

Electronic Supplementary Information

Amorphous Silicon with High Specific Surface Area Prepared by a Sodiothermic Reduction Method for Supercapacitors

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1. Materials

Metallic sodium (A. R.), magnesium powder (A. R., 100-200 mesh), tetraethylorthosilicate (TEOS, A. R.), hydrochloric acid (A. R.), hydrofluoric acid (A. R.) and sulphuric acid (A. R.) were purchased from Sinopharm Chemical Reagent Co., Ltd. The Ar gas (> 99.999 %) was supplied by Shanghai Pujiang Gas Co. Deionized water was used in the experiments. NaY zeolite was prepared from a hydrothermal reaction system with a procedure described in the literature. (L. Li, X. S. Zhou, G. D. Li, X. L. Pan and J. S. Chen, *Angew. Chem. Int. Ed.*, 2009, **48**, 6678.)

2. Experimental Section

2.1 Sample Preparation

Preparation of porous silicon by sodiothermic reduction of NaY. Porous silicon was prepared by vapor chemical reaction of metallic sodium with zeolite NaY. In an argon-filled glove box, metal Na (0.3 g) and zeolite NaY (0.3 g) were mixed and transferred into a one-end-closed glass tube. After evacuated for two hours to remove the argon and water species adsorbed in NaY, the glass tube was sealed and heated in a vacuum at a temperature of 300 °C with a ramp rate of 5 °C min⁻¹. An aluminum foil was put closely to the internal wall of the glass tube before the reaction to prevent metallic Na from reacting with the glass tube (See Figure S1). After heating at 300 °C about 20 hours, the resulting silicon-based brown aggregate was washed respectively with absolute ethanol, 2.0 mol/L HCl, and 1.0 mol/L HF solutions to remove the inorganic byproducts and unreacted zeolite.

Magnesiothermic reduction of NaY. For comparison, porous silicon was also prepared by the magnesiothermic reduction of NaY. Zeolite NaY (0.3 g) and magnesium powder (0.3 g) were put in a Corundum boat, and then heated in a tube furnace at 650 °C for 7 h under a flowing Ar. The ramp rate was kept at 5 °C min⁻¹. Then the obtained brown powder was washed respectively with absolute ethanol, 2.0 mol/L HCl, and 1.0 mol/L HF solutions. It is found that a byproduct, MgAl₂SiO₆ gel was hard to remove. Finally, porous silicon with impurities of MgAl₂SiO₆ was obtained.

Preparation of SBA-15. SBA-15 materials were synthesized using Pluronic P123 (Aldrich, molecular weight of Mw = 5800 g/mol) as a structure-directing agent and tetraethylorthosilicate (TEOS) as a silicon source, following the procedure reported by Choi *et al.* (M. Choi; W. Heo; F.

Kleitz; R. Ryoo, *Chem. Commun.* 2003, 1340.) 4.0 g of Pluronic P123 was put into 150 mL of 1.6 mol/L HCl solution with stirring. After P123 was completely dissolved, 8.4 g of TEOS was added dropwise. The mixture was stirred at 35 °C for 24 h, followed by hydrothermal treatment at 100 °C for 24 h under static conditions. The solid product was recovered by filtration, drying, and finally calcination at 550 °C for 2 h.

Preparation of porous silicon by magnesiothermic reduction of SBA-15. Silica SBA-15 (0.3 g) and magnesium powder (0.3 g) were put in a Corundum boat, and then heated in a tube furnace at 650 °C for 7 h under a flowing Ar. The ramp rate was kept at 5 °C min⁻¹. The obtained brown powder was treated respectively in absolute ethanol, 2.0 mol/L HCl, and 1.0 mol/L HF solutions. Porous silicon was recovered after washed with distilled water for 4 times and the following vacuum-drying at 80 °C for 12 h.

