Supporting Information

Title (Facile situ Synthesis of 3D Frameworks SiC&Si@CNTs Composite as an Anode Material for Lithium-Ion Batteries)

Weiming Su, Yue Liang,Yinze Zuo and Yuefeng Tang**

Experimental

Preparation of SiO_2@CNTs nano Composite

In a typical process, 0.1 g functionalized MWCNT was added in 30 ml DE-ionized water and 1.5 ml concentrated ammonia aqueous solution (25 wt.%). Following, 120 ml ethanol was added in above solution and kept ultrasonication for 1h to form a uniform suspension. Then, 0.16 g Hexadecyl trimethyl ammonium Bromide (CTAB) and 2 ml tetraethyl orthosilicate (TEOS) were added to the mixture under magnetic stirring for 12 h. Subsequently, CTAB and other impurities were washed by methanol reflux for 24 h. Afterwards, the black products were washed thoroughly with ethanol and DE-ionized water by centrifugation for 3 times. Finally, the powders were transferred to the vacuum oven for drying at 80°C overnight.

Preparation of poly-dopamine coated SiO_2@CNTs nano Composite

Typically, 500 mg as-prepared SiO_2@CNT nano composites were re-dispersed in Tris (100 ml, PH=8.5) solution. After ultrasonic dispersing, 150 mg dopamine hydrochloride was added in the mixture. The mixture was stirred vigorously for 6-48 h under room temperature. The poly-dopamine coated SiO_2@CNTs nano composites were obtained after the coating reaction. The products were washed with ethanol and water to remove the any impurities before dried at 70 °C in the vacuum oven.

Fabrication of 3D Frameworks SiC&Si@CNTs Composite

The 3D Frameworks SiC&Si@CNTs composites were synthesized by magnesiothermic reduction method. Specifically, 1 g poly-dopamine coated SiO_2@CNTs nano composites were mixed with 0.4 g magnesium powder, transferred into the porcelain boat. The boat was then placed in the tubular furnace. The furnace was heated to 450 °C for 2 h, then heated to 750 °C for 4 h at a heating rate of 5 °C min^{-1}. The all calcilation processes were applied under an argon atmosphere. Subsequently, the powder was washed with 2 M HCl and 0.1 M HF solution for 4 h. Finally, the obtained products were washed and freeze-dried for 12 h. The samples were named as SiC&Si@CNTs-1, Si&SiC@ CNTs-2, and Si&SiC@ CNTs-3 after various coated time of SiO_2@CNTs for 12 h, 24 h, and 48 h respectively. A compared sample, Si@CNTs was prepared with identical method except that as-prepared SiO_2@CNTs nano composites were not poly-dopamine coated before the magnesiothermic reduction process.

Characterization and electrochemical measurement

The obtained SiC&Si@CNTs composites were characterized with a high-resolution X-ray diffraction (XRD (Bruker D8-Advance diffractometer), scanning electron microscopy (SEM Zeiss Merlins compact) and high-resolution transmission electron microscopy (TEM Libra 120). The thermogravimetric analysis (TGA) analysis was operated from 20 to 1000 °C under air on the TGA Q5000 analyzer. Additionally, BET-surface area and pore volume were tested by N_2 adsorption at liquid nitrogen temperature using a NOVA4000 automated gas sorption system. The elements in the SiC&Si@CNTs composites were identified by Raman (RM 2000 Microscopic confocal Raman spectrometer with a 514 nm laser), X-ray spectroscopy (XPS Multilab 2000, VG, U.K) .

The batteries properties were tested by assembling CR2032 batteries. The working electrodes consisted of 80 % active material, 5 % Super P, 2.5 % styrene butadiene rubber (SBR) and 2.5 % sodium carboxymethyl cellulose (CMC). The lithium metal foil and polypropylene film were applied as reference electrode and separator. The details of cyclic voltammetry (CV), Electrochemical impedance spectroscopy (EIS) and cycling tests can be found in the previous work.[16] The current densities of cycling testes were 500 mA g^{-1} to 8 A g^{-1} and the limits potential range were between 0.001 to 1.5 V. For most electrodes, the mass loading of the active materials was 0.5-0.7 mg cm^{-2}. The SiC&Si@CNTs-1 electrode with higher mass loading of 1.27-1.53 mg cm^{-2} was fabricated and applied for application.

