Electronic Supplementary Information

Room temperature solvent-free reduction of $SiCl_4$ to nano-Si for high-performance Li-ion batteries

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Experimental Section

Preparation of nano-Si

All reagents are used without further purification. $SiCl_4$ is purchased from Energy Chemical Co. Na metal was purchased from Sinopharm Chemical Reagent Co. Ltd. In a typical procedure, stoichiometric $SiCl_4$ liquid (3.6 g), Na metal (1.95 g) and steel beads are loaded in stainless steel vessel. Ball-to-powder mass ratio is 10:1. Then, the mixture is milled in a vibratory miller (QM-3B, 180 W, Nanjing Nanda Instruments) for 1 h under pure argon atmosphere. After milling, dry brownish powder is obtained and simply washed with deionized water to remove NaCl. The obtained sample is immersed in 5 wt% hydrofluoric acid solution for 5 min and washed by two times using ethanol. Finally, the product is dried in vacuum at 60 ºC for 3 h.

Characterization

The samples are characterized by X-ray diffraction (XRD, PANalytical X'Pert3 Powder, Cu Kα), Raman spectroscopy (Jobin Yvon LabRam ARAMIS), scanning electron microscopy (SEM, Hitachi S4800), transmission electron microscopy (TEM, Tecnai F20 and HRTEM, Tecnai F20) and X-ray photoelectron spectroscopy (XPS, AXIS-Ultra spectrometer, Kratos Analytical).

Electrochemistry measurements

To prepare the working electrode, a slurry containing nano-Si, acetylene black and carboxymethyl cellulose (M_w=90,000) in mass ratio of 60:20:20 thoroughly mixed in water is pasted onto a Cu foil and dried in vacuum at 60 °C for 3 h. Coin type half-cells are assembled in an argon-filled glove-box, using a lithium foil counter electrode, 1 M $LiPF_6$ in ethylene carbonate/dimethyl carbonate = 1/1 in volume with 5 wt% fluoroethylene carbonate (FEC) as the electrolyte and polypropylene film (Celgard 2400) as the separator. The cells are tested in the voltage range of 0.005 – 1.5 V (versus Li/Li^+) at ambient temperature. Cyclic voltammetry is carried out at a scan rate of 0.2 $mV \cdot s^{-1}$. The specific capacities reported are on the mass of Si.

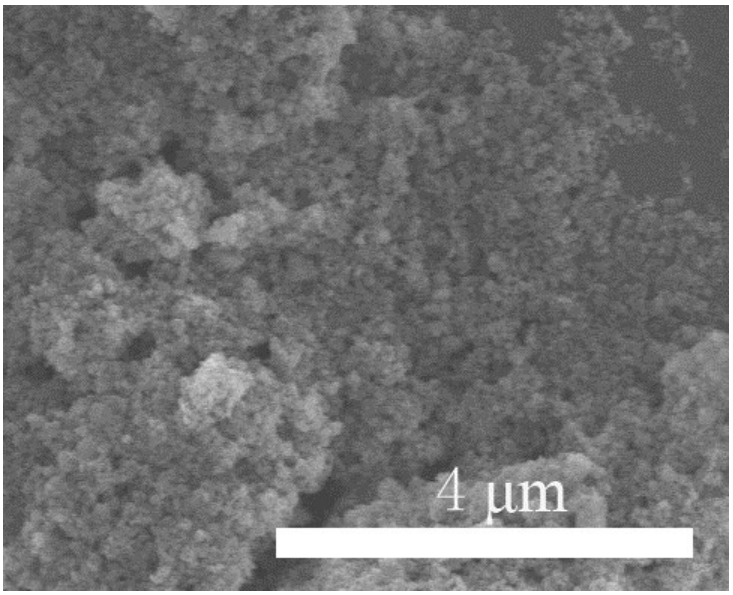

Figure S1. A low magnification SEM image of the obtained nano-Si, show absence of large particles in a large scope

