Electronic Supporting Information for:

A magnesiothermic reaction process for the scalable production of mesoporous silicon for rechargeable lithium batteries

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Experimental details.

Preparation of porous Si from SiO

Mg powder (200 mesh or < 74 μm dia.) and SiO powder (6000 mesh or <2.5 μm dia.) were obtained from, Aladdin Reagent, China and CNPC Powder Material Co., China, respectively. After thorough mixing, the Mg/SiO reactants were heated at 2°C/min in a tube furnace to 300°C for 3 h and then at 2°C/min to 500°C for up to 12 h in a flowing Ar (95 vol%)/H_2 (5 vol%) gas mixture. The powder products were immersed in a 1 M HCl solution for 6 h, followed by immersion in a 5 wt% HF solution for 5 min. The powder products were then washed with distilled water and ethanol, and vacuum-dried at 80°C for 10 h.

Electrochemical tests

CR2016 cells were assembled to perform electrochemical experiments. The electrodes were composed of 60 wt% of active material, 20 wt% of Super P carbon black, and 20 wt% of sodium alginate as a binder. The electrolyte consisted of a solution of 1M $LiPF_6$ in a mixture of carbonate-containing vinylene carbonate (Novolyte Technologies, Inc., Suzhou, China). Pure Li foils were used as counter electrodes. The cells were charged and discharged galvanostatically in a fixed voltage window from 5 mV to 1.0 V on a LAND battery test system (Wuhan Kingnuo Electronics Co., Ltd., China) at 25°C. For comparison with the Si produced via magnesiothermic reduction of SiO, Si powder (6000 mesh or <2.5 μm dia.) was obtained from a commercial vendor (CNPC Powder Material Co., China).

Materials characterization

XRD patterns were obtained at room temperature with a Rigaku D/Max-RB diffractometer using Cu Kα radiation (40 kV, 40 mA). Secondary electron microscopy (SEM) images were obtained with a Philips XL30 FEG field emission scanning electron microscope operating at 10 keV. TEM analyses were conducted with a JEOL JEM-2010 instrument operating at 200 keV. Nitrogen sorption isotherms were collected at 77 K (Micrometrics ASAP 2020 analyzer) after vacuum degassing of the samples at 200°C for 3 h. Values of specific surface area were obtained using the Brunaur-Emmett-Teller (BET) method. The Barrett-Joyner-Halenda (BJH) method was applied to absorption branches of isotherms to obtain pore size distributions.

Supporting Figures

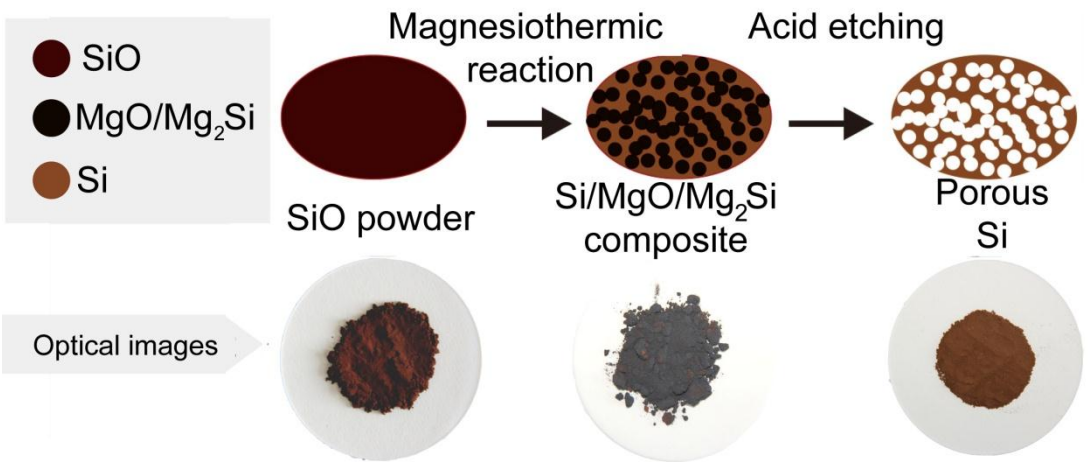

Figure S1. Schematic illustration of the formation of porous Si through magnesiothermic reaction of SiO (top row) and associated optical images of materials at each stage (bottom row).