Further, The full cells were fabricated by using SiC&Si@CNTs-1 and $LiCoO_2$ as electrodes and tested under a potential range from 2.5-4 V. The specific capacity of electrodes were calculated by whole mass including of active materials, Super P and binder.

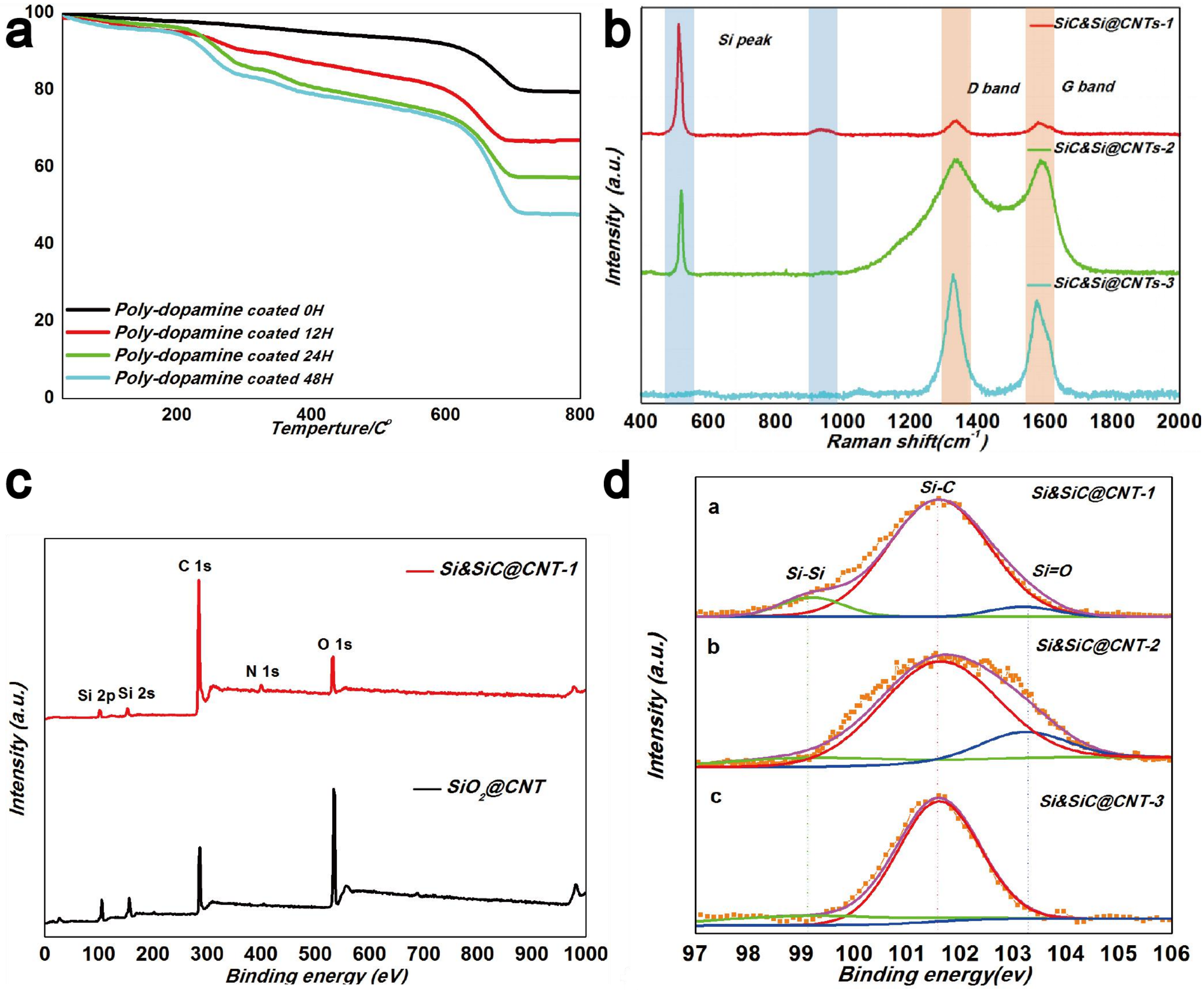


Figure. S1. a) Thermogravimetric analysis (TGA) of the SiO_2@CNTs composite poly-dopamine coated time in 0h, 12h, 24h, 48h conducted in air at scan rate of 10 °C min^{-1}. b) Raman spectra of SiC&Si@CNTs-1, SiC&Si@CNTs-2 and SiC&Si@CNTs-3 samples. c) XPS spectra of SiC&Si@CNTs-1 and SiO_2@CNTs samples. d) High-resolution XPS spectra of SiC&Si@CNTs-1, SiC&Si@CNTs-2 and SiC&Si@CNTs-3 samples.

