

Supplementary Information

Aluminothermic Reduction Enabled Synthesis of Silicon Hollow Microspheres from Commercialized Silica Nanoparticles for Superior Lithium Storage

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S1. Experimental Details

S1.1 Synthesis of Silicon Hollow Microspheres

Silicon hollow microspheres were synthesized by a solvothermal reaction. In a typical experiment, 1 g of silica, 2 g of aluminum powder (1–3 μm) and 16 g of AlCl_3 were mixed and loaded in a stainless steel autoclave. After three degassing cycles, the autoclave was filled with nitrogen. Next, the autoclave was heated at 270 $^\circ\text{C}$ for 10 h in an electric oven. After being cooled to ambient temperature, the final product, *i.e.*, silicon hollow microspheres, was collected and washed with HCl, deionized water and absolute ethanol several times. The obtained sample was then washed with HF for 10 min to remove the residual silica, and vacuum-dried at 60 $^\circ\text{C}$ overnight.

S1.2 Electrochemical Testing

A slurry was prepared by mixing silicon hollow microspheres, super P and sodium alginate at a weight ratio of 6 : 2 : 2 in deionized water, which was then coated on copper foil. After being dried in vacuum at 80 $^\circ\text{C}$ for 6 h, the working electrode was cut into a $\sim 1.3 \text{ cm}^2$ circular sheet. A CR2032 coin-type cell was assembled in an argon-filled glove box (H_2O , $\text{O}_2 < 1 \text{ ppm}$) by using Celgard 2400 polypropylene as the separator, metallic lithium as the counter/reference electrode, and 1 M solution of LiPF_6 in ethylene carbonate/diethyl carbonate (volume ratio = 1 : 1) as the electrolyte. The galvanostatic measurement was conducted on a battery tester LAND-CT2001A within a voltage range of 0.01–1.5 V at ambient temperature. The active material mass loading was 0.5–1 mg cm^{-2} for the working electrode. The CV measurement was conducted in a CHI600E electrochemical workstation within a voltage range of 0.01–1.5 V at a scanning rate of 0.1 mV s^{-1} .

S1.3 Characterizations

TEM was performed by a HITACHI HT7700 microscope operated at an accelerating voltage of 100 kV.

HRTEM was performed by a JEOL JEM-2010 microscope operated at an accelerating voltage of 120 kV. SEM was performed by a TESCAN VEGA3 microscope operated at an accelerating voltage of 20 kV. XRD was performed by a D8 Advanced X-ray diffractometer with Cu K α radiation ($\lambda = 0.154$ nm). XPS was performed by an ESCALAB 250XI spectrometer. Raman was performed by a HORIBA Jobin Yvon LabRAM HR Evolution spectrometer with 532 nm incident laser.

S2. Supplementary Figures

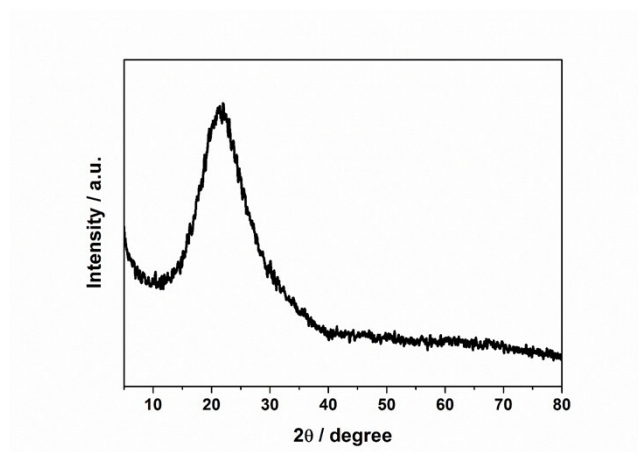


Fig. S1 – XRD pattern of silica nanoparticles showing a broad peak centered at $2\theta = \sim 22.0^\circ$ characteristic of amorphous silica (JCPDS card No. 29–0085).

