Supporting information

Nanoscale Si Coating on the Porewall of SnO_2 Nanotube Anode for Li Rechargeable Batteries

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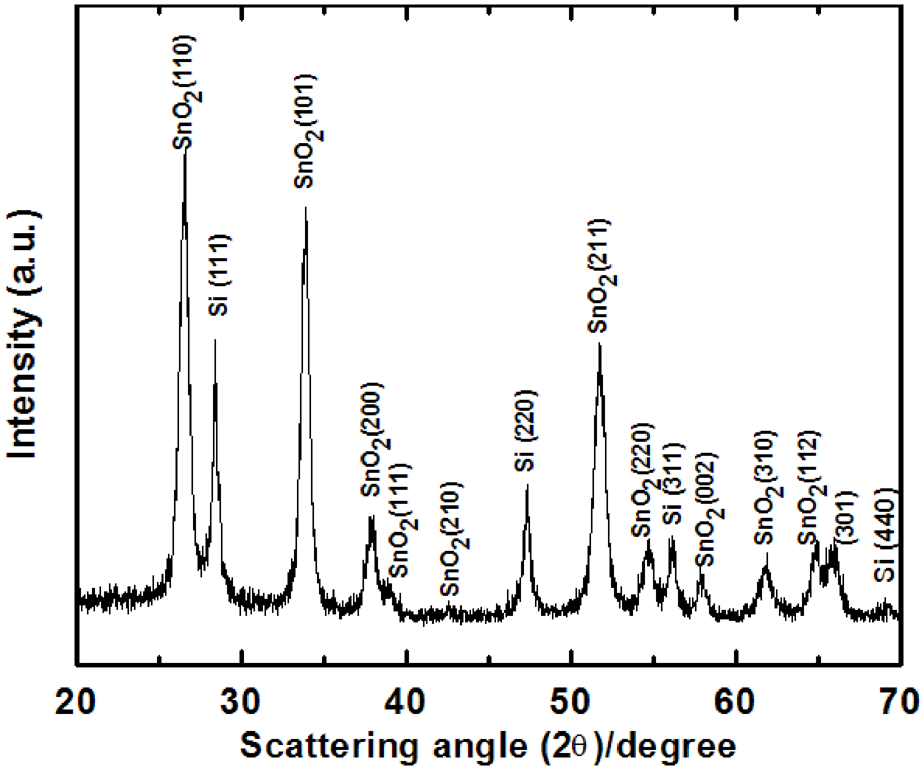
Experimental Methods

Preparation of AAO-encapsulated SnO_2 nanotubes: A porous anodized alumina (AAO) membrane (Whatman, Anodisc,φ=200-250 nm) was immersed in a 0.6M $SnCl_4$ aqueous solution (Aldrich 99%,) at ambient conditions for 4 hours. The alumina membrane was then placed above a filter paper and a vacuum was pulled for 5-10 minutes to homogenize the distribution of Sn precursor in the AAO membrane. After drying at 150 °C for 3 h in an oven, the membrane was calcined in air at 600 °C for 3h. The vacuum treatment was necessary to homogenize the distribution of precursor in the alumina membrane. For example, after equilibrating the membrane in $SnCl_4$ aqueous solution, the evaporation of water would result in the formation of a thin liquid film of $SnCl_4$ (melting point: -33°C) on the membrane walls. The application of a negative pressure would make the film thickness more uniform throughout the membrane pores and remove any air bubble that might be present inside the pores. The same is true for distributing the n-butyl-capped Si solution in the membrane. After polishing the membrane surface gently with a fine sand paper, the membrane template was removed by treatment in a 2M NaOH aqueous solution for 1h and rinsed with distilled water for several times. The SnO_2 nanotubes were recovered as an insoluble product.