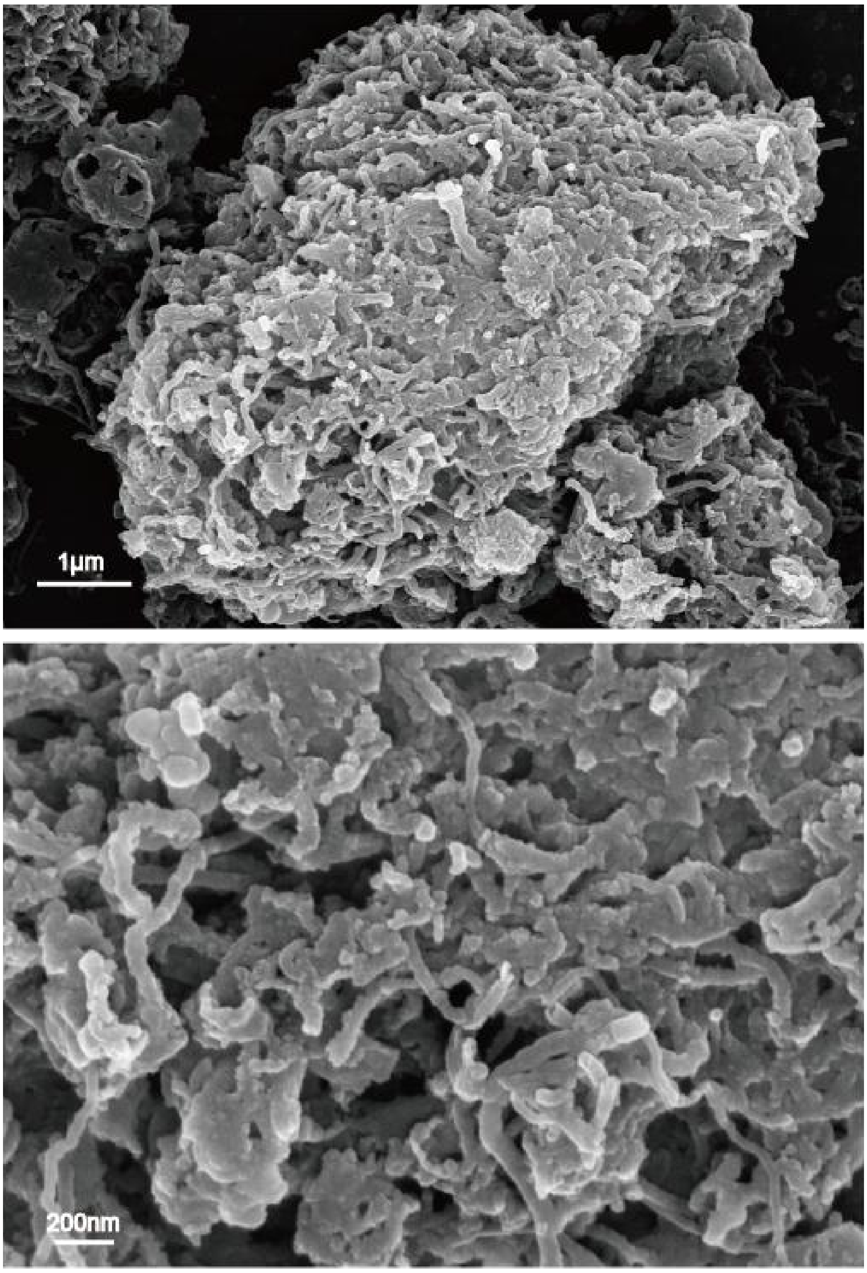
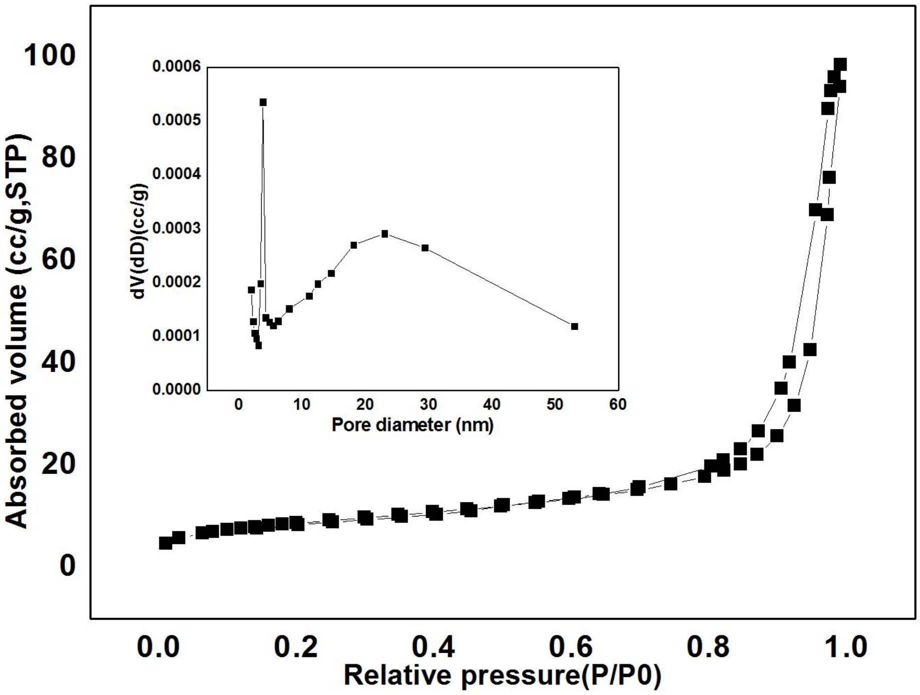
