-MWNT composite and Si/MWNT mixture at a current density of 100 mA g^{-1} for the first 40 cycles (solid symbols: Si-MWNT composite; open symbols: Si/MWNT mixture).



Scheme S1 Schematic illustration of the sample structures and their possible evolutions after cycling for the three kinds of Si-CNT materials. (A) micro Si-CNT composite, (B) nano Si-CNT composite, (C) nano Si/CNT mixture.