Characterization. Energy dispersive X-ray spectroscopy (EDX) was performed on JEM-200CX II with an accelerating voltage of 20 kV. Transmission electron microscopy (TEM) images were obtained on a JEM-200CX transmission electron microscope. The powder X-ray diffraction was collected on a Rigaku D/Max 2550 X-ray diffractometer with a Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$). The FT-IR spectra were acquired on a Nicolet 6700 FT-IR spectrometer. The X-ray photoelectron spectroscopy (XPS) was performed on a KRATOS AXIS Ultra X-ray photoelectron spectrometer. Photoemission spectra were obtained with an Mg K α radiation (1253.6 eV) and the standard deviation for the binding energy (BE) values is 0.1 eV. The nitrogen adsorption/desorption measurements were performed on an ASAP 2020 Accelerated Surface Area and Porosimetry (Micromeritics Inc., USA).

Electrochemical Tests. The working electrodes were prepared according to the method reported in the literature. (J. W. Lang, L. B. Kong, M. Liu, Y. C. Luo, L. Kang, *J. Electrochem. Soc.* 2010, **157**, A1341-A1346.) Typically, the electrodes of porous silicon were fabricated by following steps: Porous silicon (60 wt %), acetylene blacks (35 wt %) and polytetrafluoroethylene (PTFE, 5 wt %) were well mixed and grounded in an agate mortar, and then pressed onto a titanium grid ($1.0 \times 10^7 \text{ Pa}$) that was served as a current collector. The cyclic voltammetry was performed in a three-electrode system in 1.0 mol/L H₂SO₄ solution on a CHI-660D electrochemical station. Saturated calomel electrode was used as the reference electrode and a titanium grid as the counter electrode. Galvanostatic charge–discharge

was performed in the voltage range of 0 – 0.8 V at room temperature on a LAND-CT2001A instrument.

The Capacitance Calculation. The capacitances C ($F\ g^{-1}$) based on the CVs were calculated by the following equation.

$$C = (\int IdV) / (vmV),$$

where I is the current density (A), V is the potential (V), $\int IdV$ is the area of the CV loop, v is the potential scan rate ($V\ s^{-1}$), and m is the effective mass of the active electrode materials (g).

The capacitances C ($F\ g^{-1}$) based on the discharge curves were calculated by the following equation.

$$C = I\Delta t / (m\Delta V),$$

where I is the discharge current (A), Δt are the discharge time (s), ΔV is the voltage change (V) in the discharge process, and m is the mass of the active electrode materials (g).

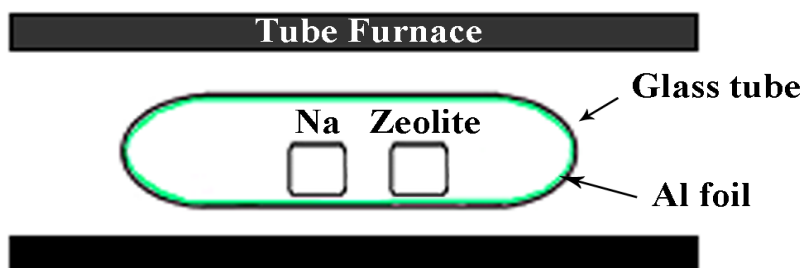


Figure S1. Schematic illustration of the container for the sodiothermic reduction of NaY.