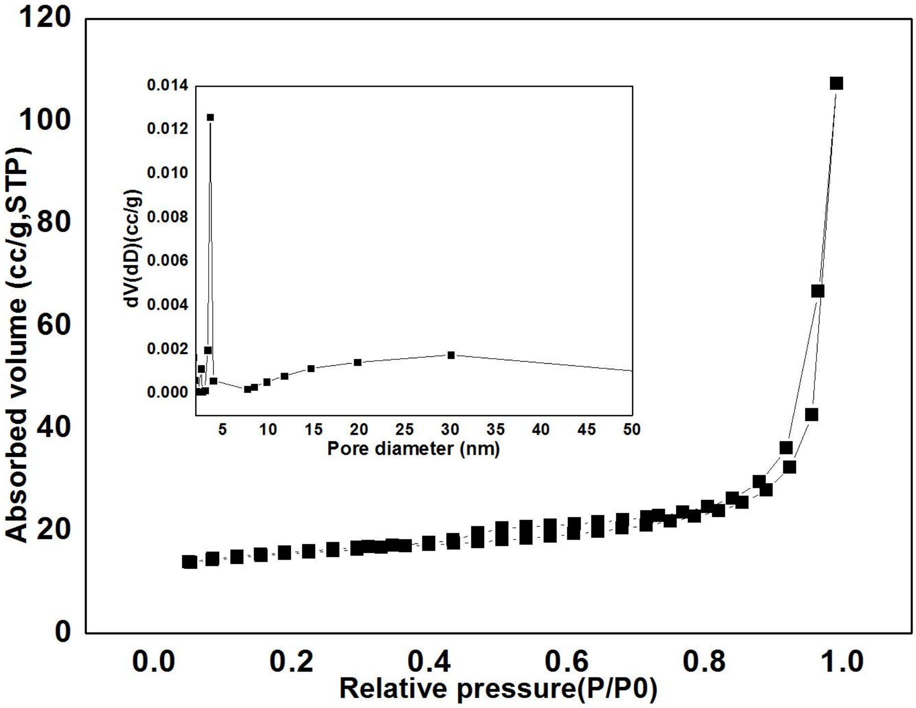