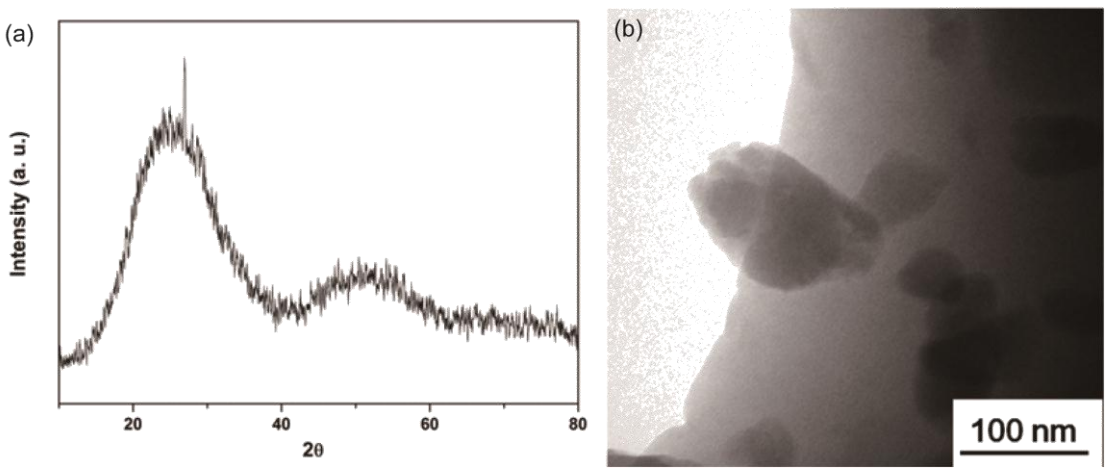

Figure S2. a, XRD pattern of SiO powder. **b,** TEM image of starting dense (nonporous) SiO powder.

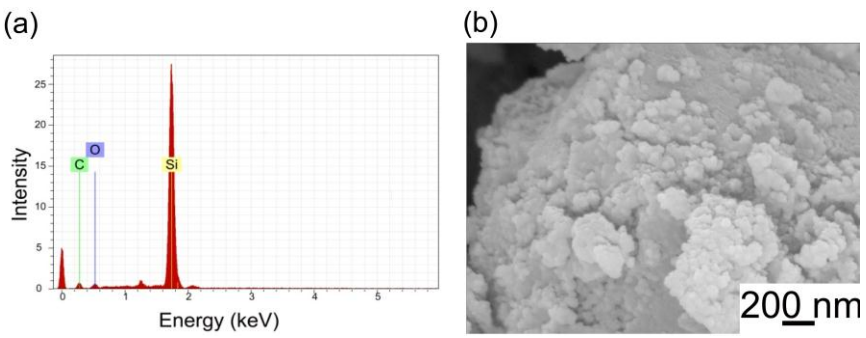

Figure S3. a and b, EDX analysis and SEM image of the silicon product prepared via reaction with Mg for 3 h at 300°C and then 12 h at 500°C, followed by acid dissolution of Mg-bearing product phases, respectively.

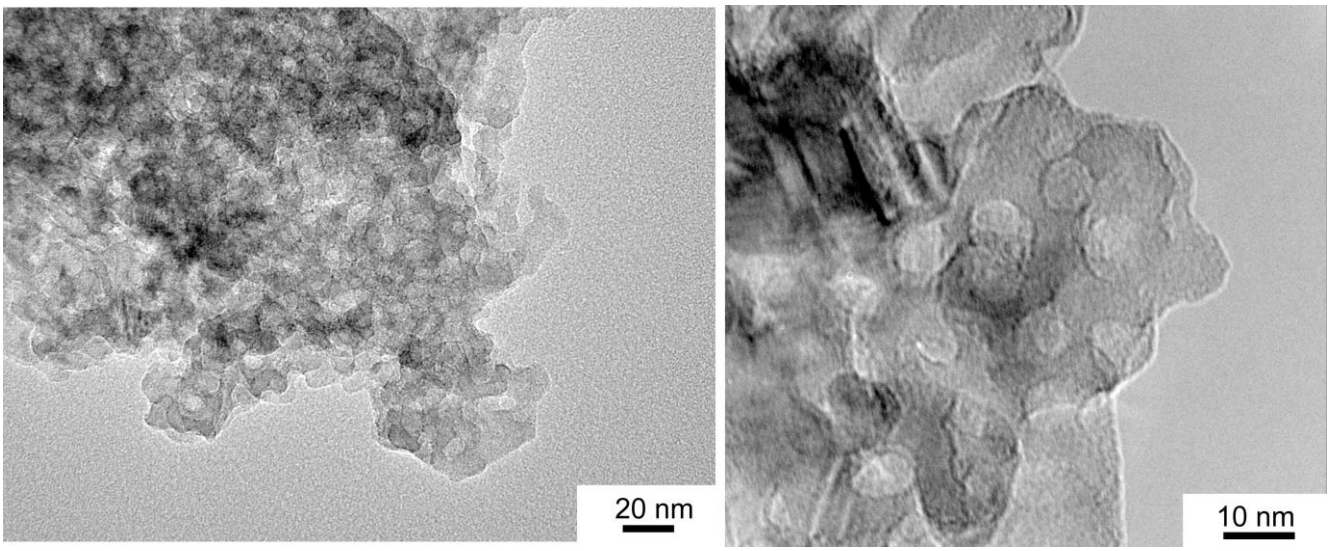

Figure S4. High resolution TEM images of silicon product, revealing its porous structure.