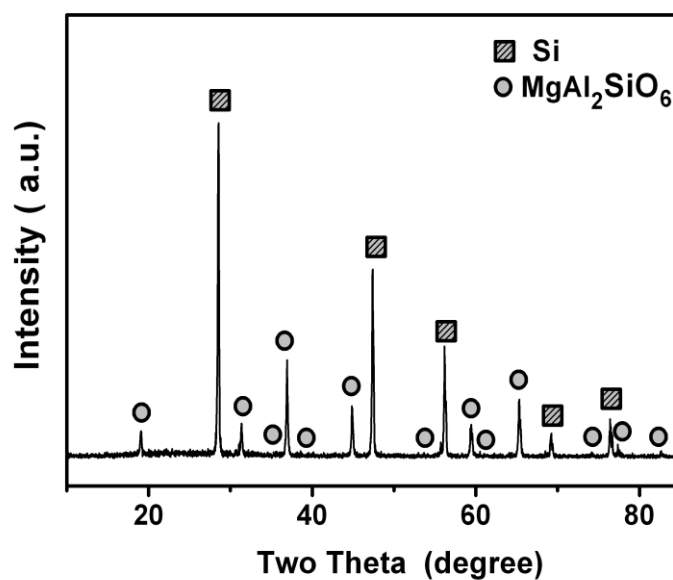


Figure S2. The XRD pattern of the sample prepared by the magnesiothermic reduction method by using zeolite NaY as a precursor.

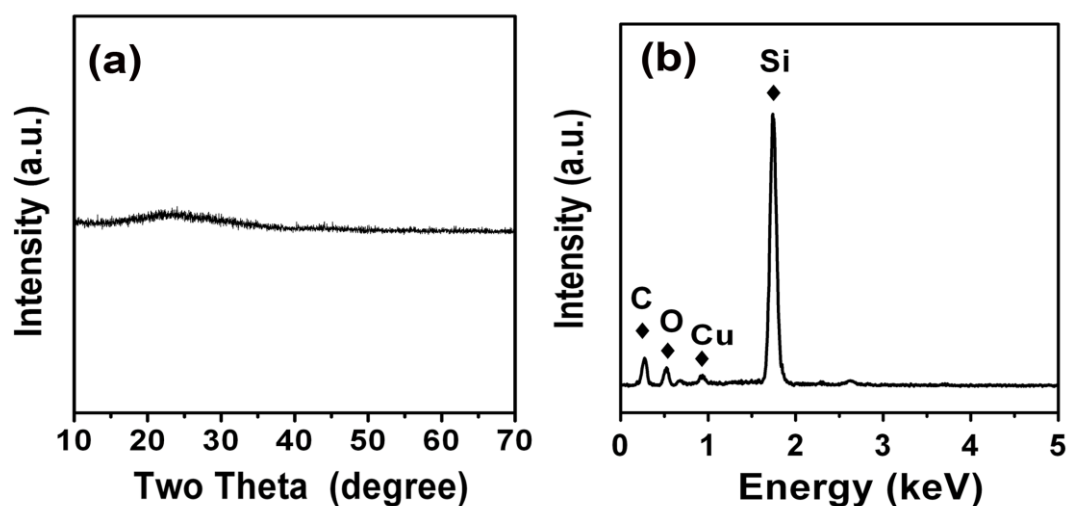


Figure S3. (a) XRD pattern and (b) EDX analysis of the sample prepared by the sodiothermic reduction method. XRD pattern indicates its amorphous nature. EDX indicates the amorphous sample mainly consists of silicon.

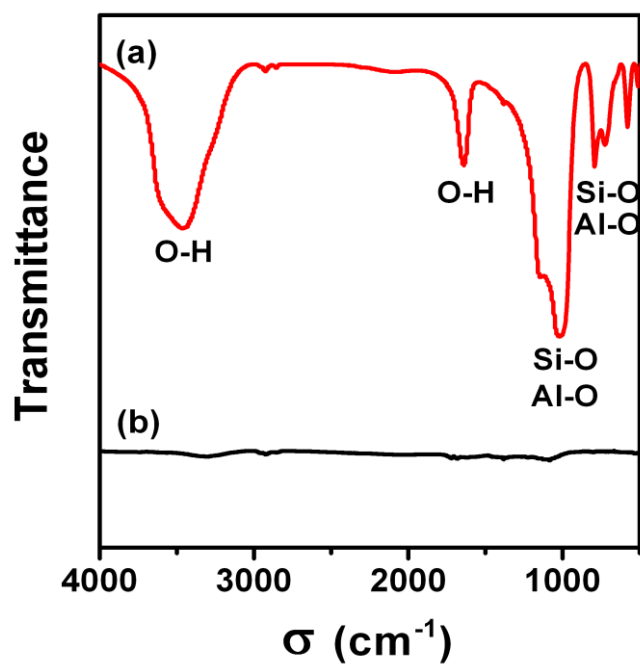


Figure S4. FT-IR spectra of (a) NaY zeolite precursor and (b) the obtained porous silicon prepared by the sodiothermic reduction method.