Figure. S2. SEM images of Si@CNTs.

(a)


Absorbed volume (cc/g,STP)
100
80
60
40
20
0
0.0
0.2
0.4
0.6
0.8
1.0
Relative pressure(P/P0)
dV(dD)(cc/g)
0.0006
0.0005
0.0004
0.0003
0.0002
0.0001
0.0000
0
10
20
30
40
50
60
Pore diameter (nm)

(b)


Absorbed volume (cc/g,STP)
120
100
80
60
40
20
0
0.0
0.2
0.4
0.6
0.8
1.0
Relative pressure(P/P0)
dV(dD)(cc/g)
0.014
0.012
0.010
0.008
0.006
0.004
0.002
0.000
5
10
15
20
25
30
35
40
45
50
Pore diameter (nm)

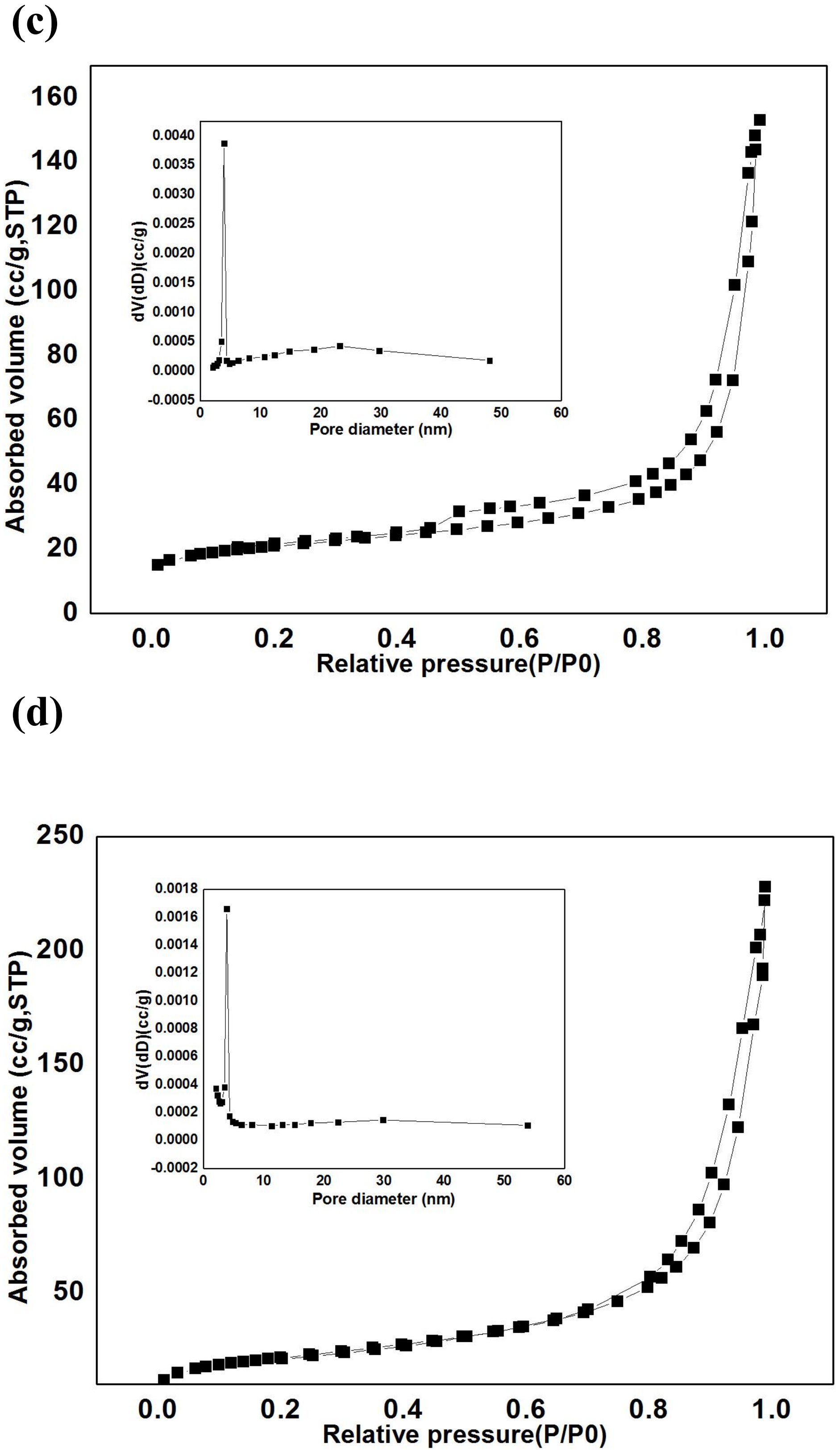


Figure. S3. N_2 adsorption–desorption isotherms of samples: (a)Si@CNTs, (b) SiC&Si@CNTs-1, (c) SiC&Si@CNTs-2 and (d) SiC&Si@CNTs-3. The inset in each figure shows the relevant pore size distribution calculated by the BJH formula.

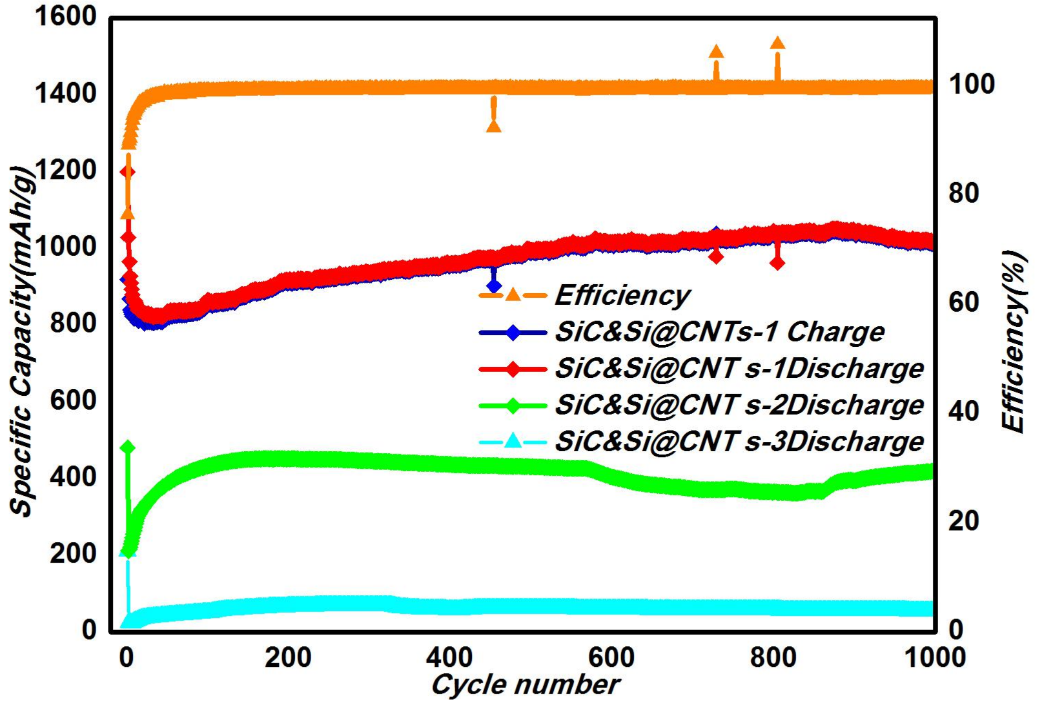


Figure. S4. Cyclability and Coulombic efficiency of the SiC&Si@CNTs-1,SiC&Si@CNTs-2 and SiC&Si@CNTs-3 electrodes at a current density of 1A g^{-1} for 1st-900th cycles.