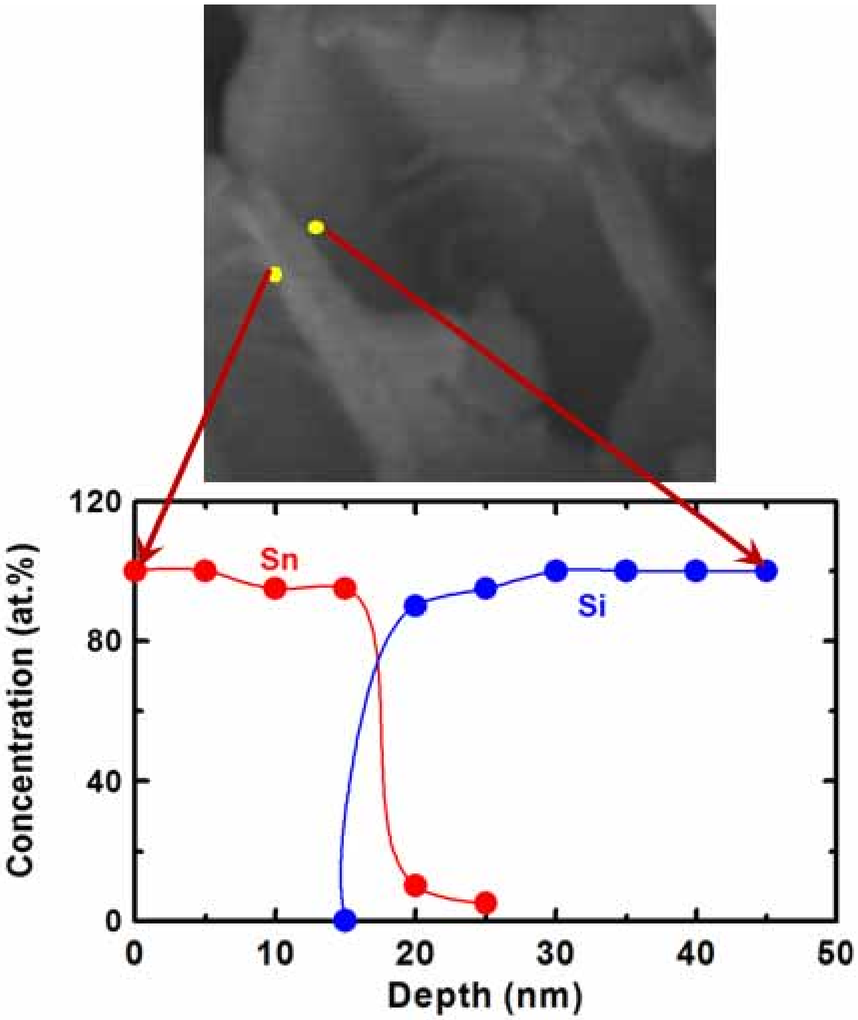
Preparation of Si-coated SnO_2 nanotubes: The calcined SnO_2 loaded template in the process described above was immersed in a butyl-capped Si solution for 30 min, and then placed over a filter paper and a vacuum was pulled for 5-10 minutes. Finally it was dried at 150^{o}C for 12h. The detailed method for preparing butyl-capped Si solution is described in Ref. 20. The immersion-drying procedure was repeated 3 times. The template was then thermally annealed in pure Ar for 3 h at 1000^{o}C. The membrane template was removed by etching in a 2M NaOH solution for 2h, and rinsed with distilled water 4 times. CHS analysis confirmed that the carbon content in the sample was 11 wt%. Since the Si was capped by carbon, it could not dissolve in 2M NaOH.

Materials characterization: The morphology and structure of Si-coated SnO_2 nanotubes were examined by scanning electron microscopy (NanoSEM 230), transmission electron microscopy (JEOL FETEM 2010), X-ray diffraction (XRD, MAX2500V) and Auger electron spectroscopy (AES, PHI-Perkin-Elmer model 10-155).