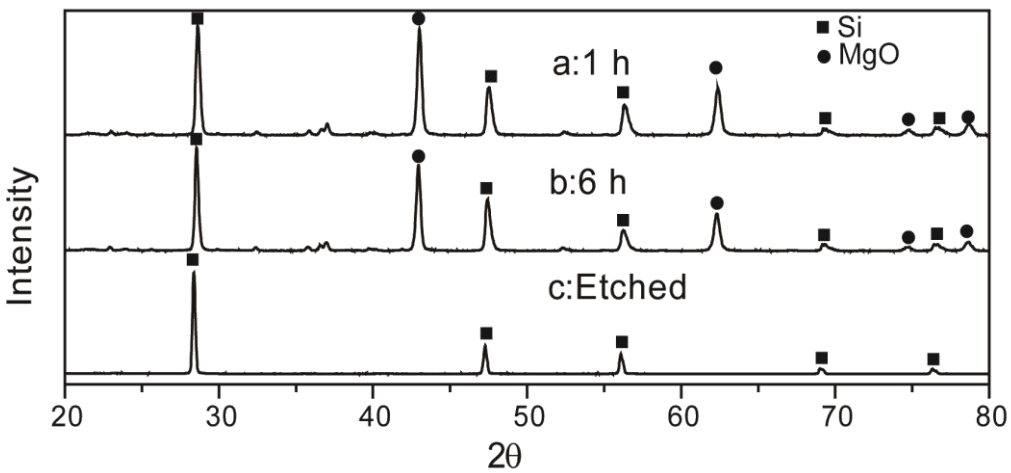

Figure S5. XRD patterns obtained from products generated by the reaction of SiO and Mg at 500°C **without the treatment at 300°C: a,** for 1 h and **b,** for 6 h. **c,** XRD pattern obtained from the product generated by etching of the sample in **b** with a HCl solution and then a HF solution.

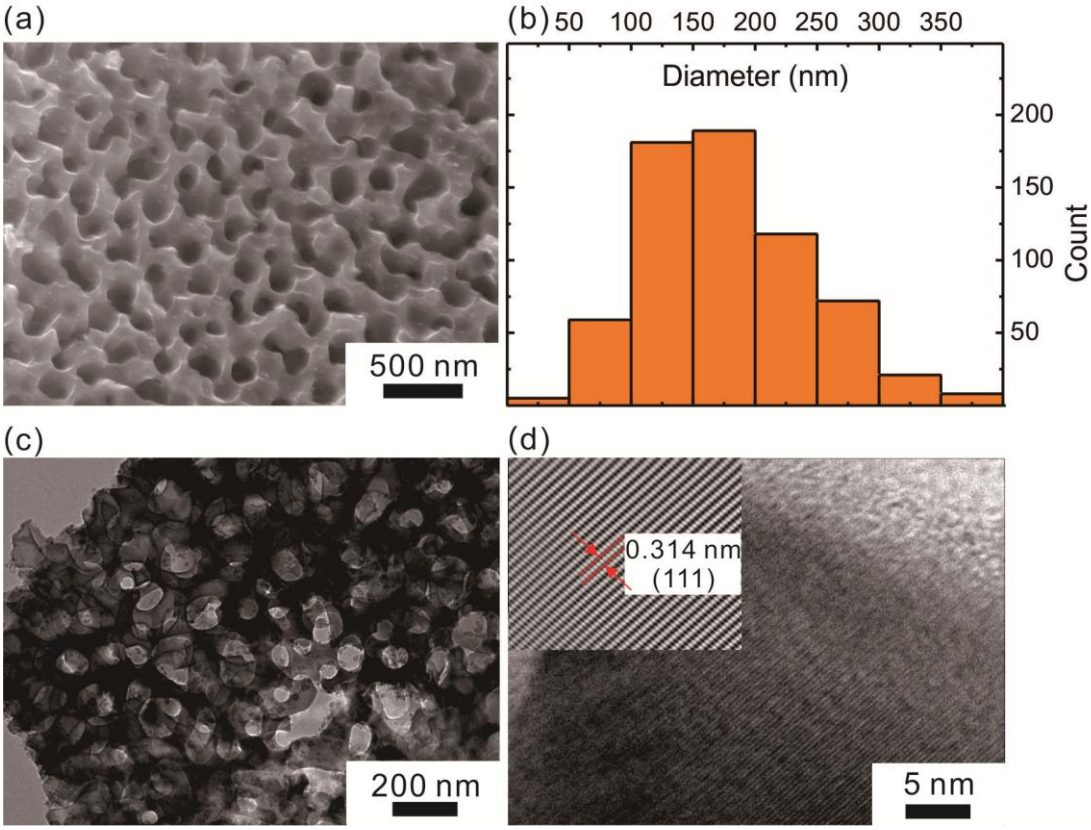

Figure S6. Characterization of the product **without the treatment at 300 °C: a,** SEM image of the product at high magnification. **b,** Pore size distribution obtained from SEM images of the product. **c, d,** Low and high magnification bright field TEM images of the silicon, respectively (the inset in **d** reveals part of the image in **d** after Fourier filtering)

