

## Supplementary Information

### Synthesis of materials

#### 1) Synthesis of porous silica from rice husk

The raw rice husk was purified by leaching with 10 wt% HCl aqueous solution for 8 h at 60°C. After leaching, rice husk was rinsed with de-ion water and dried at vacuum at 100°C. Then the rice husk was calcined in air at 700°C for 3 h to remove the organic component, and got white silica powder (*h*-Silica). As comparison, raw rice husk was just rinsed in the de-ion water, dried in vacuum and calcined in air to get the silica powder (*w*-Silica).

#### 2) Conversion of porous silica to porous silicon

0.3 g *h*-Silica or *w*-Silica and 0.3 g magnesium powder (Sinopharm Chemical Reagent Co. Ltd, 200 mesh) were mixed thoroughly. The obtained mixture was put in a steel boat, and then heated to 650°C with a ramping rate of 5°C and kept for 7 h in a tube furnace flowing through 95 vol% Ar/5 vol% H<sub>2</sub> gas. The obtained dark brown powder was etched in 2M HCl aqueous solution for 6 h, then immersed in a 5 wt% HF solution for 5 minutes. The powder in mixture was filtered out, rinsed with de-ion water and ethanol for 4 times, respectively. It was finally vacuum-dried at 80 for 12 h to obtained porous silicon. The yields of porous SiO<sub>2</sub> and Si from raw rice husk are 12.4 wt% and 4.0 wt%, respectively.

### Materials characterization

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

### Electrochemical tests

To test the properties of synthesized porous silicon, CR2016 half- cells were assembled to perform electrochemical experiments. The components of the electrodes were 60 wt% of porous silicon as 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<sub>6</sub> in a mixture of carbonate-containing vinylene carbonate (Novolyte Technologies, Inc., Suzhou, China). The active materials loading rate was ~1.00 mg/cm<sup>2</sup>. 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.

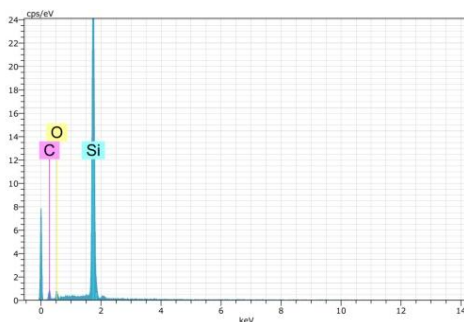


Figure S1. EDAX analysis of *h*-Silicon.

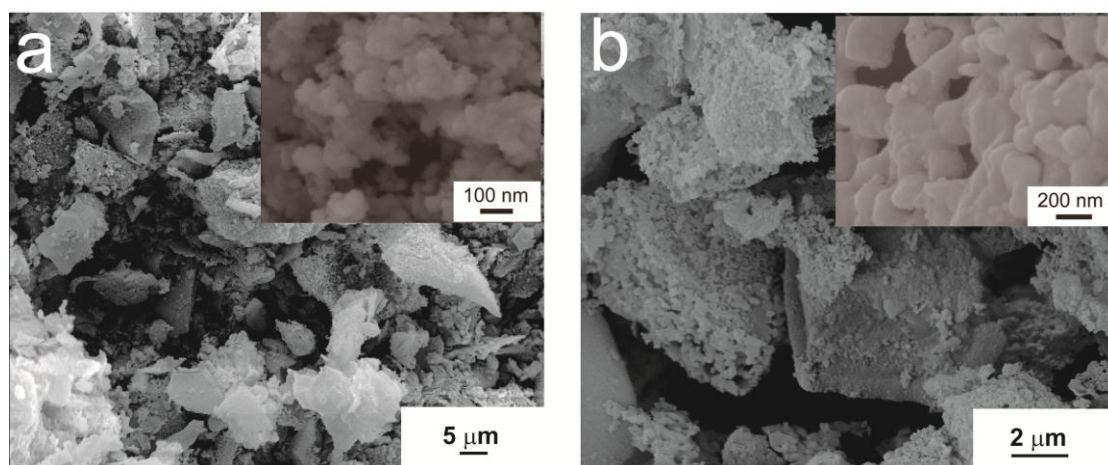


Figure S2. a, b, SE images of *h*-Silicon and *w*-Silicon, respectively (insets are images at higher magnification).