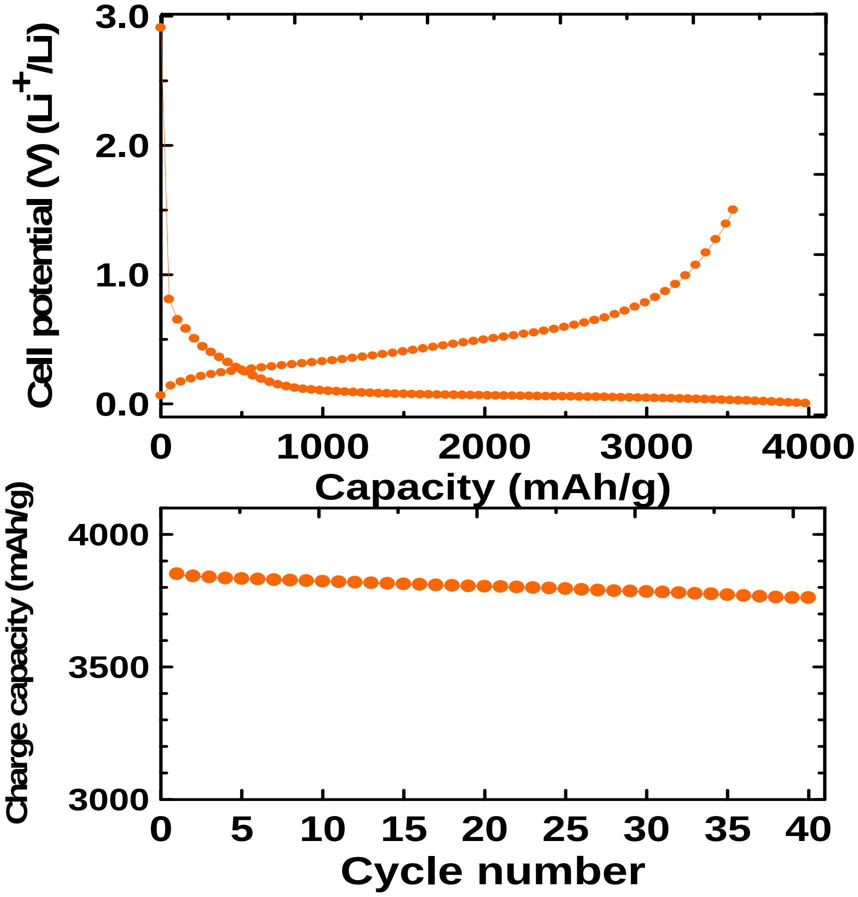
Electrochemical measurements: The electrolyte for the coin-type half cells (2016R type) was 1.1 M $LiPF_6$ in a mixture of ethylene carbonate (EC), diethylene carbonate (DEC) and ethyl-methyl carbonate (EMC) (30: 30: 40 vol. %) (Cheil Industries, Korea). The coin-type half cells were cycled at the rate of 0.2 C (1 C = 2000 mA/g) between 0 and 1.2V. The working electrode was formulated from 80 wt. % active material, 10 wt. % poly(vinylidene fluoride) binder and 10 wt. % Super P carbon black. The loading of active materials was ~13 mg. The Super P carbon black additive did not contribute to the total capacity as it functioned only as a conducting agent. Typically, five coin-cells were tested to check capacity variations at the same cycling condition which were typically < ± 6 mAh/g.



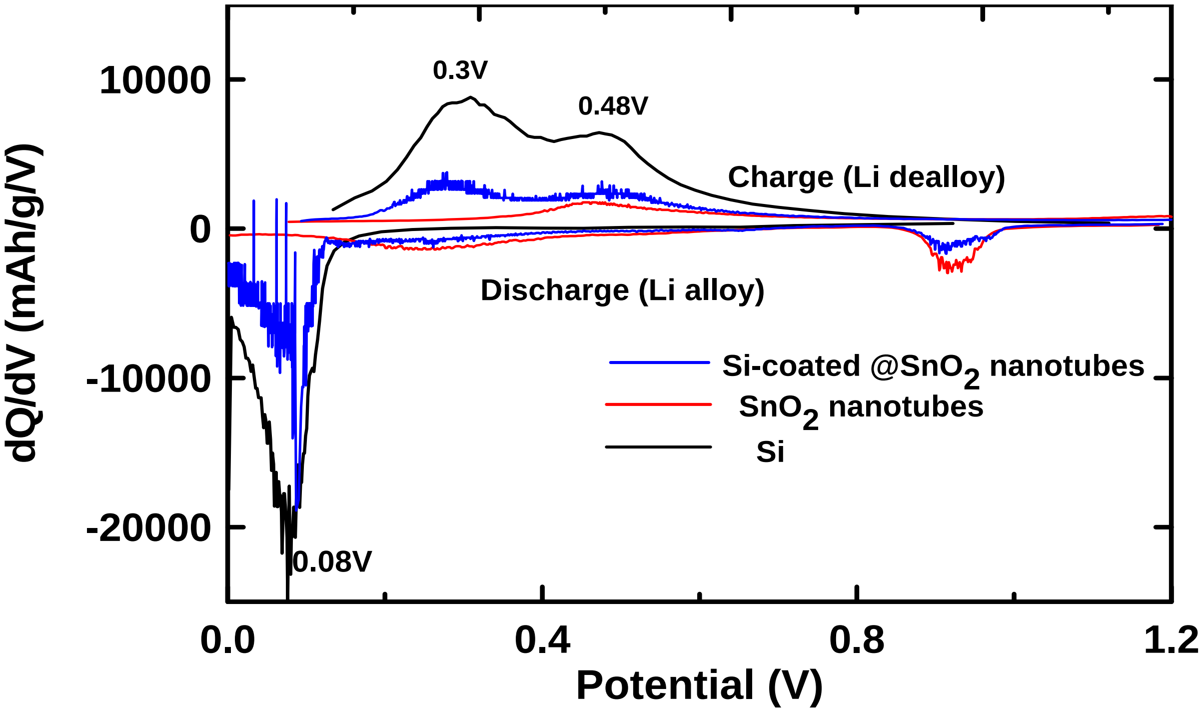
S1. XRD pattern of Si-coated SnO_2 nanotubes.



