Electronic Supplementary Information

A facile route for growth of CNT on Si@hard carbon for conductive agent incorporating anodes for lithium-ion batteries

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Experimental

Synthesis of Si@HC@CNT and Si@HC

Agarose was purchased from Sigma-Aldrich. 5 wt% of agarose aqueous solution was prepared by stirring at 95 °C. Subsequently, Si nanopowder (~100 nm, Alfa Aesar) and $Ni(NO_3)_2 \cdot 6H_2O$ (Sigma-Aldrich) were added to the agarose solution. The concentrations of Si nanopowder and Ni precursor are 0.5 wt% and 0.01 wt%, respectively. After mild stirring at 95 °C for 2 h, the solution was moved to a petri dish for cooling at room temperature for 1 h. The resultant product was dried at 70 °C in a convection oven for 12 h. Subsequently, carbonization process of the agarose encapsulating Si composites (denoted as Si@agarose) was conducted in a quartz tube furnace with ramping rate of 5 °C min^{-1}. The Si@agarose was heated to 200 °C for 1 h under argon atmosphere for stabilization. Then, temperature was increased to 900 °C for 2 h to enhance electrical conductivity and to increase the carbon quality of hard carbon encapsulating Si (denoted as Si@HC). During the carbonization process, we switched the gas in the tube furnace with acetylene gas (10% diluted in argon) and conducted CNT growth on the surface of Si@HC for 3 min. For Si@HC, all experimental processes are the same as above, except for addition of $Ni(NO_3)_2 \cdot 6H_2O$ into the initial solution.

Physical characterization

Si@HC and Si@HC@CNT were characterized by a scanning electron microscope (SEM, S4800, Hitachi) operating at 10 kV. The crystalline structure of Si@HC and Si@HC@CNT were analysed with a powder X-ray diffractometer (MPD) using Cu Kα radiation (λ=1.54 Å) between 20° and 90° at a scan rate of 0.01° s^{-1}. Raman spectra were obtained from a JASCO spectrometer (NRS-3000) to investigate the characteristics of the carbon coating layer using a He-Ne laser operating at $\lambda = 632.8$ nm. To characterize the morphologies of the Si@HC@CNT, high resolution transmission electron microscope (HR-TEM, JEOL, JEM-2100F) operating at 200 kV was employed. The carbon contents were measured by an elemental analyzer (Flash EA 1112, Thermo Electron Corp.).

Electrochemical measurements

Electrochemical test was performed using coin-type half (2016 R-type) assembled in an argon-filled glove box. The Si@HC@CNT anodes were composed of active materials, poly(acrylic acid)/sodium carboxymethyl cellulose (50/50 wt%/wt%, Aldrich) binder at a weight ratio of 90:10. The Si@HC anodes were composed of active materials, carbon black (Super P), poly(acrylic acid)/sodium carboxymethyl cellulose (50/50 wt%/wt%, Aldrich) binder at a weight ratio of 80:10:10.The resulting slurry was coated on a Cu current collector and dried in a vacuum at 150 °C for 2 h. The mass loading of active materials was ~3.5 mg cm^{-2} for both anodes. The coin-type half cells consisted of lithium metal as a counter electrode, a polyethylene separator, and 1.3 M $LiPF_6$ in ethylene carbonate/diethyl carbonate (EC/ DEC, 3/7 v/v) with 10 wt% fluoroethylene carbonate (FEC) as the electrolytes. The cell performance was examined using a cycle tester (Wonatech). The coin-type half cells were cycled at a rate of 0.05 C between 0.005 V and 2 V for an initial cycle, and at a rate of 0.2 - 20 C between 0.01 and 2 V for other cycles. The AC impedance (frequency range = 10 mHz to 1 MHz at an amplitude of 10 mV) and cyclic voltammetry of cells were obtained using a potentiostat/galvanostat (VSP classic, Bio-Logic).

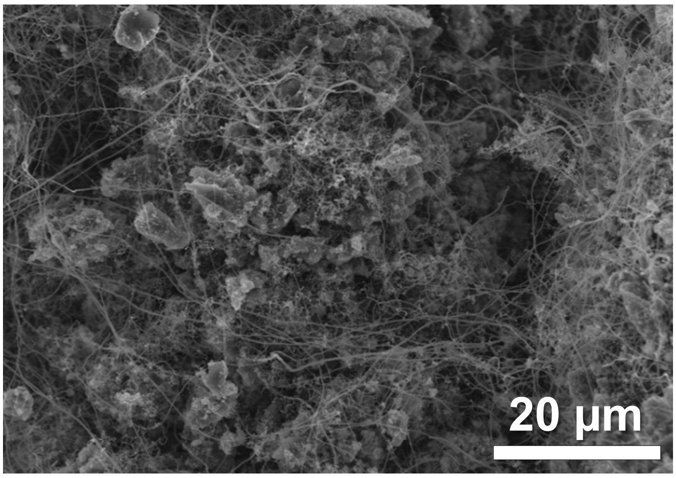

Fig. S1 Low magnified SEM image of as-synthesized Si@HC@CNT. CNT was uniformly grown on the Si@HC over entire regions.