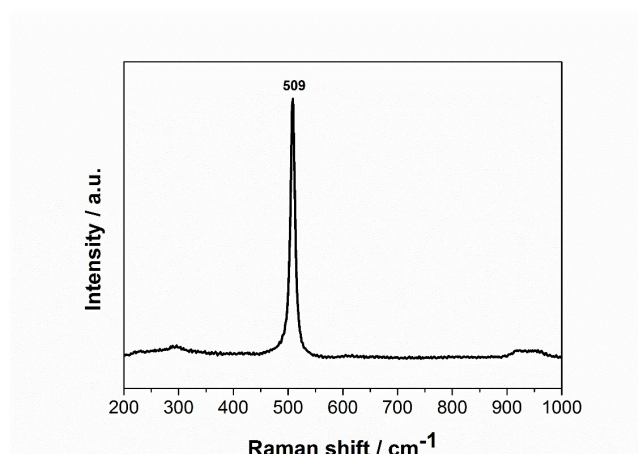


Fig. S2 – Raman spectrum of silicon hollow microspheres showing a sharp peak residing at 509 cm^{-1} is attributed to the first-order optical phonons of crystalline silicon (*Adv. Funct. Mater.*, 2007, **17**, 1765), which shifts from 520 cm^{-1} for bulk silicon to a lower frequency indicating the silicon hollow microspheres are composed of numerous nanocrystals (*Phys. Rev. B*, 2000, **61**, 16827).

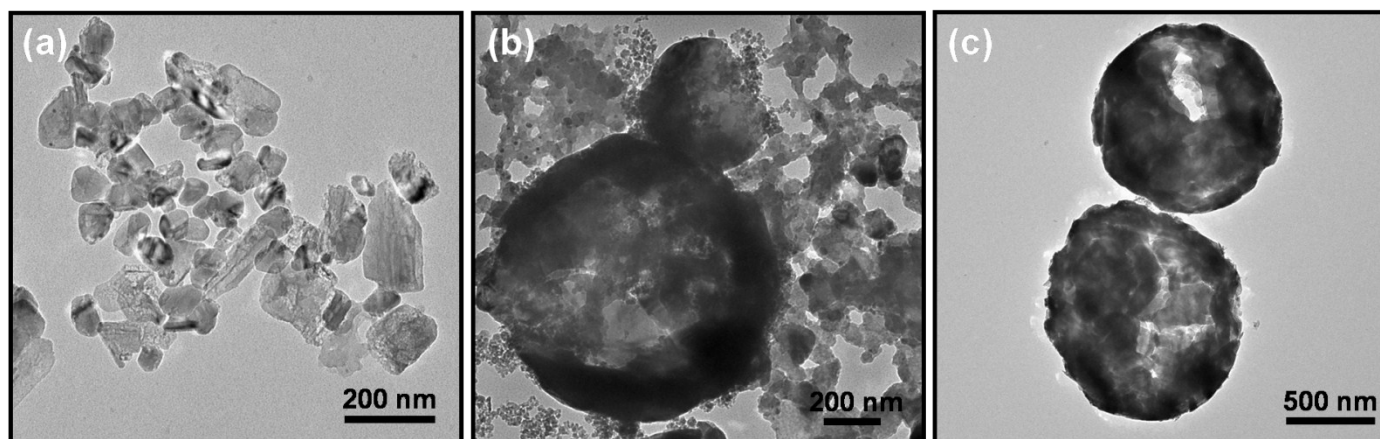


Fig. S3 – TEM images of silicon hollow microspheres obtained by aluminothermic reduction at different temperatures: (a) 230 °C, (b) 250 °C and (c) 270 °C.