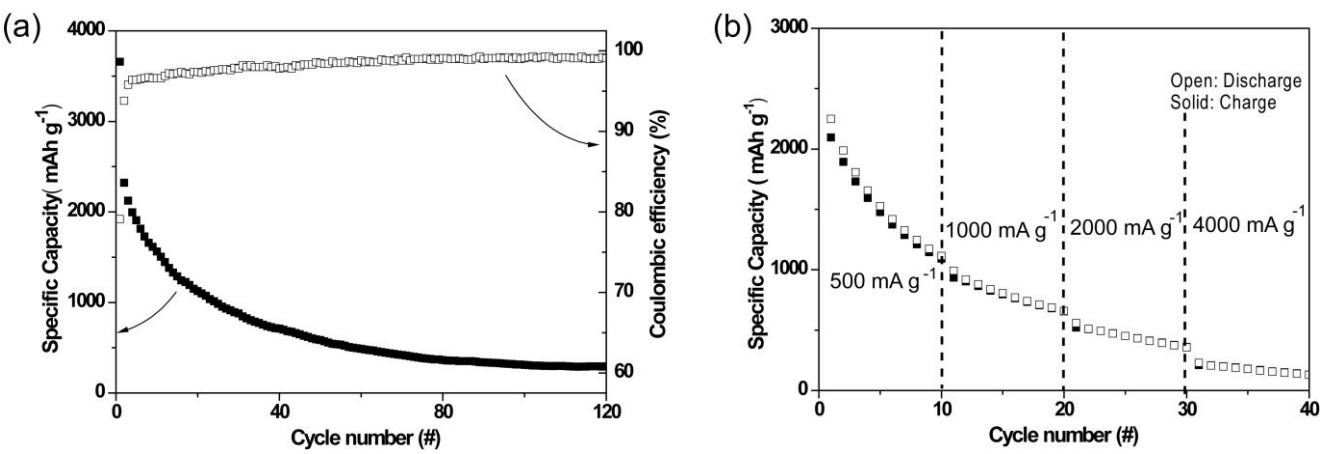

Figure S7. a, b, Cycling performance and rate performance of the product **without the treatment at 300°C,** respectively**.**

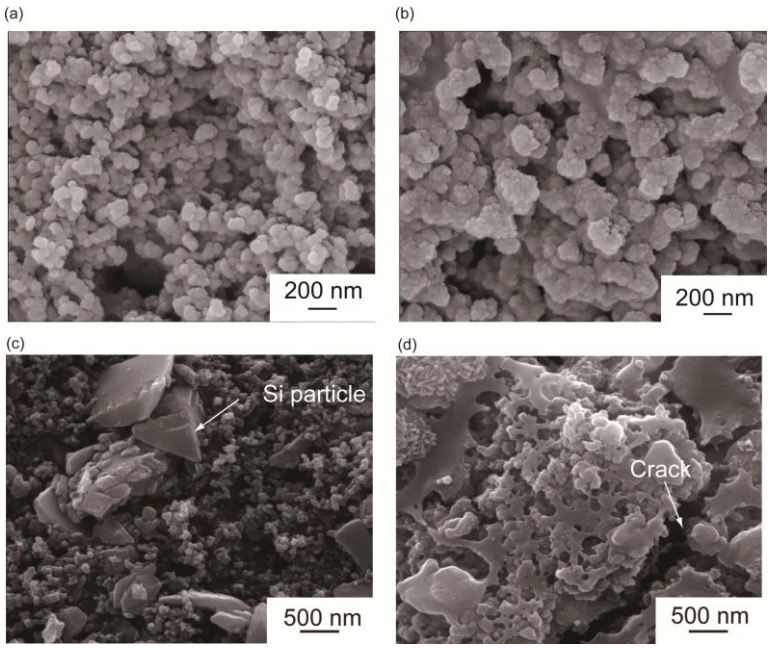

Figure S8. SEM images of porous nanocrystalline silicon-based electrodes **a,** before the cycling and **b,** after the cycling. SEM images of solid silicon-based electrodes **c,** before the cycling and **d,** after the cycling.