

Supporting Information

In-situ growth of carbon nanotubes wrapped Si composites as anodes for high performance lithium ion batteries

Jianbin Zhou,^a Yang Lan,^a Kailong Zhang,^a Guoliang Xia,^a Jin Du,^a Yongchun Zhu*^a and Yitai Qian*^a

^a Hefei National Laboratory for Physical Science at Microscale and Department of Chemistry, University of Science and Technology of China, Hefei, 230026, P.R. China. Tel: +86-551-63601589; E-mail: ychzhu@ustc.edu.cn, ytqian@ustc.edu.cn.

Experimental Section

Preparation of CNTsWS

Commercial Si particles with diameters ranging from several to tens micrometers and CuCl are purchased without further treatment. In a typical synthesis process, 0.6 g of Si powder and 0.4 g of CuCl were mixed by ball milling method for 3 h under argon condition. And then, the mixture was transported into tube furnace at 400 °C for 5 h with controlled C₂H₂ (C₂H₂: 10% and Ar: 90%) airflow speed of 8 ml/min. The heating rate was 10 °C/min. After that, the collected Sample was washed with diluted HNO₃ solution and then washed with deionized water 3 times and ethanol 1 time. Finally, the products were dried in vacuum oven at 60 °C overnight. Then, CNTsWS can be obtained.

Preparation of in-situ formed CNTs

To obtain the in-situ formed CNTs, dilute HF solution was used to remove Si that in CNTsWS at room temperature.

Preparation of CNTs/Si

Commercial Si particles and commercial CNTs were mixed with a weight ratio of 0.76: 0.24 by ball milling method for 3 hours, and then CNTs/Si can be obtained.

Material characterization

The crystal phase, morphology and composition of products were characterized by X-ray diffraction (XRD, Philips, X'pert X-ray diffractometer with Cu K α , $\lambda=1.54182$ Å), transmission electron microscopy (TEM, Hitachi H7650), Scanning electron microscopy (SEM, JEOL-JSM-6700F), Raman spectroscopy (Lab-RAM HR UV/VIS/NIR). Thermogravimetric analysis (TGA, SDT-Q600, under atmospheric conditions, heating rate of 10 °C/min).

Electrochemical characterization

Half cells (2016 R-type) were used to test the electrochemical properties of the samples. To prepare working electrode, the active materials, acetylene black and carboxymethylcellulose sodium were homogeneously mixed with water with a weight ratio of 70: 20: 10. And then, the slurry was coated on a copper foil and dried at 80 °C for 12 h in a vacuum oven. The mass of the active materials was measured to be ~2 mg/cm². It should be noted that all the specific capacity

mentioned in our manuscript is calculated based on the mass of active materials. For assembling the half cells, lithium foil, Celgard 2400 and a solution of 1 M LiPF₆ in a mixture of ethylene carbonate/dimethylcarbonate (EC/DMC; 1:1 by Volume) and 5 wt% fluoroethylene carbonate (FEC) was used as the counter electrode, the separator and the electrolyte respectively. Cyclic voltammogram (CV) was carried on electrochemical workstation (CHI660D) at a scanning rate of 0.1 mV/s in the voltage window of 0.01-1.5 V. Galvanostatic charge/discharge test was conducted on a battery tester (LANDCT2001A) at various current densities. The electrochemical impedance spectroscopy (EIS) was also conducted on a CHI660D electrochemical workstation at an alternating current (AC) voltage of 0.005 V in the frequency window from 100 KHz to 0.1 Hz.

(1) TG was conducted to investigate the thermal behavior of CNTsWS, CNTs/Si and bare Si and evaluate the weight ratio of CNTs content. According to Fig. S1, the weight loss before 300 °C can be ascribed to the absorbed air and H₂O by the sample. In the temperature section ranging from 300 °C to 650 °C, the weight loss can be mainly attributed to the loss of CNTs, as which become unstable after 300 °C in air condition. Therefore, the carbon content in CNTsWS and CNTs/Si is measured to be 23.6 wt% and 23.3 wt%, respectively. The carbon content in CNTs/Si is identical with that in CNTsWS within experimental error range. At the same time, also most no carbon content can be detected from bare Si.

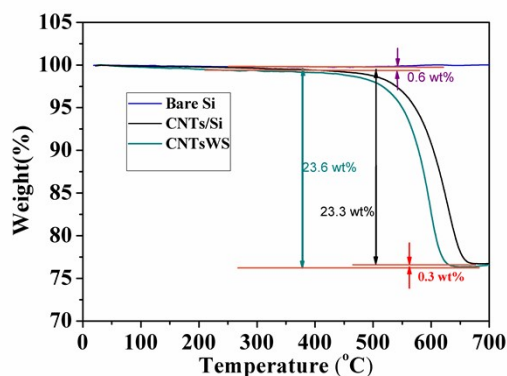


Fig. S1 TG curves of CNTsWS, CNTs/Si and bare Si.

