Supporting Information

Improving cyclic performance of Si anode for lithium-ion batteries by forming an intermetallic skin

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Experimental Section

50 mg nanosized Si (average particle size $\leq$ 50nm, 98%, Laser synthesized from vapour phase, Alfa Aesar) was put in a petri dish and coated by Ni in an EMITECH K575X turbo sputter-coater. Oxides on the Ni target were removed before sputtering. The coating thickness was controlled to be 1, 4, and 6 nm. In the cases of 4 and 6 nm Ni-coating, Ni sputtering was carried out twice, with a 2 and 3 nm coating each time, respectively; after the first round of Ni coating, the Si powders were redistributed in the petri dish to increase the chance of Si particles being coated because some Si surfaces facing down may not have been coated during the first coating run. Because the fast release of the vacuum may result in blowing off the powder, the gas valve was controlled to increase Ar flow gradually. The Ni-coated samples were then transferred to a tube furnace (Lindberg/Blue M) and annealed at 800 °C for 1 h under H_2/Ar flow to allow the Ni to react with the surface of the Si, forming an intermetallic surface on the Si particles. The resulting products were denoted as Si@1nm $NiSi_x$, Si@4nm $NiSi_x$, and Si@6nm $NiSi_x$ for the samples with sputtering 1, 4, and 6 nm Ni, respectively.

The as-prepared samples were characterized by powder X-ray diffraction (XRD) on a Bruker D8 DISCOVER diffractometer with Cu Kα radiation. Scanning electron microscopy (SEM) was performed on a Hitachi S-4800, equipped with a Bruker Quantax EDS system. X-ray photoelectron spectroscopy (XPS) spectra of samples were obtained using an HP5950A ESCA spectrometer with monochromatic Al Kα radiation as the X-ray source. Transmission electron microscopy (TEM) was carried out on a Hitachi H-9000-NAR operating at an acceleration voltage of 300 kV. Charge/discharge performance was characterized by 2032-tpye coin cells that were assembled in an argon-filled glove box with oxygen and moisture content below 1 ppm. Electrodes were prepared by mixing the as-prepared nickel silicide-coated Si as the active material, poly(acrylic acid) as a binder, and carbon black as a conductor with a weight ratio of 70:15:15 to form a slurry. The resulting slurries were coated onto a Cu foil using the doctor blade method. After drying and pressing, the Cu foil was cut into disks (1.11 cm in diameter) with typical electrode material loadings of ca. 1 mg., and 1 M $LiPF_6$ dissolved in ethylene carbonate/ethyl methyl carbonate (40:60, v/v) was employed as an electrolyte. Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) spectra of the as-prepared anodes were measured on a PARSTAT 4000 electrochemical station by using a three-electrode cell that consisted of the nickel silicide-coated Si electrode as a working electrode, a lithium disk as a counter electrode, and a lithium ring as a reference electrode. CV was carried out at a scanning rate of 0.1 mV s^{-1}, while EIS was tested between 100,000-0.1 Hz with an amplitude of 10 mV.

(a)

S4800 10.0kV 6.7mm x110k SE(M) 1/6/2014 21:14   500nm

(b)

