Electronic Supplementary Information:

High Tap Density Secondary Silicon Particle Anodes by Scalable Mechanical Pressing for Lithium-ion Batteries

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Materials and Methods

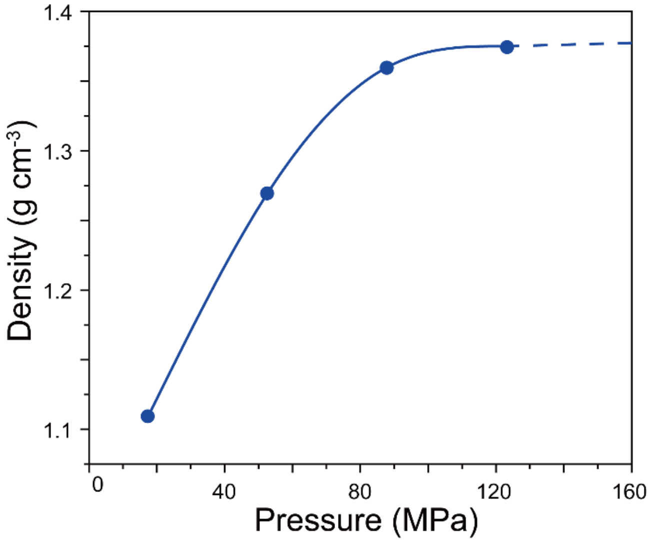
Si@ SiO_2 nanoparticles synthesis. In the large scale of synthesis we used here, ~20 g Si nanoparticles (SiNPs, <100 nm, from MTI, Inc.) were firstly well dispersed in 2.5 L ethanol with ultrasonication. Afterward, 500 mL of DI water and 50 mL of concentrated ammonium hydroxide was added consequently. Vigorous stirring was applied then with mechanical stirring machine to make sure all chemicals mix sufficiently. Under stirring, 100 mL of Tetraethoxysilane (TEOS, Aldrich) was added to initiate the hydrolysis reaction. After 5 hours, when the 100 mL of TEOS was almost fully reacted, another 100 mL of TEOS was added to continue the hydrolysis reaction so that adequate thickness of SiO_2 coating can be attained. The whole reaction was performed at room temperature and run overnight. After the completion of reaction, Si@SiO_2 nanostructures were collected by suction filtration and washed with 1 L of DI water. The as-obtained Si@SiO_2 was dried in vacuum oven for 3 days to guarantee that fully dried powder was obtained. It is noted that this just performs as the starting materials for the demonstration of mechanical process. In practical points of view, if we hope to economically obtain the Si@SiO_2 nanostructure, we can firstly use rice husks as the source for Si nanoparticle production.[1] Afterward, sacrificial SiO_2 layers can be created by thermally oxidize the surface of Si nanoparticle.

Mechanical process for producing micro-sized SC. The as-obtained Si@SiO_2 powder was pressed into pellets with dry press machine (MTI, Inc.), any additives (e.g. CNT) can be mixed with the powder before applying pressure. Different pressure, various from 17.6 MPa to 123 MPa (as shown in Figure 1b, supplementary Figure S1) was applied to obtained pellets with different density. Since pellets were made, they were calcined at 600 °C for 2 hours to strongly bridge the Si@SiO_2 particles together. Then, high energy mechanical milling was exploited to break pellets into micro-sized cluster. 20 minutes of milling was performed to produce cluster with size in the range of 1 μm to 15 μm.