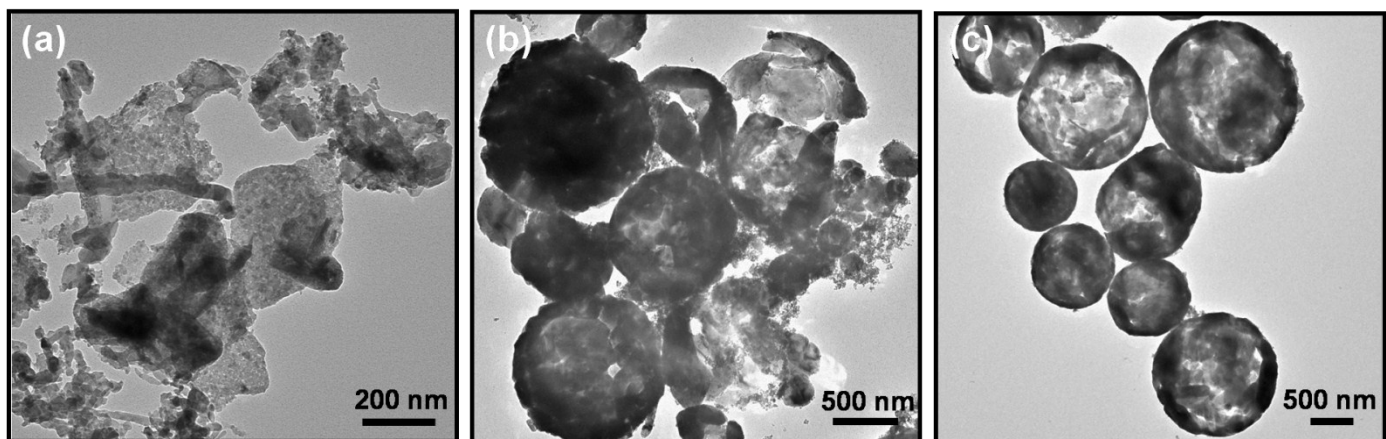


Fig. S4 – TEM images of silicon hollow microspheres obtained by aluminothermic reduction at different $\text{SiO}_2/\text{Al}/\text{AlCl}_3$ ratios: (a) 1 g/2 g/4 g, (b) 1 g/2 g/8 g and (c) 1 g/2 g/16 g.

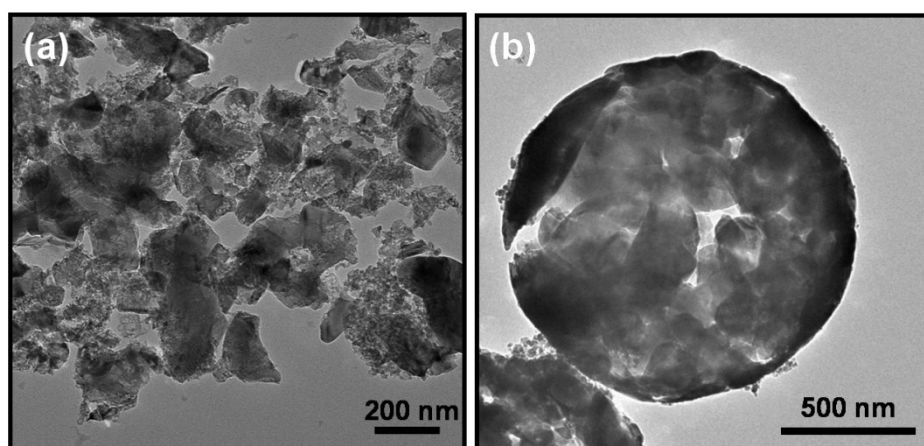


Fig. S5 – TEM images of silicon hollow microspheres obtained by aluminothermic reduction at different aluminum powder sizes: (a) 44–145 μm and (b) 1–3 μm .