Fig. S2 SEM images of Si@HC@CNT electrodes. (a) Top-view SEM image, (b) magnified top-view SEM image, (c) cross-section SEM image and (d) magnified cross-section SEM image. SEM image in the inset shows CNTs on the Si@HC@CNT (scale bar: 200 nm).

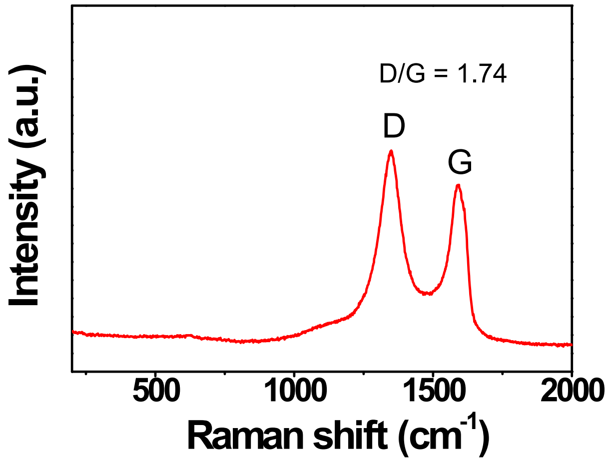

Fig. S3 Raman spectrum of as-synthesized Si@HC@CNT.

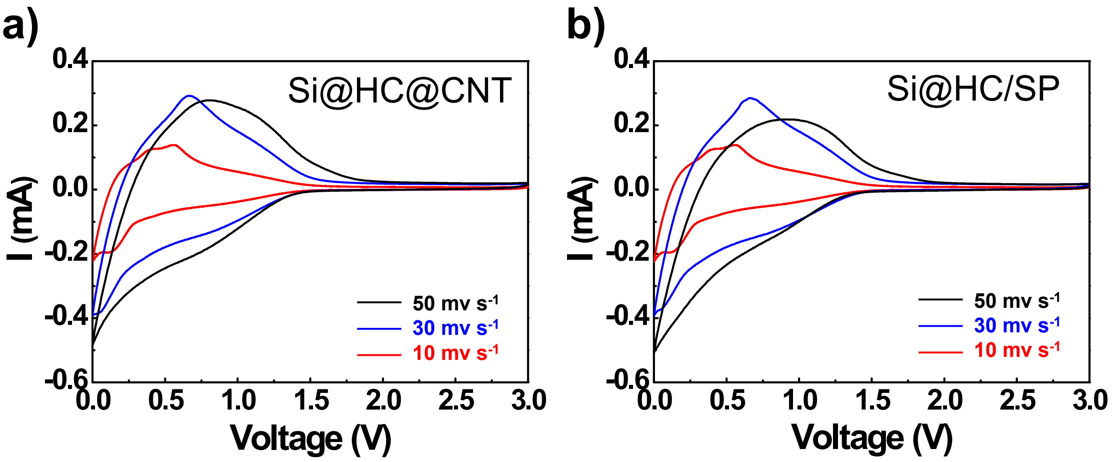

Fig. S4 CV curves of Si@HC@CNT and Si@HC/SP at various scan rates.

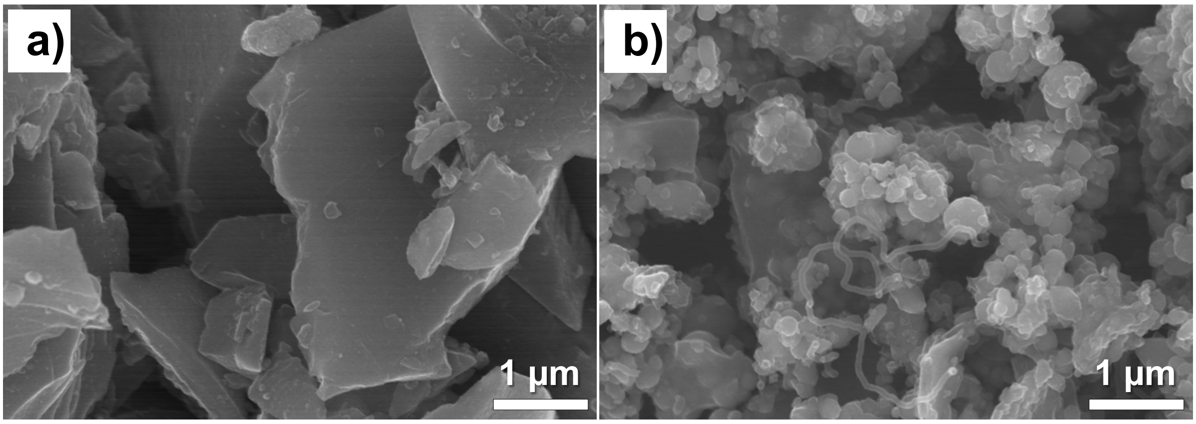

Fig. S5 SEM images of as-synthesized Si@HC@CNT with different Si contents: (a) 5 wt% and (b) 35 wt%. These samples are synthesized without CVD process.