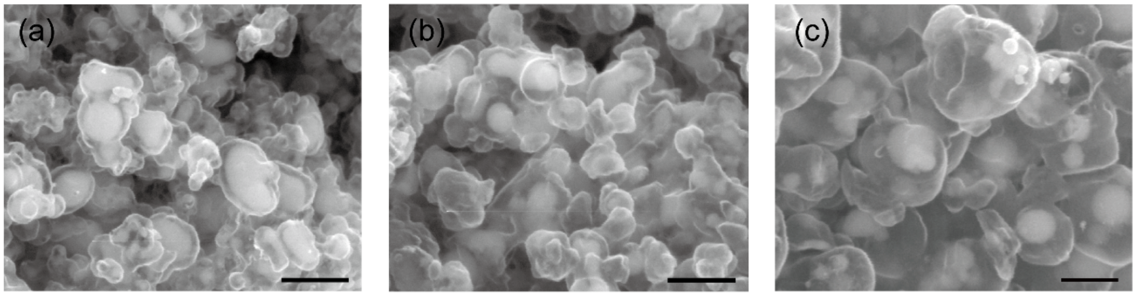
Carbon coating & SiO_2 etching. Typically, 1 g of SC were dispersed in 180 mL DI water first, followed by the addition of 6 mL of cetyl trimethylammonium bromide (CTAB, Aldrich, 0.01 M) and 0.6 mL concentrated ammonia hydroxide (Aldrich, 28%). The solution was then vigorously stirred with stir bar at 340 rpm for 30 minutes to assure proper surface modification. Next, 250 mg resorcinol (Aldrich) and 350 μL formaldehyde (Aldrich, 37 wt% in water) was successively added into solution to initiate the reaction. The thickness of carbon shell can be flexibly controlled by the amount of resorcinol and formaldehyde added into the system, while proportion between resorcinol and formaldehyde was fixed. The figure S.2 shows the different thickness of carbon shells synthesized under different amount of reagent added, 250 mg, 500 mg, and 1 g of resorcinol respectively. The reaction was kept going for 6 hours to guarantee the completion of reaction. Then, suction filtration was performed to separate the resorcinol-formaldehyde resin (RF) coated cluster before they were dried in vacuum oven for 24 hours. The RF polymerization is well known as a mature technique. The reaction used here can be linearly scale up. In a lab scale, 30 g of cluster sample can be coated in one beaker. The RF shell can then be carbonized under Ar flow at 800 °C for 2 hours. To etch the SiO_2 sacrificial layers away, clusters were stirred in 5 wt% aqueous hydrofluoric acid (Aldrich) for 30 minutes followed by suction filtration to separate the cluster. Control on etching time for removal of SiO_2 is important since long time etching might also remove some of the Si.

Synthesis of CNT-embedded nano-Si SC. First of all, to well disperse CNT in aqueous solution, 2g of multiwall(MW) CNT (NTP, Inc.) was pretreated in 200 mL of HNO_3: H_2SO_4= 3:1 (M_w) acid mixture at 90 °C for 1.5 hours. Suction filtration was then conducted to separate MWCNT and acid before dispersing MWCNT back into 300 mL DI water. Afterwards, dialysis was performed to neutralize MWCNT solution until pH reach the range of 5-7. The concentration of as-obtained MWCNT was determined by evaporating a specific volume of solution and weighting the mass of MWCNT. ~8 wt% of MWCNT was mixed with Si@SiO_2 starting materials in order to get uniformly-mixed CNT-Si@SiO_2. Sample was then dried before conducting further mechanical processes.

