Electronic Supplementary Material (ESI) for Energy & Environmental Science

Supplementary Information

Scalable approach to multi-dimensional bulk Si anodes via metal-assisted chemical etching

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1. Materials and Methods

Commercially available Si powder was immersed in a solution of 5-20 mM silver nitrate ($AgNO_3$) and 5 M HF for a controlled time. Immediately after rinsing, the silver deposited silicon powder was immersed in an etchant consisting of 5 M HF and 1.5% H_2O_2 at 50 ^oC for 1-3 hr to produce silver catalyzed etched Si materials. Depending on the deposition time of silver nitrate, the size of silver particles was varied (Fig. S1(a-c)). During electroless deposition of silver, nanopits were also observed by etching in HF solutions. When the silicon powder having various silver particle sizes was soaked into an etchant, composed of 5 M HF and 1.5% H_2O_2, at 50 ^oC for 1 hr, nanoporous silicon nanowires, which protrude out from intact silicon core, were produced with different length and pore size (Fig. S1(d-f)). In addition to size of silver catalyst, the concentration of H_2O_2 that act as an oxidant is another controllable parameter to tune the Si morphology. As the H_2O_2 concentrations of

1.0, 1.5, and 2.0% were used at a fixed HF concentration (5 M), shallow nanopits, Si nanowires, and Si macropores were prepared, respectively (Fig. S2). To obtain multi-dimensional Si powders that nanoporous Si nanowires protrude out from microscale Si matrix, silver deposited Si samples were etched in a 5 M HF and 1.5% H_2O_2 at 50 ^oC for 3 hr. As-synthesized Si powders were immersed in 5% HF for 1 min to remove silicon oxide onto the surface of etched Si, and followed by drying in a vacuum oven at 100 ^oC for 2 hr to remove water completely. Subsequently, the etched Si samples were coated by carbon by thermal decomposition of acetylene gas at 700 ^oC for 20 min in quartz furnace.

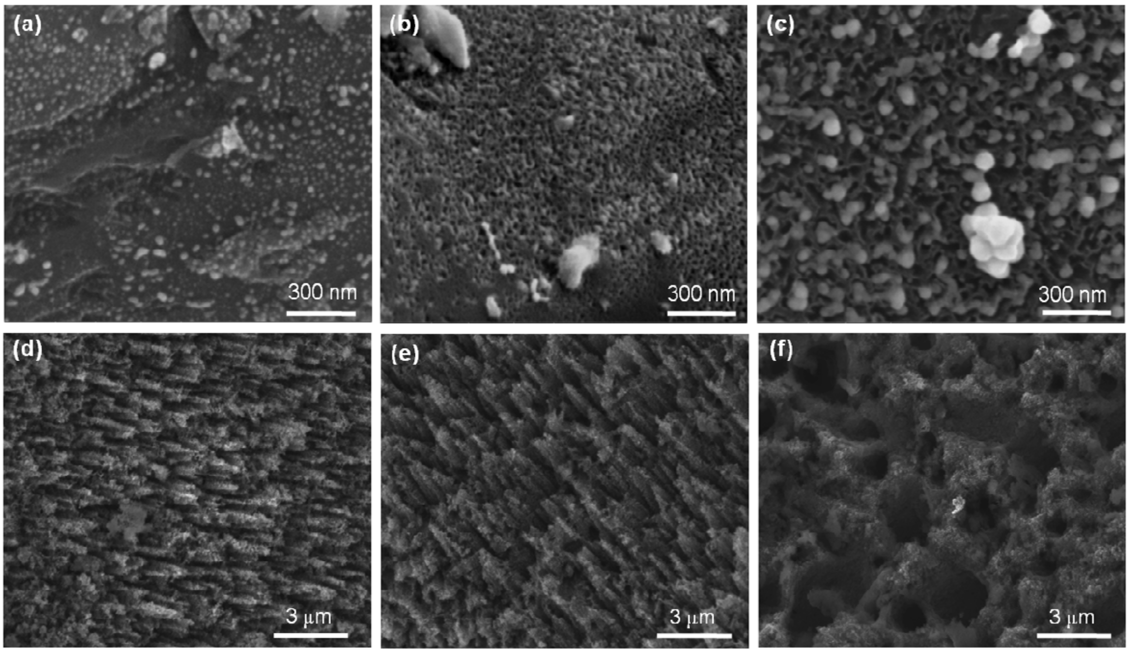

Fig. S1 Morphologies of Si surfaces according to the size of silver nanoparticles. SEM images of silver deposited Si powders prepared by three different silver nitrate concentrations of (a) 5 mM, (b) 10 mM, and (c) 20 mM. Immediately after silver deposition, the samples were immersed in an etchant consisting of 5 M HF and 1.5% H_2O_2 at 50 ^oC for

1 hr to etch the Si surfaces using silver catalyst. SEM images of the samples etched from samples seen in Fig. S1(a-c) show (d) short Si nanowires, (e) long nanoporous Si nanowires, and (f) macroporous Si structures, respectively.