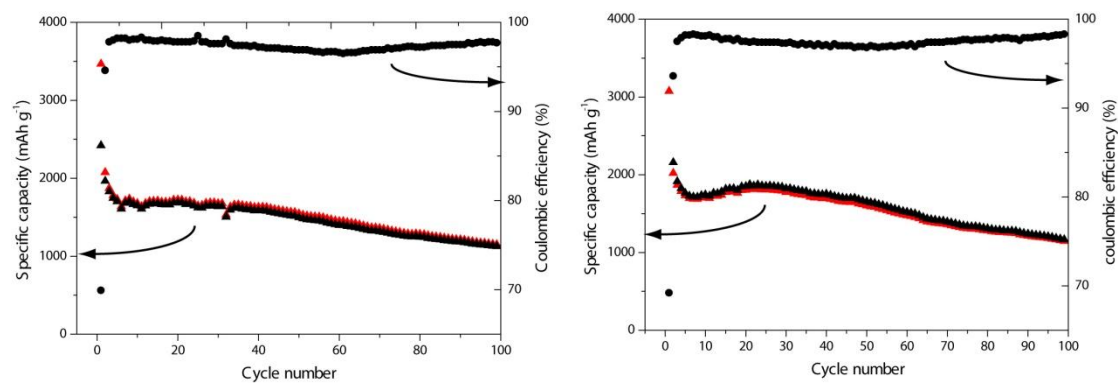


Figure S3. The cycling performance of another two *h*-silicon samples, showing the repeatability of our measurements.

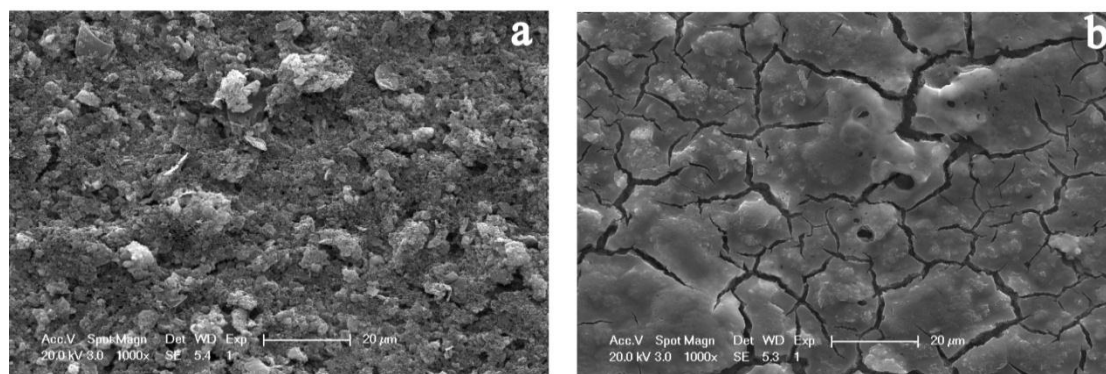


Figure S4. SEM images of mesoporous anodes composed of *h*-silicon a) before and b) after the cycling.

Table S1. The cycle and rate performance of mesoporous *h*-Silicon compared with other porous Si

Reference No	BET ( $\text{m}^2 \text{g}^{-1}$ )	Anode Materials	Capacity after 50 cycles ( $\text{mAh g}^{-1}$ )	Rate at 1C ( $\text{mAh g}^{-1}$ )	Rate at 2C ( $\text{mAh g}^{-1}$ )	Rate at 4C ( $\text{mAh g}^{-1}$ )
This work	150	Mesoporous Si	1370 (1.0 C)	1863	1555	1150
1	112	Hollow porous Si	ca.1700 (0.5 C)	ca.1400	–	ca.800
2	–	Macroporous Si	ca.1800 (0.1 C)	1430	590	–
2	–	Silver-coated Si	ca.2500 (0.1 C)	1610	800	–
3	–	Mesoporous Si	ca.1500 (2.0 C)	–	–	–
4	-	Mesoporous Si	ca.750 (0.4C)	-	-	ca.375
5	93.4	Mesoporous C/Si	594 (0.1C)	270	-	-
6	46.9	Porous silicon	240	ca.120	90	-

Note: 1C=1000  $\text{mA g}^{-1}$

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