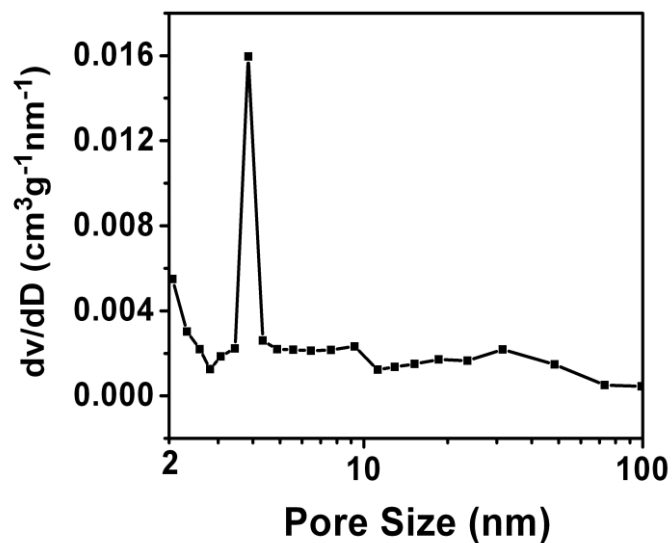


Figure S5. BJH pore size distribution curve for the porous silicon by sodiothermic reduction of NaY.

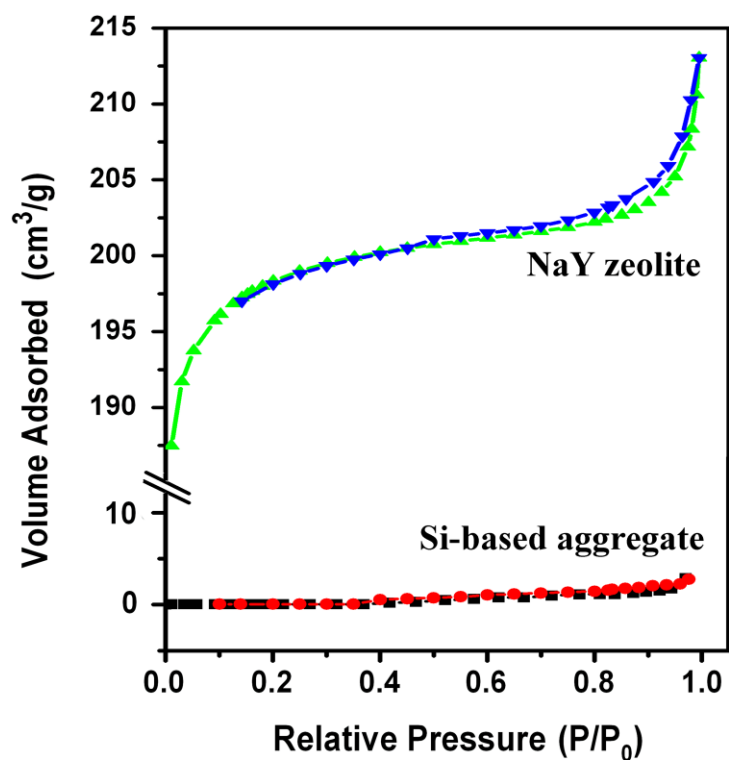


Figure S6. Nitrogen adsorption/desorption isotherms for the NaY precursor and its sodiothermic reduction product (silicon-based aggregate) without acid-washing treatment.

