Supporting Information

Helical Silicon/Silicon Oxide Core-Shell Anodes Grown onto the Surface of Bulk Silicon

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Experimental Section

Preparation of Si/SiOx urchin-like structures: Bulk Si powder (Sigma-Aldrich, 10-20 μm in size) was cleaned in acetone and isopropyl alcohol and dried under nitrogen. PS-*b*-P4VP copolymer was purchased from Polymer Source, and was used without further purification (M_n,PS = 35.0 *kg/mol*, M_n,P4VP = 21.0 *kg/mol*, M_w/M_n = 1.09). The PS-*b*-P4VP copolymers were dissolved in toluene at 60 ^oC for 1 hr and cooled to room temperature to make a 0.7 wt% polymer solution. Subsequently, chloroplatinic acid (H_2PtCl_6, Sigma-Aldrich) was loaded to the polymer solutions with a molar ratio of metal to pyridine of 0.8 and stirred for 24 hr. Next, bulk Si powder (1 g) was added to Pt-incorporated PS-b-P4VP solution (5 mL) with stirring for 3 hr, and subsequently, n-hexane, non-solvent for both blocks, was dropped to form bulk Si uniformly coated with micellar film. When the Si powder containing the Pt-incorporated micelles was exposed

to oxygen plasma (SPI Plasma Prep II, 50 watts) for 20 min, Pt-decorated Si particles were obtained with the removal of all polymers. In addition, high-temperature annealing (500 ^{o}C for 2 hr in an Ar) can also be used to remove polymers. The Pt-coated Si was transferred to quartz tube furnace (1050 ^{o}C for 2 hr in an Ar stream) to grow 1D Si/SiOx nanostructures onto the surface of Si particle. In order to coat the carbon layer on the urchin-like Si/SiOx electrodes, acetylene gas that used as a carbon source, was thermally decomposed at 850 ^{o}C for 30 min in quartz furnace.

Characterization of Si/SiOx urchin-like electrodes: Pt-incorporated PS-*b*-P4VP thin films, Pt-decorated Si, Si/SiOx urchin-like structures were characterized by SEM (NanoSEM 230, FEI) operating at 10 kV. The crystal structures of Si/SiOx sample were measured by high power X-ray diffractometer (XRD) on a Rigaku D/MAX at 2500 V using Ni-filtered Cu Kα radiation. Raman spectra (WITEC, Alpha-300M) were obtained to determine the dimensional ratio of diordered (D) band to the graphene (G) band (I_D/I_G) for carbon-coated electrodes. A He-Ne laser operating at λ = 632.8 nm was used as the excitation source. For HR-TEM measurements, urchin-like Si/SiOx samples were dispersed in ethanol by ultra-sonication, and transferred onto Formvar-coated copper grids. TEM images were taken in the bright-field (or dark-field) mode using JEM 2100 (JEOL) operated at 200 kV accelerating voltages.

Electrochemical performance: Electrochemical experiments were performed using coin-type half cells (2016R type) by assembling in an Ar-filled glove box. Cabon-coated bulk Si and Si/SiOx urchin-like electrodes were used as the working electrodes and lithium metal foils as the counter electrodes. The electrolyte was $LiPF_6$ (1.3 M) with ethylene carbonate/diethylene carbonate (EC/DEC, 30:70 vol%, Panax starlyte, Korea). The coin-type half cells were cycled at a rate of 0.1 and 0.2 C between 0.02 and 1.2 V. The

electrode was composed of carbon-coated Si/SiOx nanostructured electrodes (70 wt%), Super P carbon black (15 wt%), and polyacrylic acid/sodium carboxymethyl cellulose (wt/wt = 50/50, 15 wt%, Sigma-Aldrich).