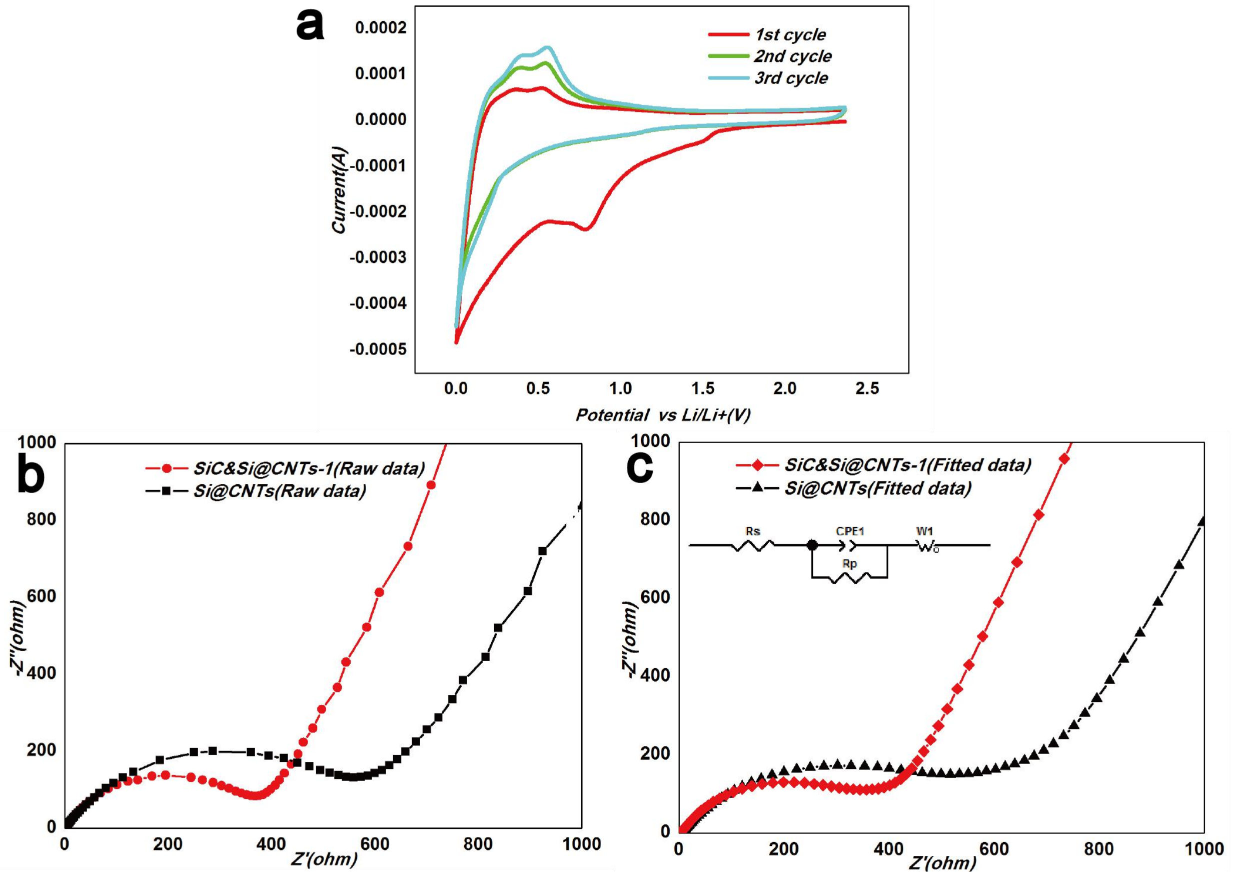


Figure. S5. (a) Cyclic voltammogram of the SiC&Si@CNTs-1 electrode measured at a scan rate of 0.1 mV s^{-1}. (b) Electrochemical impedance spectroscopies of Si@CNTs and SiC&Si@CNTs-1 electrodes. (c) Electrochemical impedance fitted spectroscopies and equivalent circuit of Si@CNTs and SiC&Si@CNTs-1 electrodes.