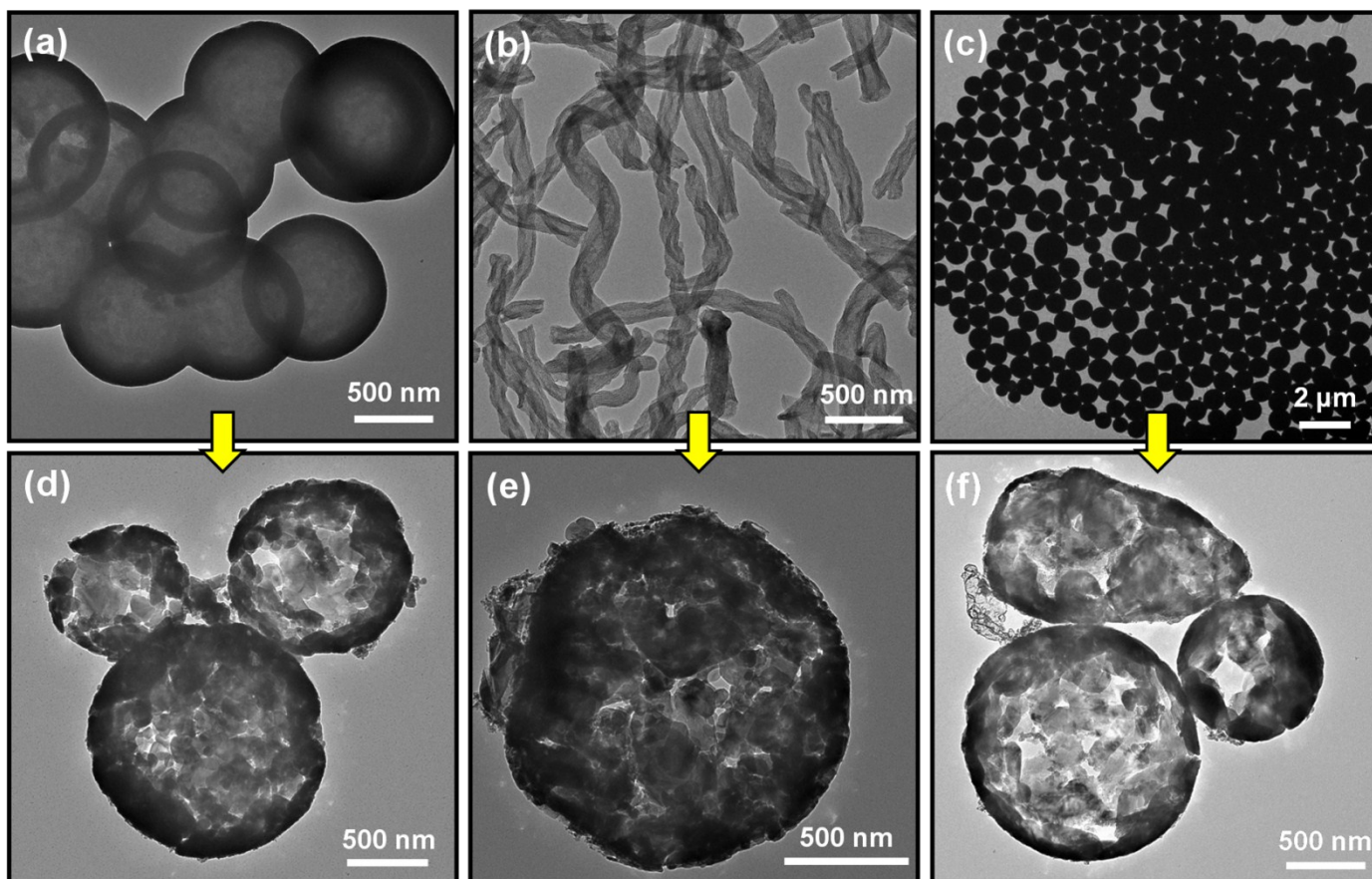


Fig. S6 – TEM images of silicon hollow microspheres obtained by aluminothermic reduction from different silica sources: (a) silica hollow microspheres, (b) silica nanotubes and (c) silica nanospheres.