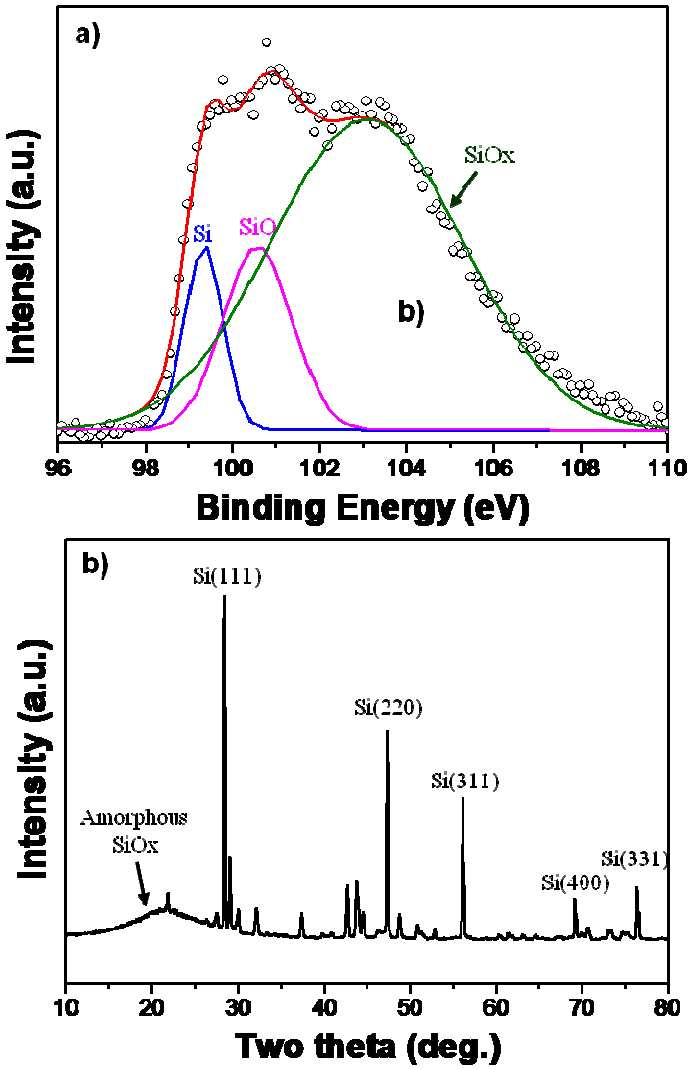

Figure S1. Characterization of Si/SiOx urchin-like structures consisting of Si/SiOx nanocoils grown onto the surface of bulk Si particles. a) XPS spectra confirms that Si/SiOx urchin-like structures are composed of silicon and SiOx ($1 < x < 2$). b) XRD pattern indicates that Pt-Si alloy (unassigned peaks) acted as a catalyst to grow crystalline Si and amorphous SiOx onto the surface of bulk Si particles.

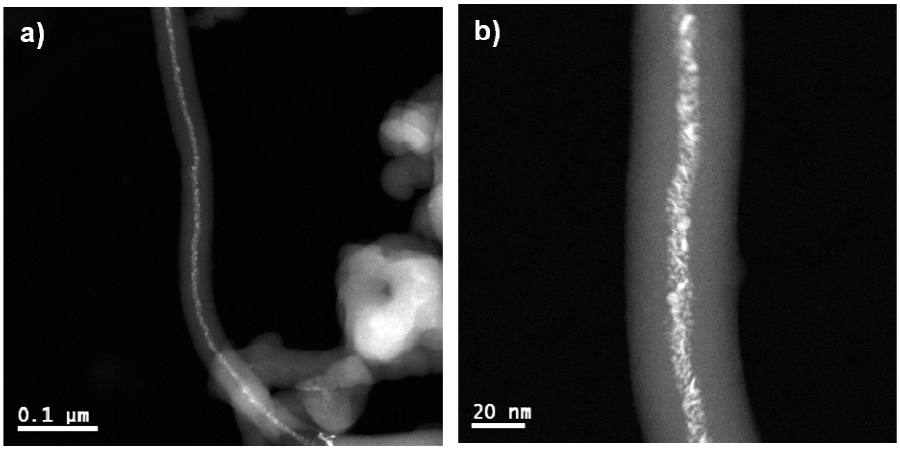

Figure S2. Dark-field TEM image showing a) straight nanowires consisting of crystalline Si core and amorphous SiOx shell and b) the magnified TEM image. The crystalline Si having higher electron density than amorphous SiOx was seen as brighter spots.