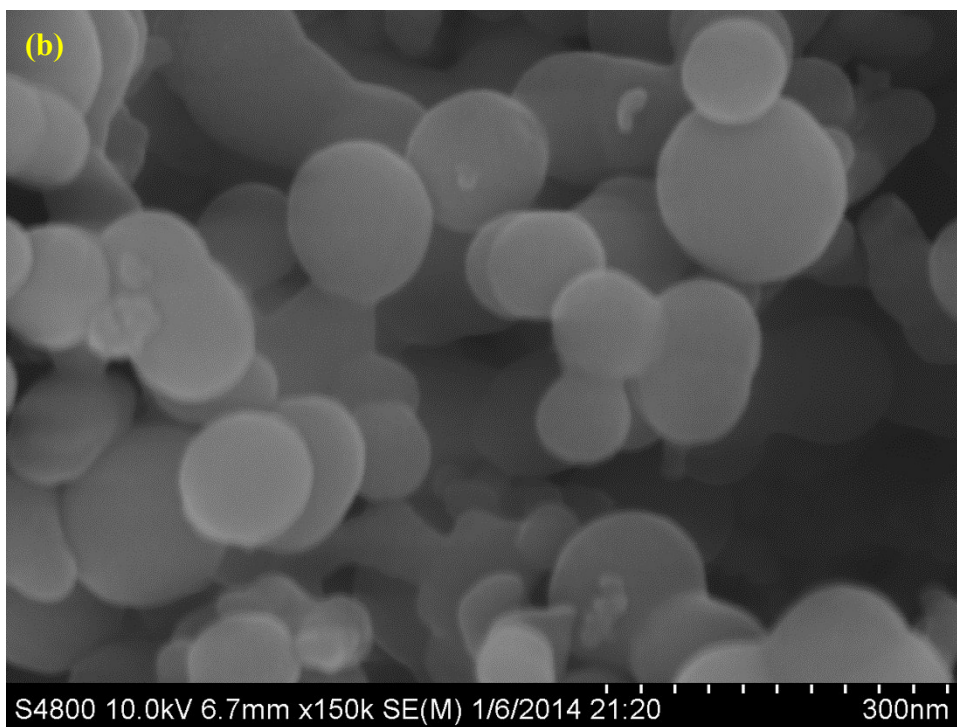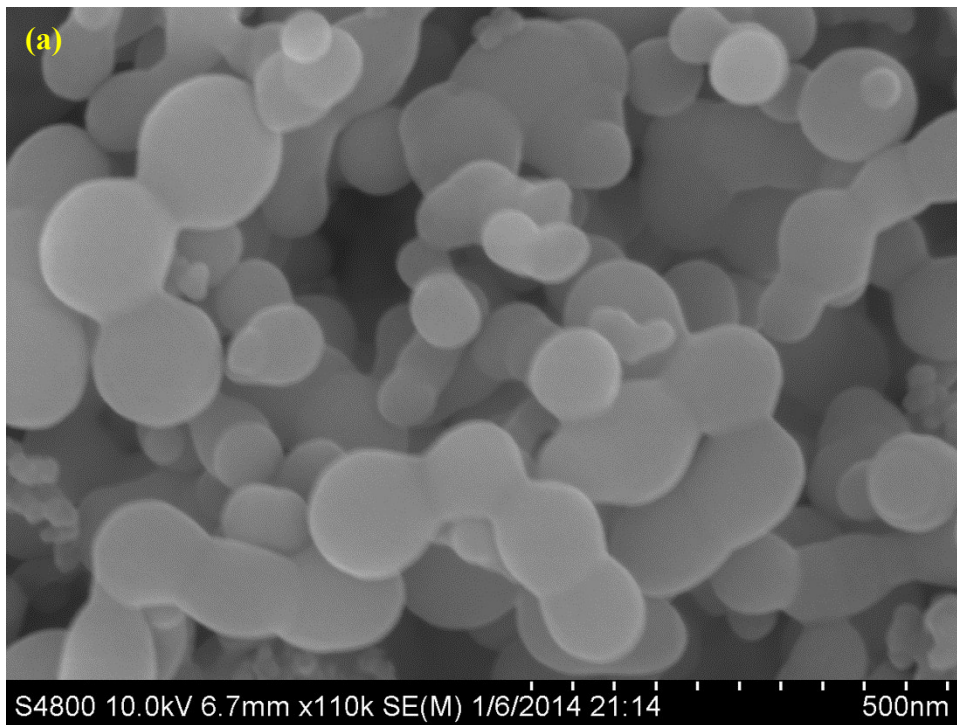S4800 10.0kV 6.7mm x150k SE(M) 1/6/2014 21:20   300nm