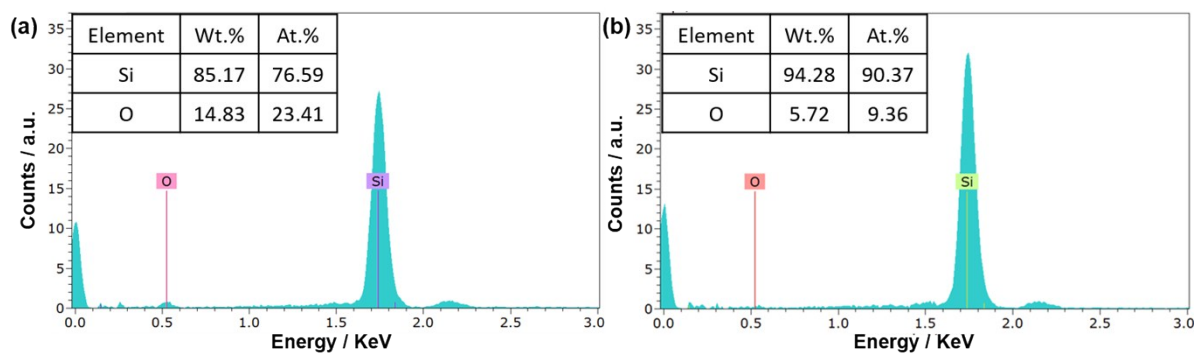


Fig. S7 – SEM EDS spectra of silicon hollow microspheres (a) before and (b) after HF washing. As seen from this figure, the Si/O mass ratio of the as-synthesized silicon hollow microspheres (without HF washing) is roughly 85 : 15. After HF washing, this value is increased to 94 : 6, which means a substantial fraction of pure silicon can be obtained by aluminothermic reduction combined with HF washing.

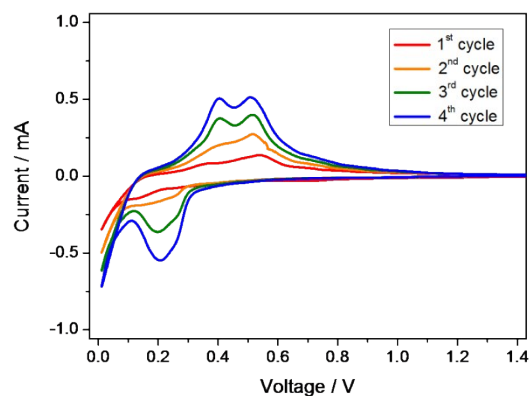


Fig. S8 – Representative CV curves of silicon hollow microspheres over a potential window of 0.01–1.5 V at a scan rate of 0.1 mV s^{-1} . The main cathodic peak in the range of 0.01–0.30 V is related to the formation of the Li_xSi phase (Li alloy). In contrast, the two overlaid peaks during the anodic scan at 0.42 and 0.52 V correspond to the phase transition from $\alpha\text{-Li}_x\text{Si}$ to $\alpha\text{-Si}$ (Li de-alloying).

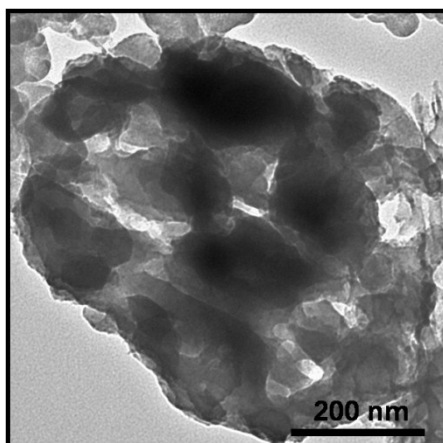


Fig. S9 – TEM image of silicon hollow microspheres after the cycling test at 0.5 A g^{-1} for 50 charging/discharging cycles.