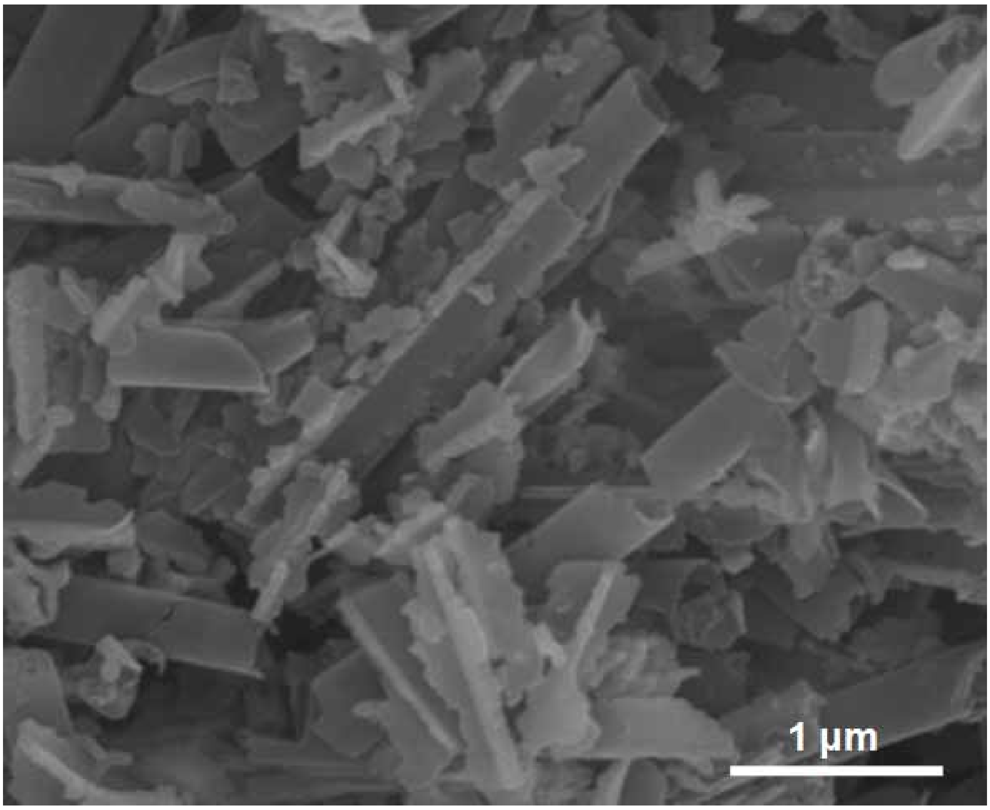
S 2. SEM image of Si-coated SnO_2 nanotubes and Auger depth profiling of Sn and Si elements from the exterior to the interior of the nanotube.



S3. Voltage profiles (top) and charge capacity (lithium dealloy) of the Si nanoparticles prepared by a method in the experimental (botom) in coin-type half cells at the 0.5C rate in coin-type half cells. Fisrt Charge and Discharge capacities were 3980 mAh/g and 3535 mAh/g, respectively, correspding to coulombic efficiency of 88%. Since Si nanoparticles were obtained from butyl-capped Si, final Si nanopraticles were capped with carbon.



S4. Differential curves of Si-coated SnO_2 nanotubes, SnO_2 nanotubes and Si nanoparticles during the first cycle.



S5. TEM images of SnO_2 nanotubes after cycling for 90 times at a rate of 0.5C.