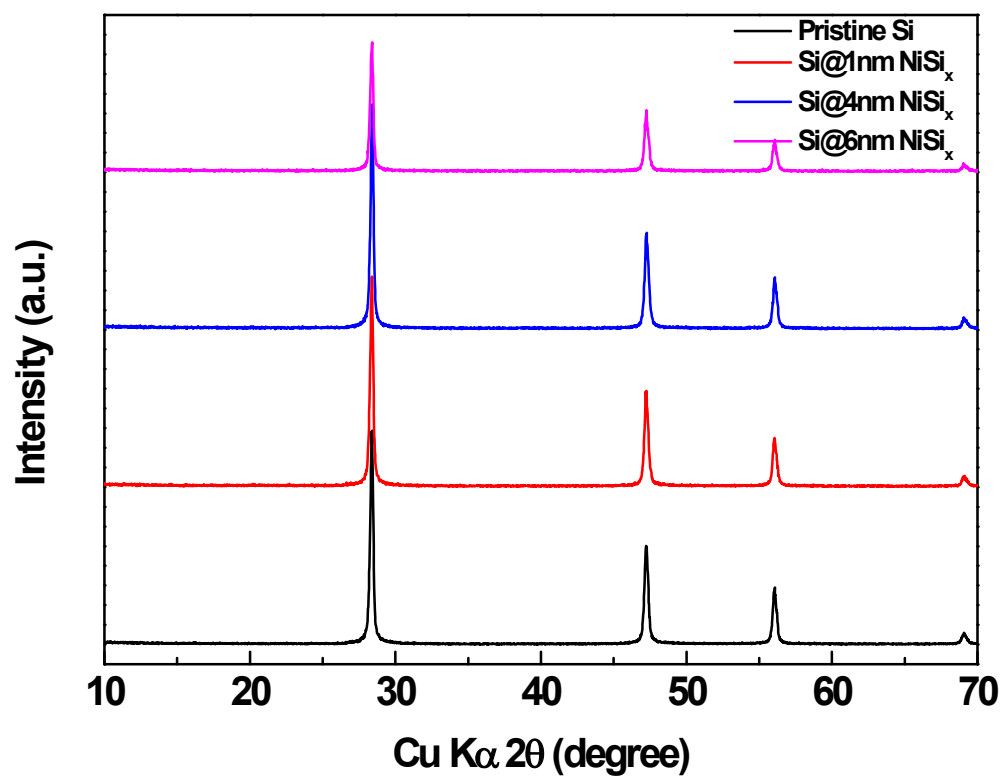Figure S1. SEM images of (a) pristine Si nanoparticles and (b) $NiSi_x$-coated Si nanoparticles.

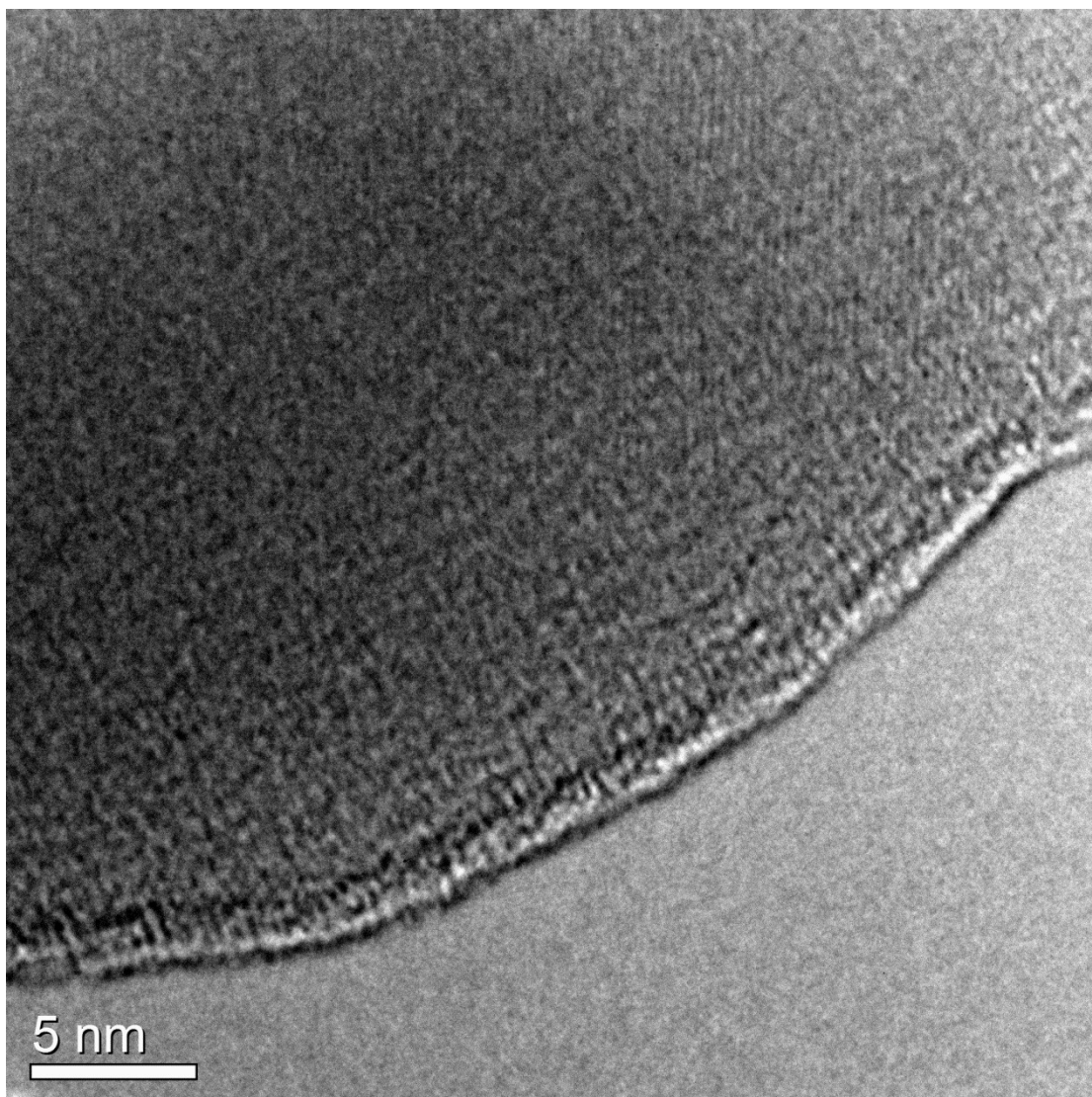Figure S2. XRD patterns of pristine Si and NiSi$_x$-coated Si with various coating thicknesses.