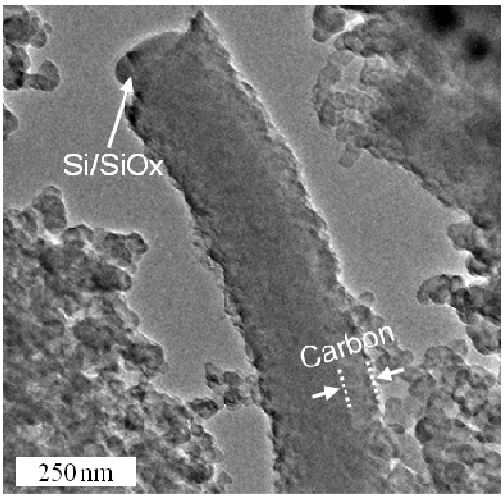

Figure S3. HR-TEM image of Si/SiOx 1D nanostructures. It shows that the Si/SiOx structures were not significantly changed after 70 cycles.

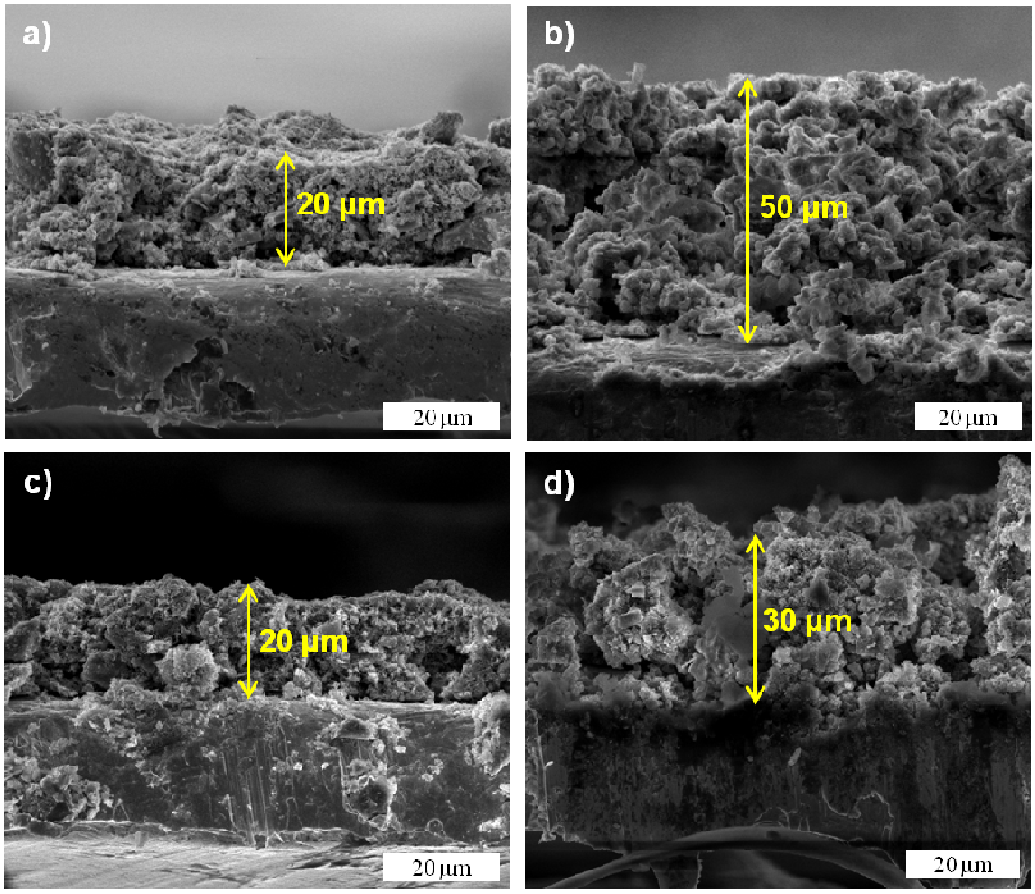

Figure S4. SEM images showing thickness of active layers before lithiation and after lithiation. Thickness of carbon-coated bulk Si layers a) before lithiation and b) after lithiation to 0 V. Thickness of carbon-coated Si/SiOx layers c) before lithiation and d) after lithiation to 0 V. The Si/SiOx active materials showed less volume expansion than bulk Si electrodes.