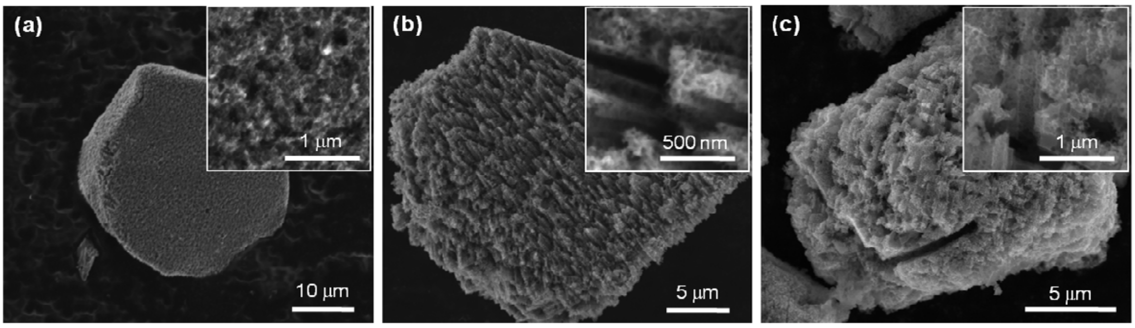

Fig. S2 Morphologies of Si surfaces according to the concentrations of H_2O_2. SEM images of Si powders chemically etched with three different H_2O_2 concentrations of (a) 1.0%, (b) 1.5%, and (c) 2.0% at a fixed HF concentration of 5 M. All samples were silver deposited in 10 mM $AgNO_3$ and 5 M HF plating solution for 3 min. H_2O_2 acts as an oxidant to etch the Si and the concentration of H_2O_2 enables to control the morphologies of Si powder. The corresponding SEM images show that Si nanopits (from 1.0% H_2O_2), porous Si nanowires (from 1.5% H_2O_2), and macroporous Si structures (from 2.0% H_2O_2) were synthesized. The insets show the magnified Si morphologies.

2. Effect of carbon-coating temperature on the electrochemical performance of Si electrodes

We investigated the effect of carbon coating condition on the electrochemical performance. The SEM images of mSi carbon-coated at 700, 900, and 1000 ^{o}C do not show the distinct difference (Fig. S3(a-c)). Therefore, Raman and FT-IR spectrum were obtained to characterized three different samples. Figure S3d shows the Raman spectra of multi-dimensional Si carbon coated with decomposition of acetylene gas at 700, 900, and 1000 ^{o}C. From the two peaks appearing at ~1360 (D band) and ~1580 cm^{-1} (G band), the dimensional ratio of the D and G bands of samples carbon coated at 700, 900, and 1000 ^{o}C are 2.5, 2.1, and 3.1, respectively. The FT-IR spectrum of sample prepared at relative low temperature (700 ^{o}C) shows incomplete decomposition of acetylene molecules appearing at ~1640 cm^{-1}, which is associated with the vibration of carbon (vinyl bonds) skeleton of the sample (Fig. S3(e)). In case of samples coated at 1000 ^{o}C, incomplete decomposition of acetylene gas was not observed, but lower degree of graphitization was obtained due to small amount of oxygen remaining carbonization process (Fig. S3(d & e)). All three samples were prepared with a similar carbon content of ~ 30wt% at three different temperatures. In order to compare the electrochemical performance of three samples, galvanostatic discharge/charge experiments were carried out. Figure 6f shows the voltage profiles of the three c-mSi anodes at 0.1 C rate between 1.2 V and 0.01 V. The first cycle discharge capacities are 3200, 2440, and 2290 mAh/g for the electrodes of multi-dimensional Si carbon-coated at 700, 900, and 1000 ^{o}C, respectively, with the corresponding first charge capacities of 2630, 2150, and 1900 mAh/g. Therefore, the coulombic efficiencies in the first cycle are 65%, 88%, and 85% for the three different Si samples carbon-coated at 700, 900, and 1000 °C, respectively. The cycling performance of samples with high degree of graphitization is superior to that of low degree samples (Fig. S3(g)).