Table S1. (Fitting results of cells with Si@CNTs and SiC&Si@CNTs-1 as anodes)

Sample	Rs [Ω]	Rct [Ω]	W
Si@CNTs	2.55	637	794.3
SiC&Si@CNTs-1	1.145	420.2	437.9

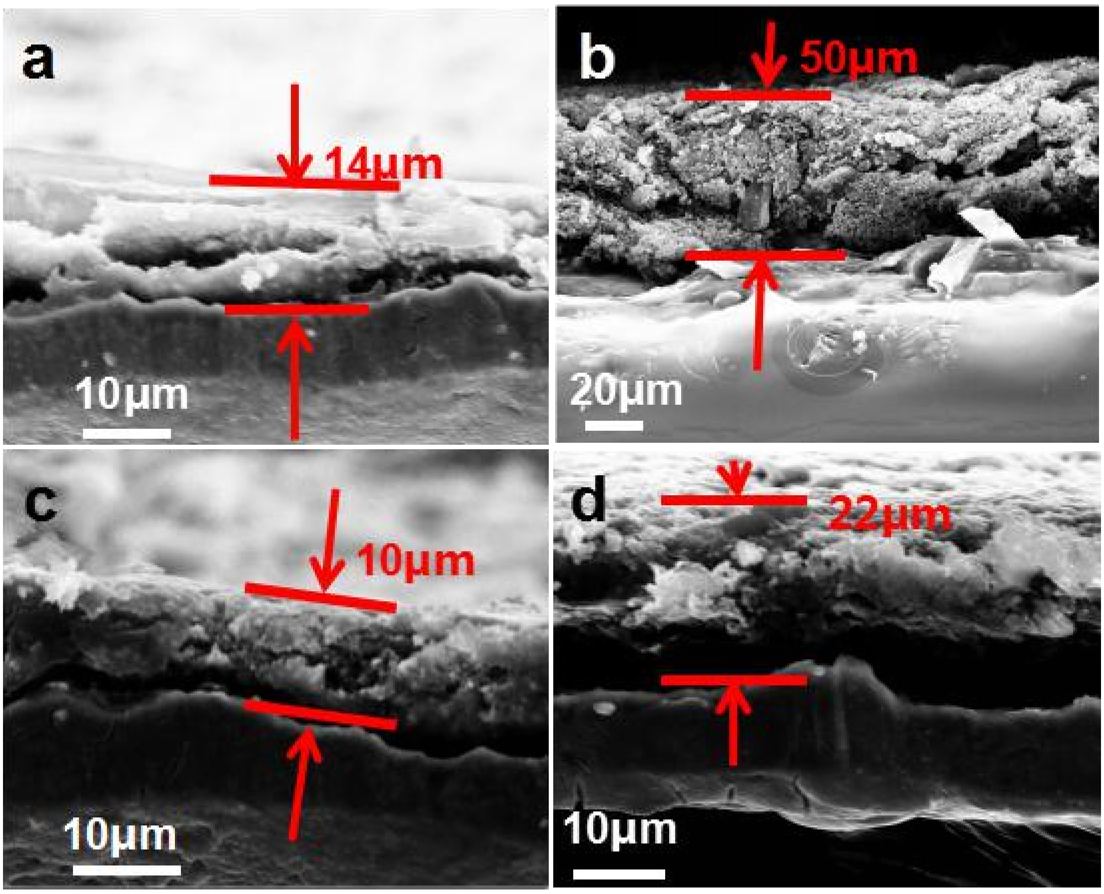


Figure. S6. (a) Cross sectional view SEM images of the Si@CNTs prior to cycling, (b)at the fully lithiated state following cycling, (c) 3D framework SiC&Si@CNTs-1 composites prior to cycling, (d) at the fully lithiated state following cycling.