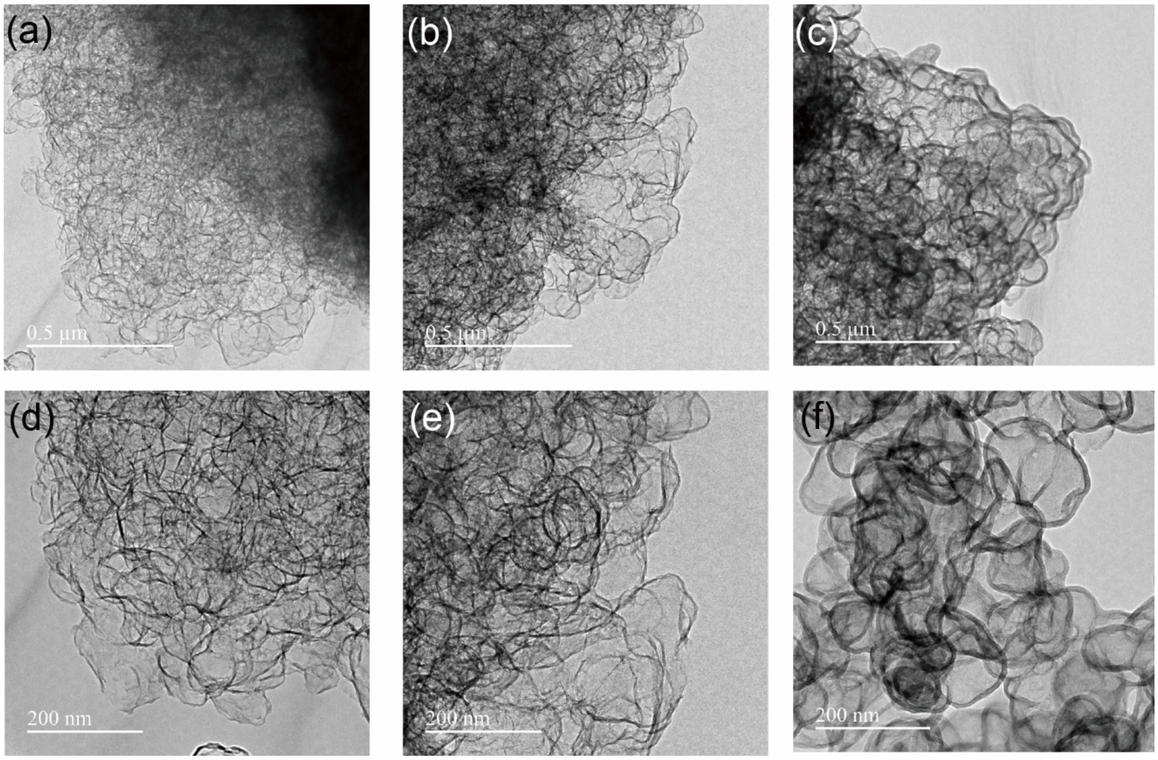
Cell preparation and electrochemical characterization. Prior to the slurry coating process, as-obtained SC was mixed with carbon black (Super P, TIMCAL, Switzerland), and polyvinylidene difluoride (PVDF, Kynar HSV 900) in the mass ratio of 65:20:15. N-methylpyrrolidone (NMP) was added as solvent and stirring was performed overnight. Then, slurry was cast on 1 cm^2 copper foil and dried @ 60 °C. To guarantee that the electrodes were fully dried, they were kept in vacuum oven at 100 °C for 4-5 hours and then kept in Argon-filled glove box for 1 day. Coin cells (2032) were assembled here for electrochemical test. Lithium metal foil was perform as counter electrode. Here, 1.0 M $LiPF_6$ in 1:1 w/w ethylene carbonate/diethyl carbonate (BASF) was used as electrolyte, while 10 vol% fluoroethylene carbonate, 1 vol % vinylene carbonate (Novolyte Technologies) was added for stabilizing cycling. Arbin battery tester was used here for Galvanostatic cycling, the voltage cutoffs for Si/Li cell were 1 V and 0.01 V (vs Li^+/Li) for charging and discharging, respectively. The rate capability was calculated based on the theoretical capacity of Si (1C = 4.2 mA mg^{-1}) while the specific capacity based on the total mass of SC (include the mass of carbon shell). For the measurement of Electrochemical Impedance Spectroscopy (EIS), BioLogic VMP3 system was used, frequency range was set from 1 MHz to 50 mHz.



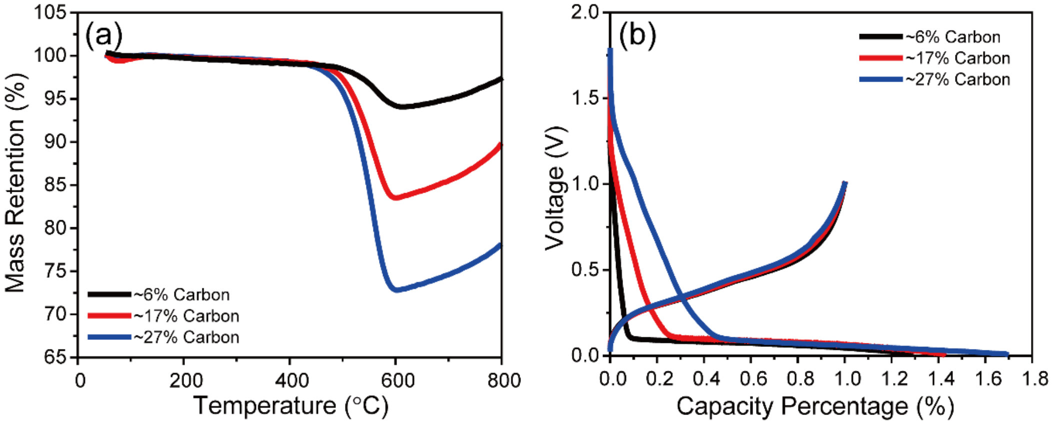
Supplementary Figure S1 Density of pellets versus pressure plot corresponding to Figure 1b, showing the evolution trend of density with increasing pressure.