(2)

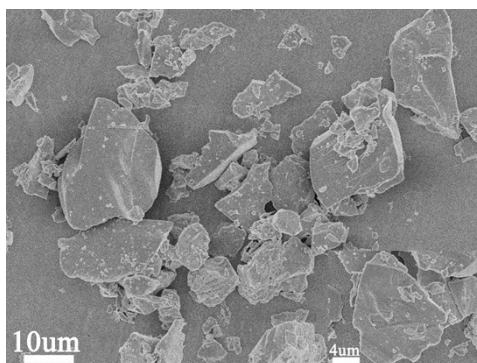


Fig. S2 SEM images of commercial Si particles.

(3) In contrast experiment, simply mixed commercial CNTs and Si hybrids (CNTs/Si) were also prepared by ball-milling method with the same C/Si weight ratio as CNTsWS. As illustrated

in SEM images of CNTs/Si (Fig. S3), CNTs/Si shows much difference from CNTsWS without uniformly CNTs coating on Si.

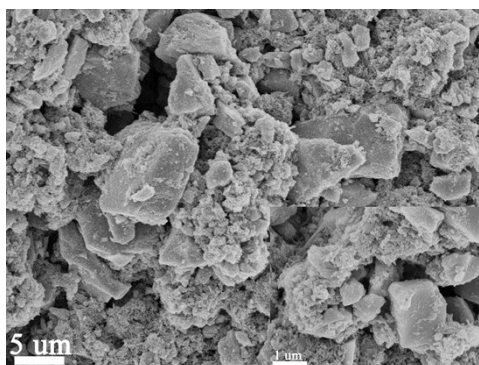


Fig. S3 SEM image of CNTs/Si hybrids.

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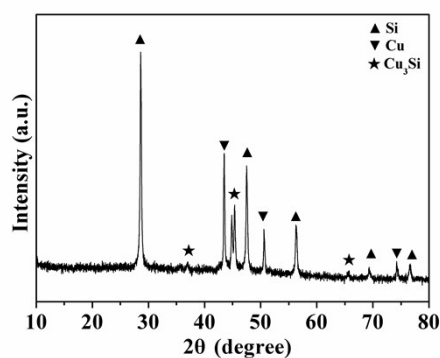


Fig. S4 XRD pattern of the product from reaction between Si and CuCl at 400 °C under Ar atmosphere.

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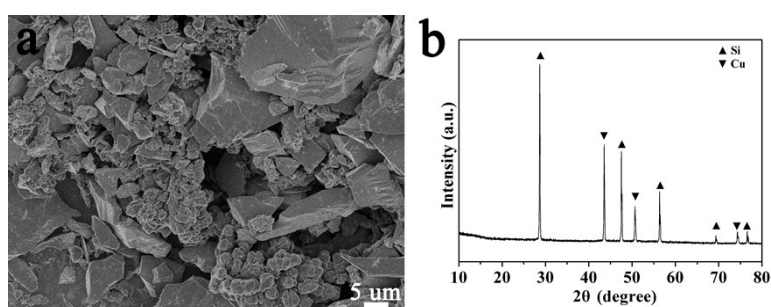


Fig. S5 SEM image (a) and XRD pattern (b) of product obtained from the contrast experiment with the mixture of commercial Cu and Si at 400 °C under C_2H_2 condition.

(6) The CV curves of CNTsWS in the first 5 cycles (Fig. S6†), which are constant with the typical electrochemical characteristics of Si/CNTs composites. The sharp peak below 0.1 V appearing in the 1st cycle represents the alloy reaction of crystallized Si and Li^+ . In the subsequent cycles, the peak below 0.1 V is replaced by the peak at 0.21 V due to the

amorphization of crystalline Si after the initial process of lithiation. The predominant peaks at 0.34 V and 0.55 V from 1st to 5th cycle in the anodic part represent the lithium extraction potential, which can be assigned to the reaction between Li and Si and the formation of amorphous Si.

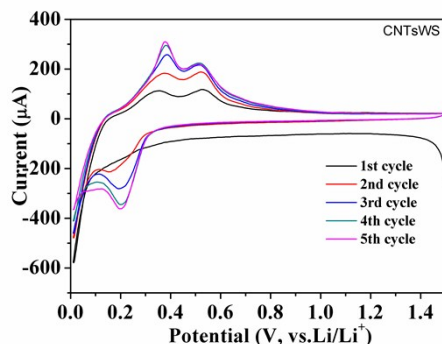


Fig. S6 CV curves of CNTsWS.

- (7) We have ever used dilute HF solution to remove the Si in CNTsWS to obtain the pure in-situ formed CNTs and assembly cells to test the electrochemical properties of in-situ formed CNTs electrode. The XRD (Fig. S7a†) and SEM image (Fig. S7b†) of in-situ formed CNTs show the purity of them after treatment with HF solution. Fig. S7c and Fig. S7d† reveal the cycling performance of in-situ formed CNTs at the current densities of 0.9 A/g and 1.8 A/g, respectively. The discharge capacity of CNTs remains 216.7 and 118.9 mA h/g at 0.9 A/g after 80 cycles and 1.8 A/g over 500 cycles, respectively. From above results, the in-situ formed CNTs only contribute the very little part of the capacity to the whole electrode, indicating that Si provide the main capacity in CNTsWS electrode.