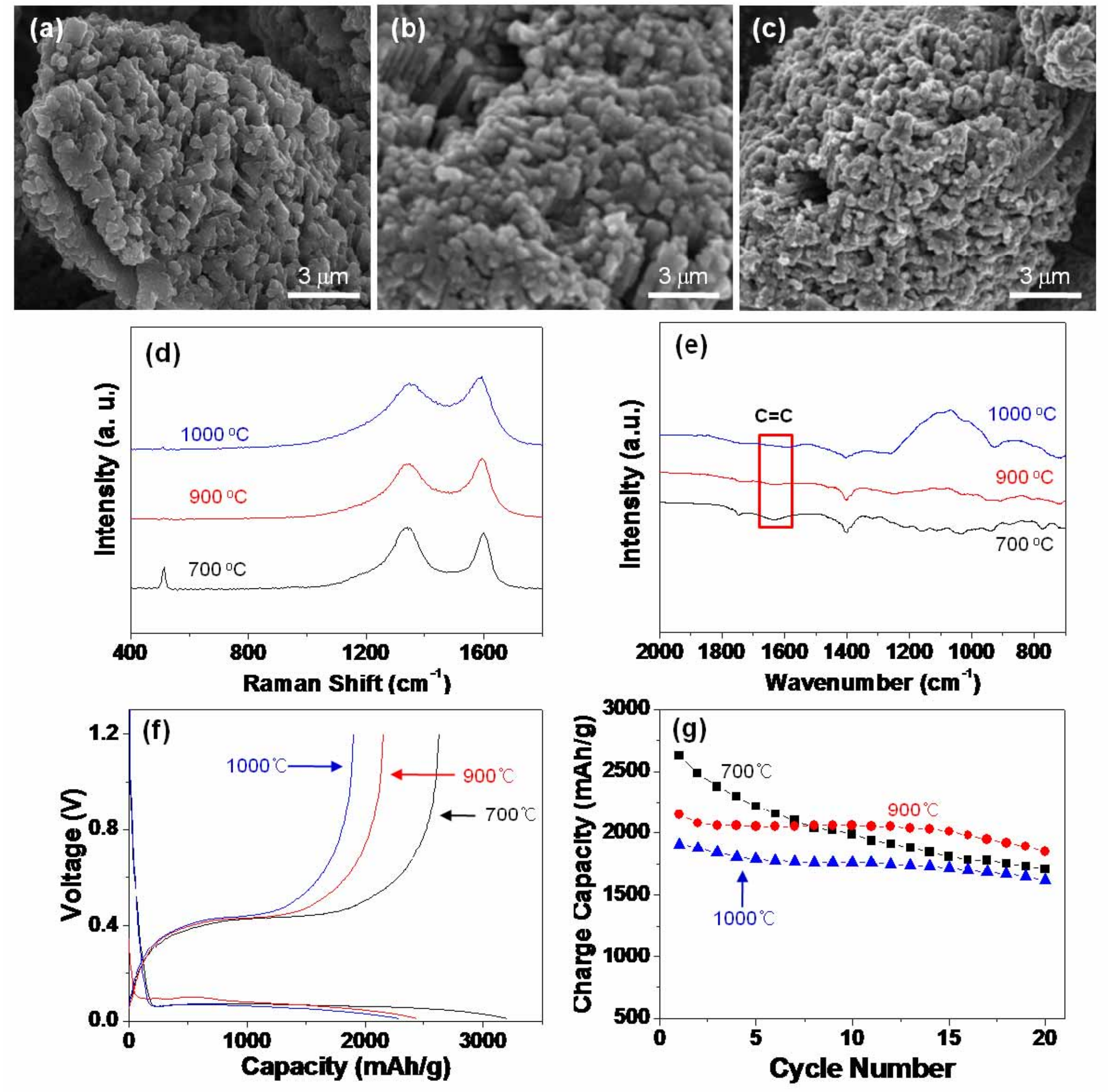

Figure S3. Effect of carbon-coating temperature on the electrochemical performance. SEM images showing mSi carbon-coated at (a) 700, (b) 900, and (c) 1000 ^{o}C. (d) Raman spectra of Si anodes coated with carbon at 700, 900, and 1000 ^{o}C. (e) The corresponding FT-IR spectrum of each anode materials. (f) Voltage profiles for the first galvanostatic cycles of the c-mSi at the 0.1 C rate. All three samples have a similar carbon content of ~28 wt%. (g) Charge capacity versus cycle number for the carbon-coated Si at the 0.1 C rate. The carbon coating condition affects the initial capacity and cycling retention. Square, circle, and triangle symbols represent the carbonization temperature of 700, 900, and 1000 ^{o}C, respectively.

Reference

S1. Svatoš, A., & Attygalle, A. B. Characterization of Vinyl-Substituted, Carbon-Carbon Double Bonds by GC/FT-IR Analysis, *Anal.Chem.* **69**, 1827-1836 (1997).