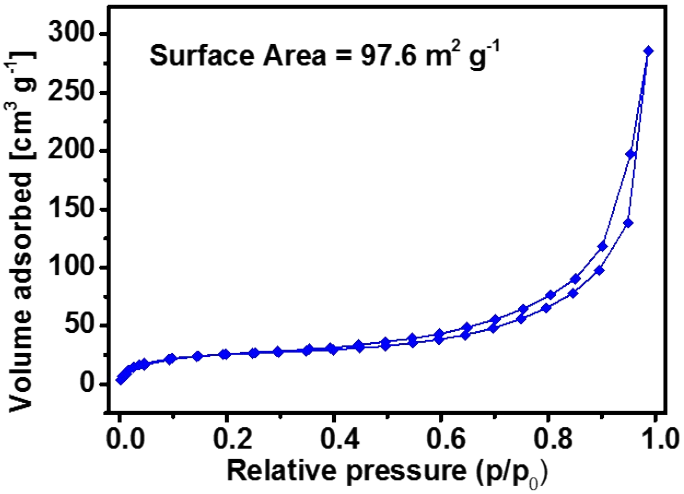

Figure S2. The N_2 sorption isotherm of the obtained nano-Si

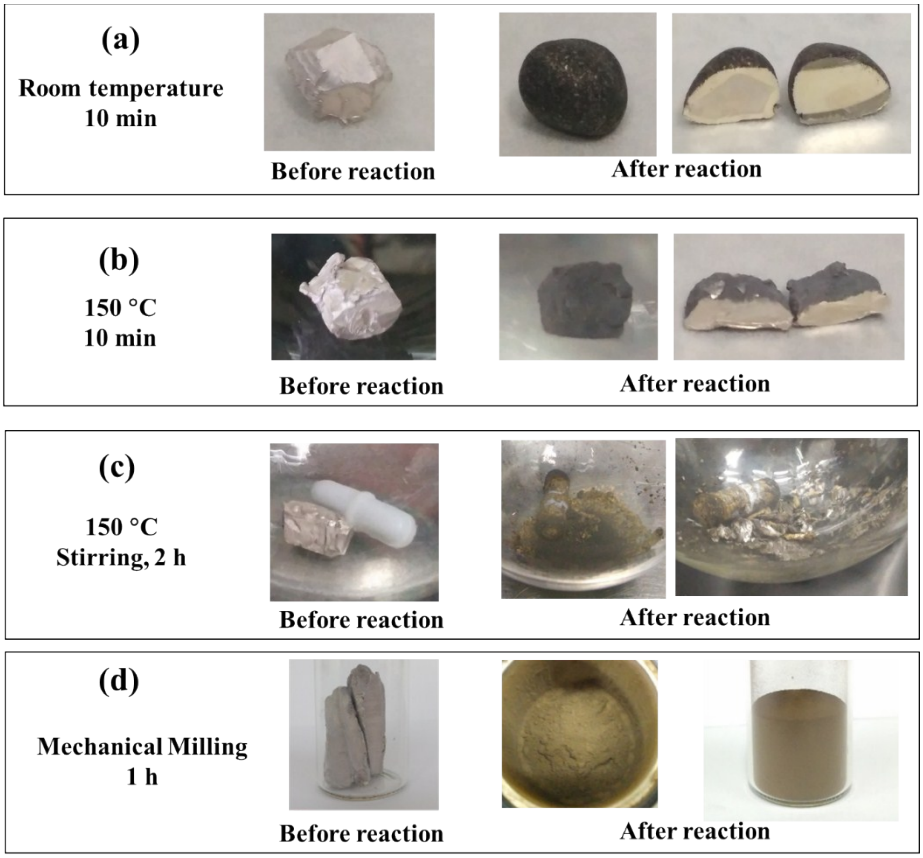

Figure S3. Photographs showing the result of four typical reaction conditions. (a) Direct reaction at room temperature, (b) Direct reaction at 150 °C, (c) Stirring at 150 °C and (d) Mechanical milling for 1 h.