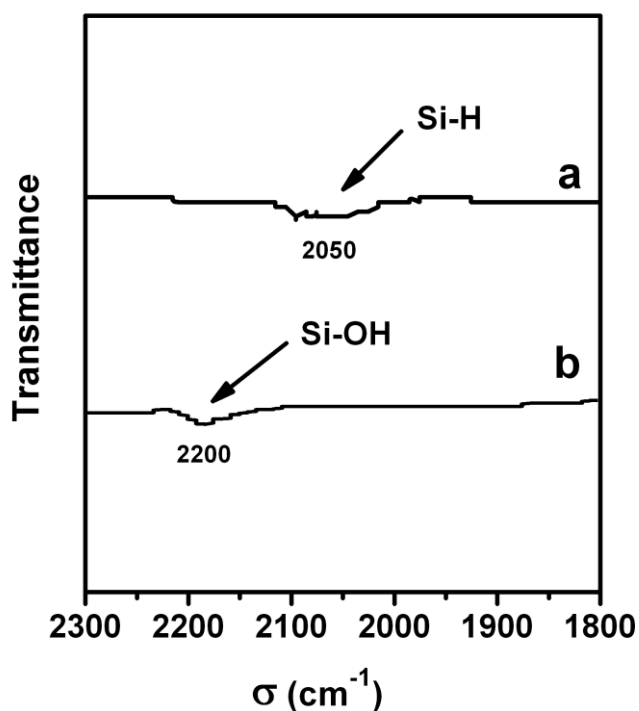


Figure S7. FT-IR spectra for the porous silicon prepared by the sodiothermic reduction method before (line a) and after (line b) exposed to air. The stretching vibrations of H-Si in the region of 2050 cm^{-1} are detected for the fresh porous silicon sample. But when the porous silicon material is left in air for 48 hours, the HO-Si stretching bands in the region of 2200 cm^{-1} are detected. These results demonstrate that H-Si groups can be oxidized easily to HO-Si groups in air. This means the existence of HO-Si groups in the surface of our porous silicon sample.

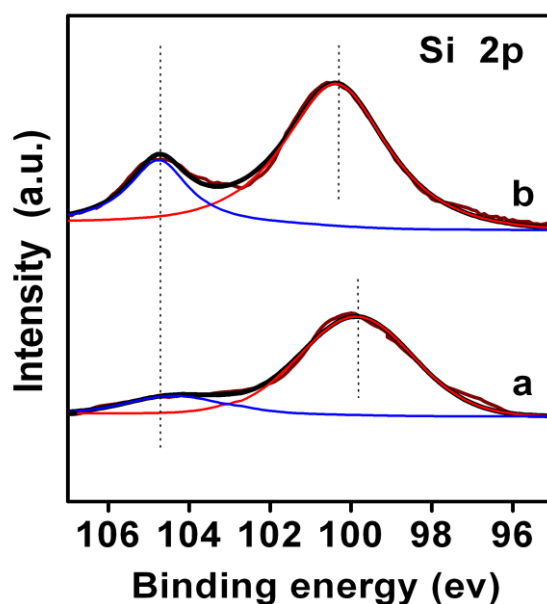


Figure S8. XPS spectra for the porous silicon prepared by the sodiothermic reduction method before (line a) and after (line b) exposed to air. After exposing porous silicon for 48 hours in air, the 2p peak of XPS spectra has shifts to higher energy position compared with that of the fresh porous silicon, while the peak intensity at the region of 104.6 eV, corresponding to the Si-O band increased. These results also demonstrate that the existence of Si-OH groups on the surface of porous silicon after exposed to air.