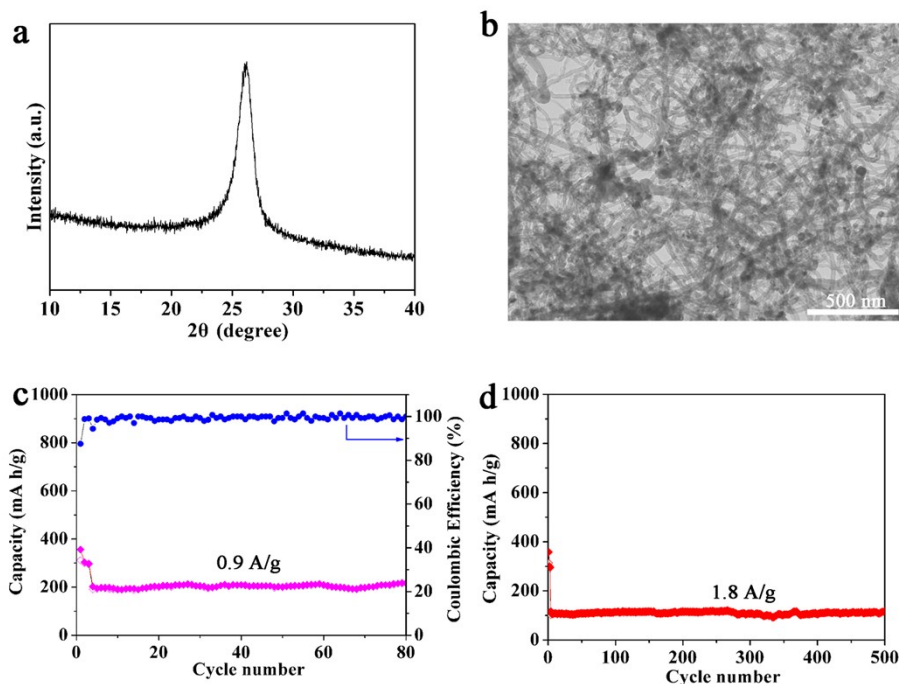


Fig. S7 The XRD (a) and SEM image (b) of in-situ formed CNTs. The cycling performance of in-situ formed CNTs at the current density of 0.9 A/g (c) and 1.8 A/g (d).

(8) The morphology variation of CNTsWS and commercial Si based electrodes were investigated after cycling at 0.9 A/g. As shown in Fig. S6, the surface of the CNTsWS electrode was much smoother than that of Si after 80 cycles. At the same time, Fig. S6b clearly displayed the huge breakage on the surface of Si electrode, which may be caused by the huge variation. In contrast, the huge breakage can not be observed on the surface of CNTsWS electrode, indicating the well persevered integrity of electrode because of the in situ formed CNTs. Therefore, it is reasonable to speculate that CNTsWS could effectively release the volume change and keep the integrity of electrodes, resulting in the enhanced electrochemical performance.

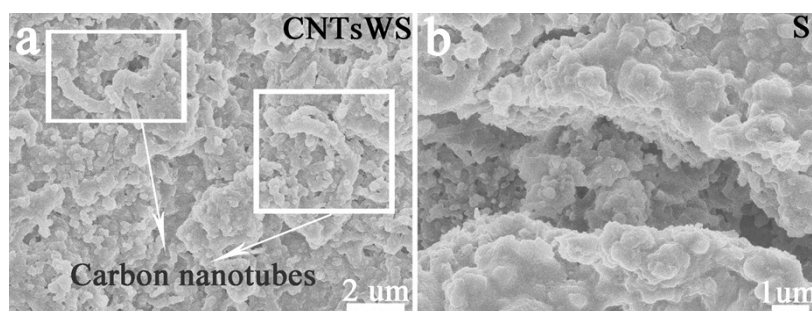


Fig. S8 SEM images of CNTsWS (a) and commercial Si (b) electrodes after 80 cycles at 0.9 A/g.

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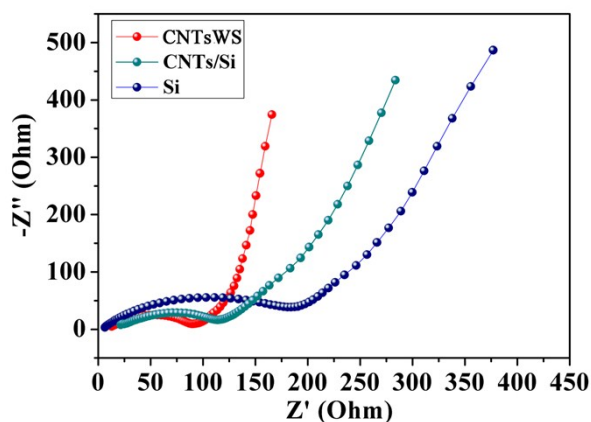


Fig. S9 Electrochemical impedance spectra of electrodes made of CNTsWS, CNTs/Si and commercial Si.