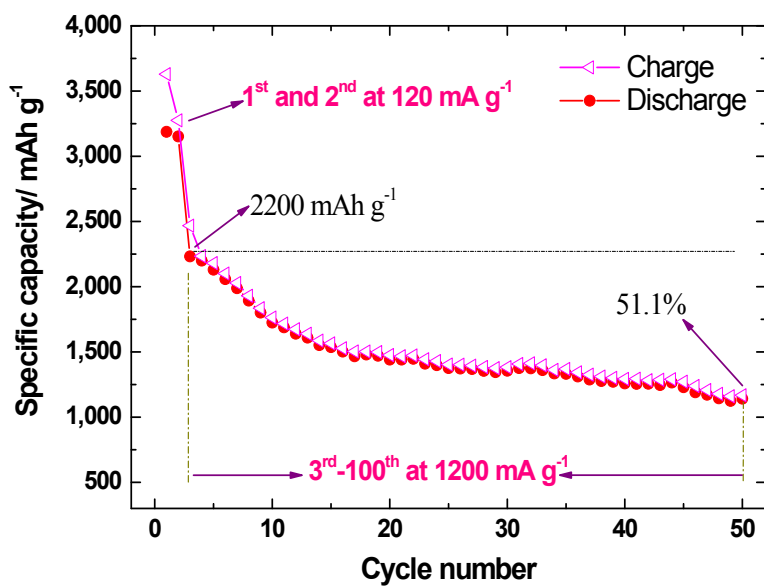Figure S3. TEM image of 6 nm NiSi$_x$-coated Si.

Figure S4. Cyclic performance of the Si@Ni that was prepared by coating 6 nm Ni on the Si surface but without the subsequent annealing. The Si@Ni delivered an initial capacity of 3187.6 mAh g^{-1} at 120 mA/g, and retained 1141.8 mAh g^{-1} at the 50th cycle. Compared with the Si@6 nm NiSi$_x$, the Si@6 nm Ni showed a higher initial capacity but a poorer cyclic performance (84.8% vs. 51.2%). Note that the Si@6 nm Ni delivered an initial capacity even higher than that of the pristine Si (2881.3 mAh g^{-1}), which is due to the improved electrical conductivity associated with the coated Ni surface.