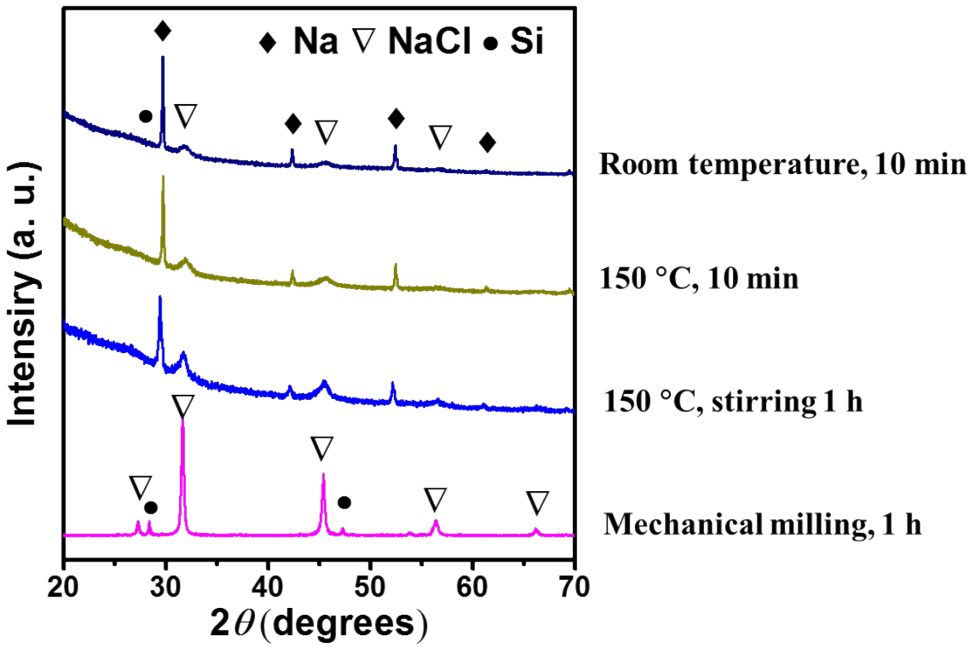

Figure S4. XRD patterns of the products obtained in four typical reaction conditions. Only mechanical milling results in complete conversion of Na metal.

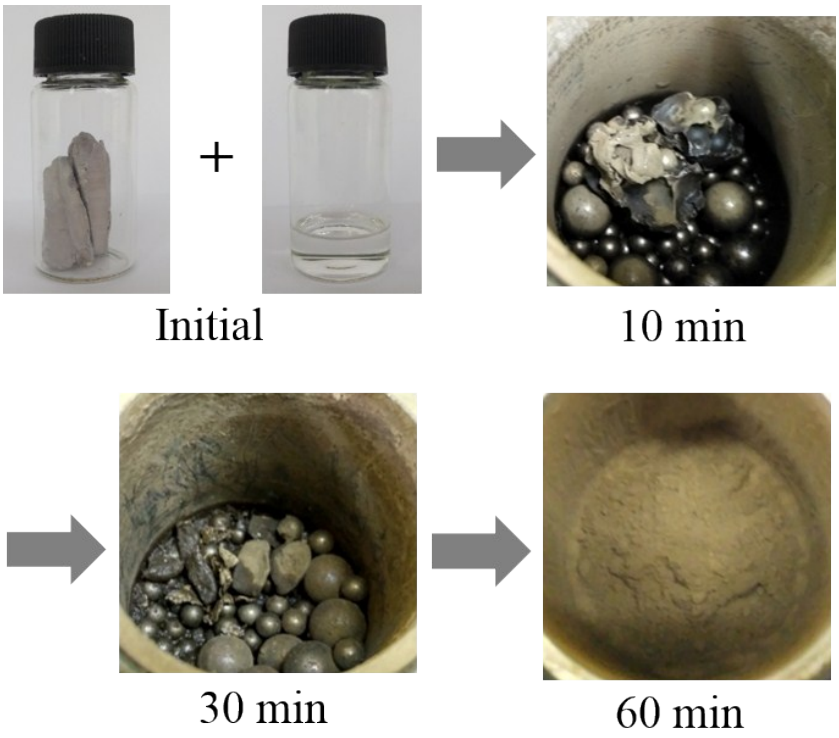

Figure S5. Photographs showing the reaction at different stages during the mechanical milling process.

Table S1. $SiCl_4$ reduction by solution based methods reported in literature

Solvent	Reducing agent	Reaction condition	Ref
THF	Naphthalene sodium	380 ºC, high pressure, $(CH_3)_3$(dodecyl)NBr, Ar, 24 h	1
Glyme	Naphthalene sodium	Ar, 24 h	2
THF	Sodium cyclopentadienide	Ar, 7 h	3
THF	Crown ether potassium	Ar, 20 h	4
Toluene	Liquid NaK alloy	Reflex, Ar, 4 h	5
Toluene	Na dispersion liquid	385 ºC, >100atm, Ar, 72-168 h	6
Glyme	KSi	Reflex, N_2, 48-96 h	7
Glyme	NaSi	Reflex, Ar, 24 h	8
Toluene and THF	$LiAlH_4$	Sonication, $(Octyl)_4NBr$, Ar, 3 h	9

Table S2. Performance comparison bewteen our pristine nano-Si anode with the state of the art pristine Si based anodes

Anode materials	Size (nm)	Current density ($A \cdot g^{-1}$)	Cycles	Gravimetric capacity ($mAh\ g^{-1}$)	Volumetric capacity ($mAh\ cm^{-3}$)	Ref
Si nanoparticles	35	4.2	100	1700	850	10
Si nanoparticles	50	3.0	1000	900	Not reported	11
Si nanoparticles	10	0.9	40	2900	Not reported	1
Si nanotube	40	0.84	900	1300	1460	12
Si nanowire	70	2.1	200	1706	1023	13
Si nanowires	100	0.14	100	676	1014	14
Si hollow sphere	80	2.0	100	1318	Not reported	15
Porous Si	50	3.6	500	1100	Not reported	16
Porous Si	60	0.2	300	952	Not reported	17
Si nanoparticles	25	2.1	100/500	1950/1600	1560/1280	Our work

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