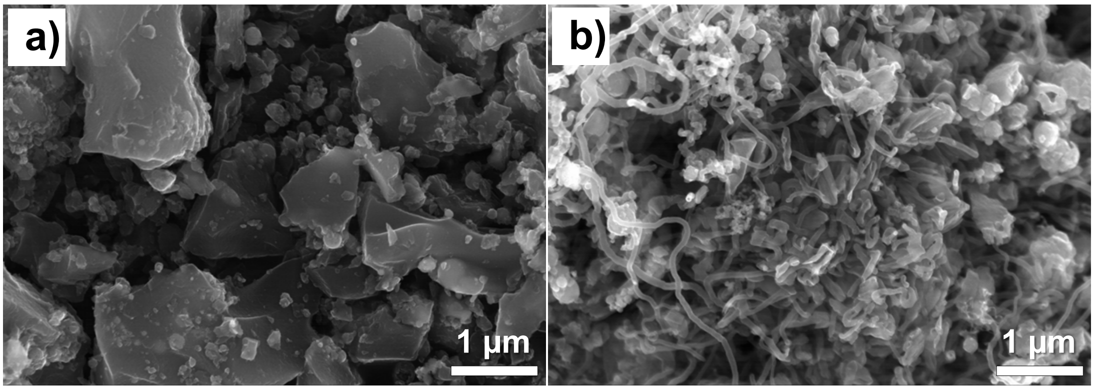

Fig. S6 SEM images of as-synthesized Si@HC@CNT at different CVD conditions: (a) without CVD process and (b) with CVD process for 5 min. Si contents for both samples are fixed at 23 wt%.

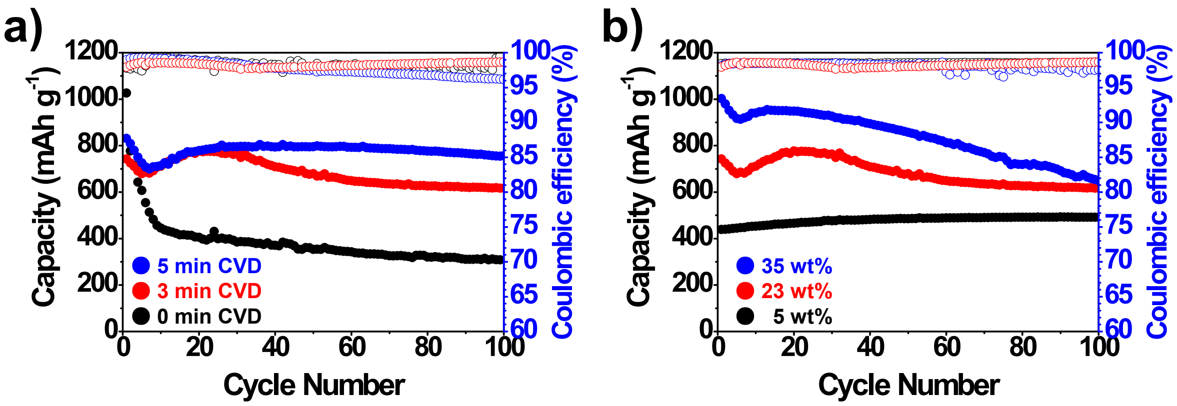

Fig. S7 Cycle performances of as-synthesized samples with (a) different CVD conditions (Si content of 23 wt%) and (b) different Si contents (CVD time: 3 min) at 0.5/0.5 C discharge/charge. No additional conductive agent (super P) was added to all electrodes.

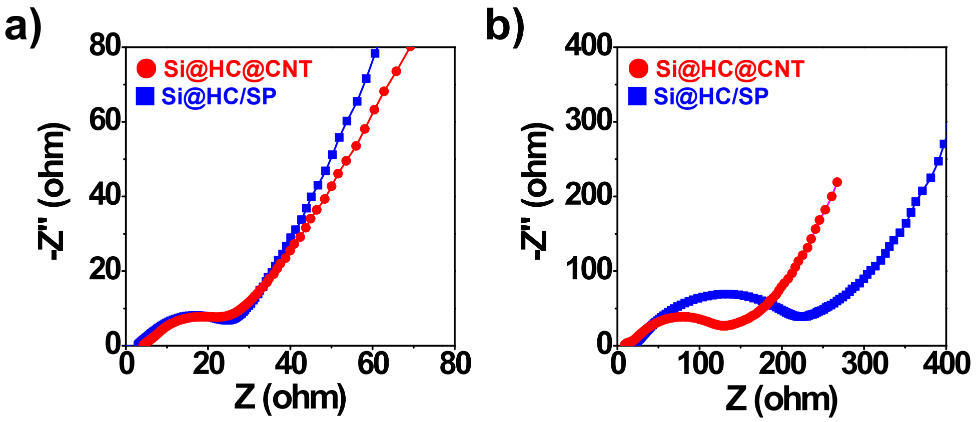

Fig. S8 Nyquist plots of the electrochemical impedance spectra of Si@HC@CNT and HC@CNT/SP. EIS spectra of both electrodes (a) after 1st cycle and (b) after 500th cycles at a rate of 0.5 C