S4800 10.0kV 10.1mm x3.50k SE(M) 9/5/2014 19:39   10.0um

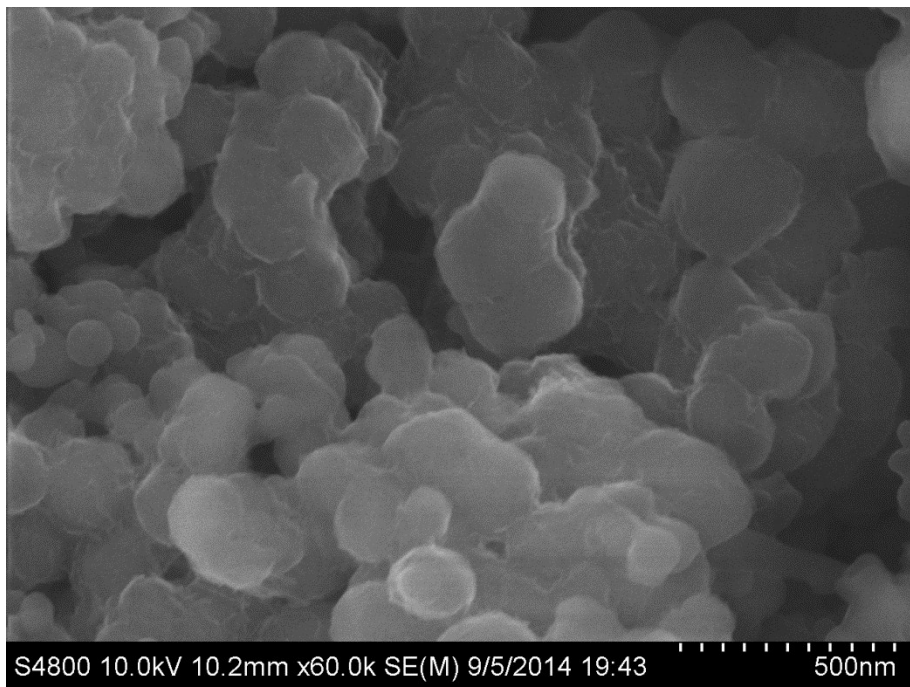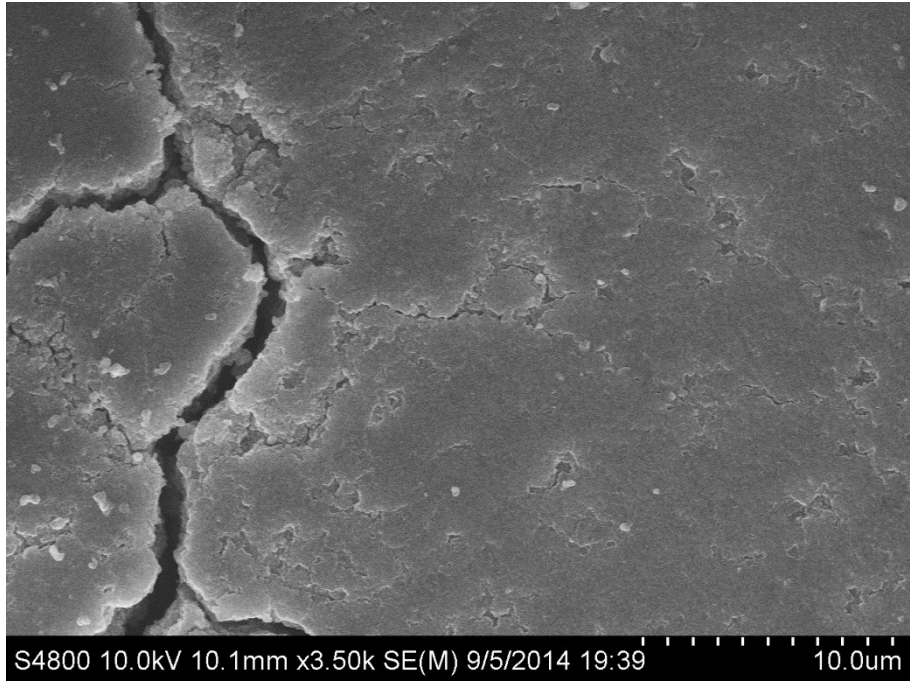S4800 10.0kV 10.2mm x60.0k SE(M) 9/5/2014 19:43   500nm