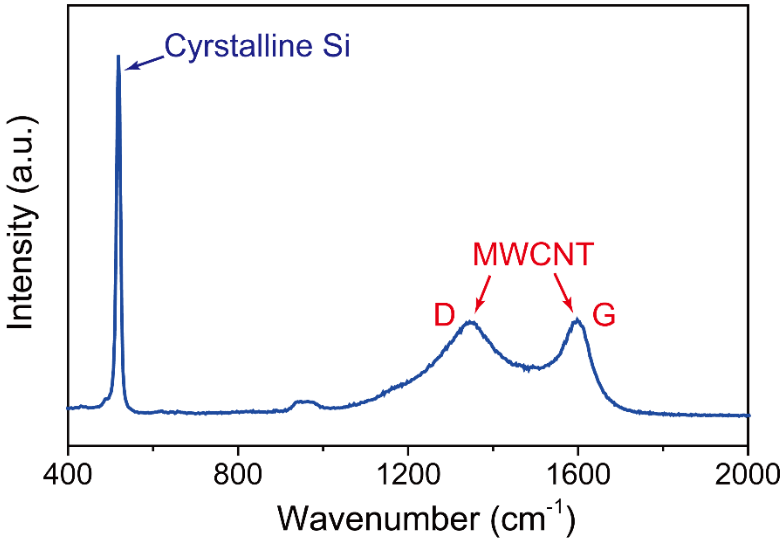
Supplementary Figure S2 SEM images of the surface of SC with different volume of void space. (a) With ~100% void volume versus initial volume (b) ~350% (c) ~500%. The percentage of void space is estimated by weight gain after SiO_2 coating. Figure (a) refers to the cycling performance in figure 3a with not enough void space, (b) refers to the cycling performance in figure 3a with enough void space. Scale bar: 200 nm



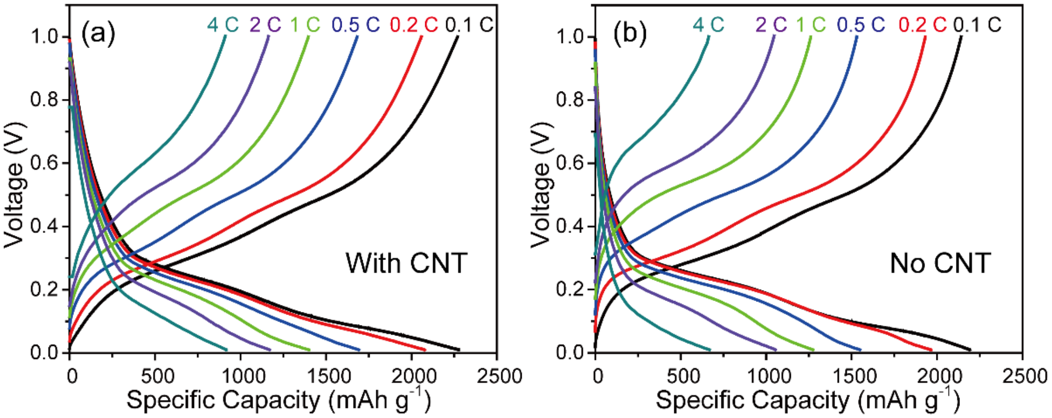
Supplementary Figure S3 Transmission electron microscopy (TEM) images of pure carbon framework with (a, d) ~2 nm (b, e) ~4 nm (c, f) ~10 nm of carbon shell. Si nanoparticles were fully removed to clearly show the morphology of carbon framework.



Supplementary Figure S4 (a) Weight loss of nanostructured Si SC with different carbon ratio by Thermogravimetric analysis. Temperature was scanned from room temperature to 800 °C, at the rate of 5 °C/min. (b) Normalized first cycle voltage profile Si SC with different carbon ratio. Showing the effect of carbon amount on first Coulombic efficiency.



Supplementary Figure S5 Raman spectroscopy of CNT-integrated nano-Si SC, showing the peak of crystalline Si and MWCNT.



Supplementary Figure S6 Typical charge/discharge voltage profile of cells with/without integrated CNT at different c-rate. Cells were cycled between 1 V and 0.01 V.

1. N. Liu, K. Huo, M. T. McDowell, J. Zhao and Y. Cui, *Sci. Rep.*, 2013, **3**, 1919.