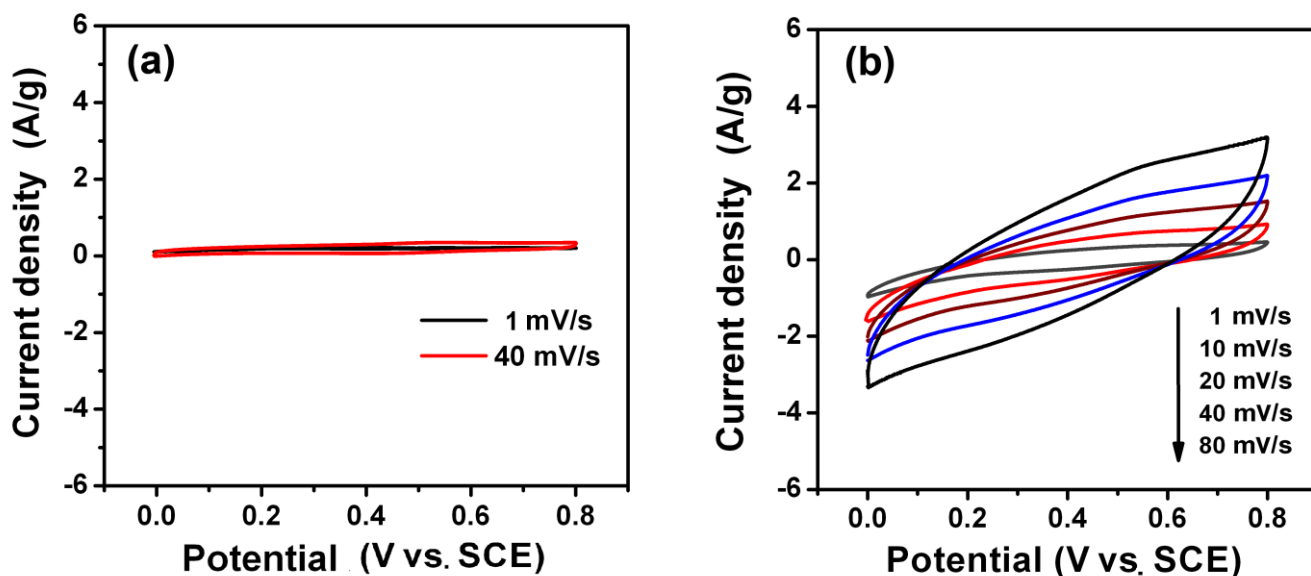


Figure S9. CV curves of (a) commercial silicon powder and (b) porous silicon by magnesiothermic reduction of SBA-15 in 1.0 mol/L H_2SO_4 solution at different scanning rates. At the scanning rate of 1 and 40 mV/s, the specific capacitances for (a) commercial silicon powder were calculated to be 15 and 5 F/g, respectively. At the scanning rate of 1, 10, 20, 40 and 80 mV/s, the specific capacitances for (b) porous silicon were calculated to be 102, 80, 65, 51, 40 F/g, respectively.

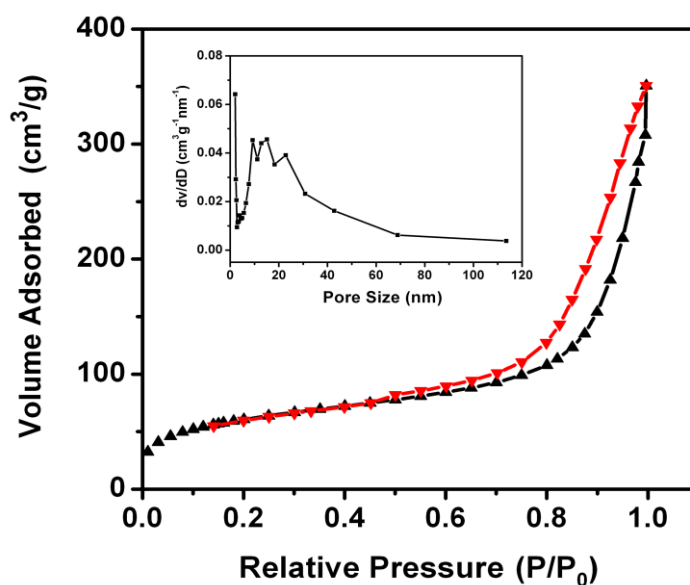


Figure S10. Nitrogen adsorption / desorption isotherm and the pore size distribution for the sample of porous silicon by magnesiothermic reduction of SBA-15. Inset shows the BJH pore distribution curve of corresponding porous silicon.