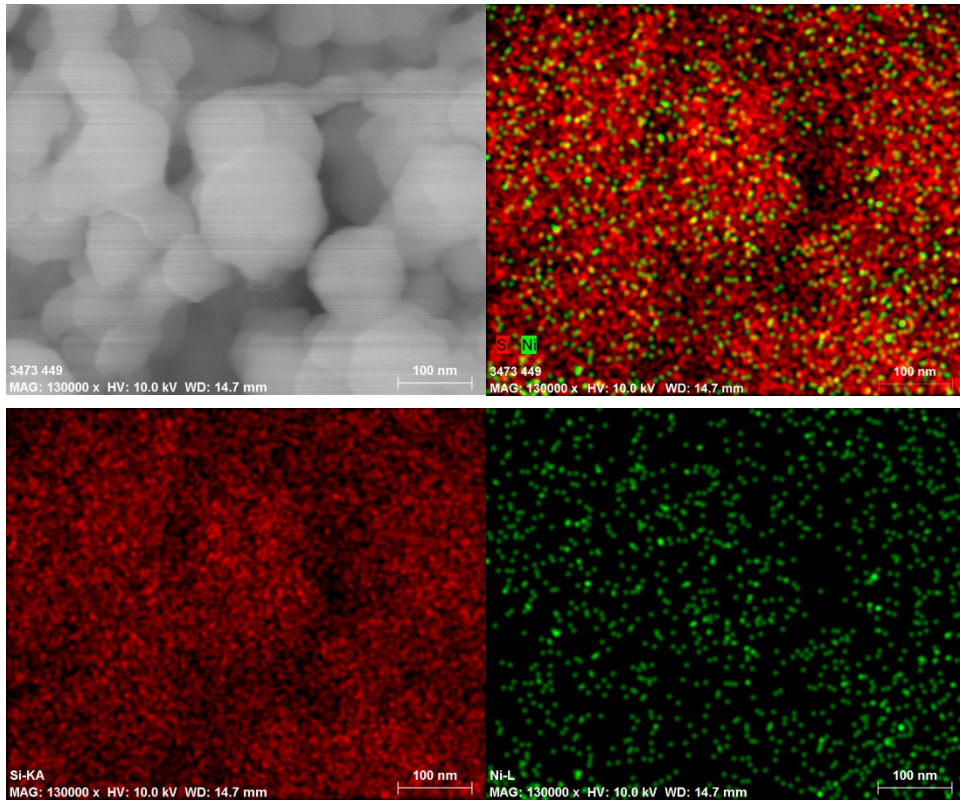Figure S5. SEM images of the Si@6nm NiSix electrode after 50 cycles.

Figure S6. SEM image and EDS mapping of the Si@6nm NiSix electrode after 50 cycles.
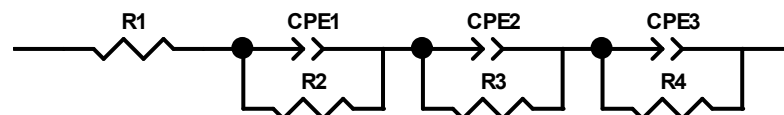
Figure S7. Equivalent circuit with three time constants.

Table S1 Fitting results of sample Si@6nm NiSi$_x$ at various charge states.

SOC	R1	CPE1-T×10^{-5}	CPE1-P	R2	CPE2-T×10^{-5}	CPE2-P	R3	CPE3-T×10^{-3}	CPE3-P	R4
4h[a]	3.02(1.0)[b]	4.5(3.7)	0.73(0.6)	39.8(4.8)	3.67(3.6)	0.86(1.1)	153.5(2.3)	2.69 (2.2)	0.72 (2.2)	139.8(2.6)
6h[a]	2.98(1.1)	5.0(3.9)	0.72(0.6)	40.2(5.5)	3.77(3.7)	0.86(1.1)	140.7(2.5)	3.32 (2.4)	0.74(2.4)	110.5(2.8)
Full	3.00(1.6)	7.1(5.0)	0.68(0.8)	52.4(10.2)	4.41(4.9)	0.85(1.9)	138.9(4.8)	3.65 (3.6)	0.84(3.0)	88.4(3.7)

[a] The anode was charged at a current density of 240 mA g^{-1}.

[b] The values in the brackets are the relative errors (percentages) of the corresponding fitting results.