

## Supplementary Information

# Large-scale fabrication of micro-sized bulk porous silicon as a high performance anode for lithium-ion batteries

Wei He<sup>a</sup>, Huajun Tian<sup>a\*</sup>, Fengxia Xin<sup>a</sup> and Weiqiang Han<sup>a,b\*</sup>

<sup>a</sup>*Ningbo Institute of Materials Technology and Engineering, Chinese Academy of Sciences, Ningbo 315201, P. R. China*

<sup>b</sup>*School of Physical Science and Technology, Shanghai Tech University, Shanghai200031, P. R.China*

\*Corresponding Author:

E-mail address: [tianhuajun@nimte.ac.cn](mailto:tianhuajun@nimte.ac.cn); [hanweiqiang@nimte.ac.cn](mailto:hanweiqiang@nimte.ac.cn)

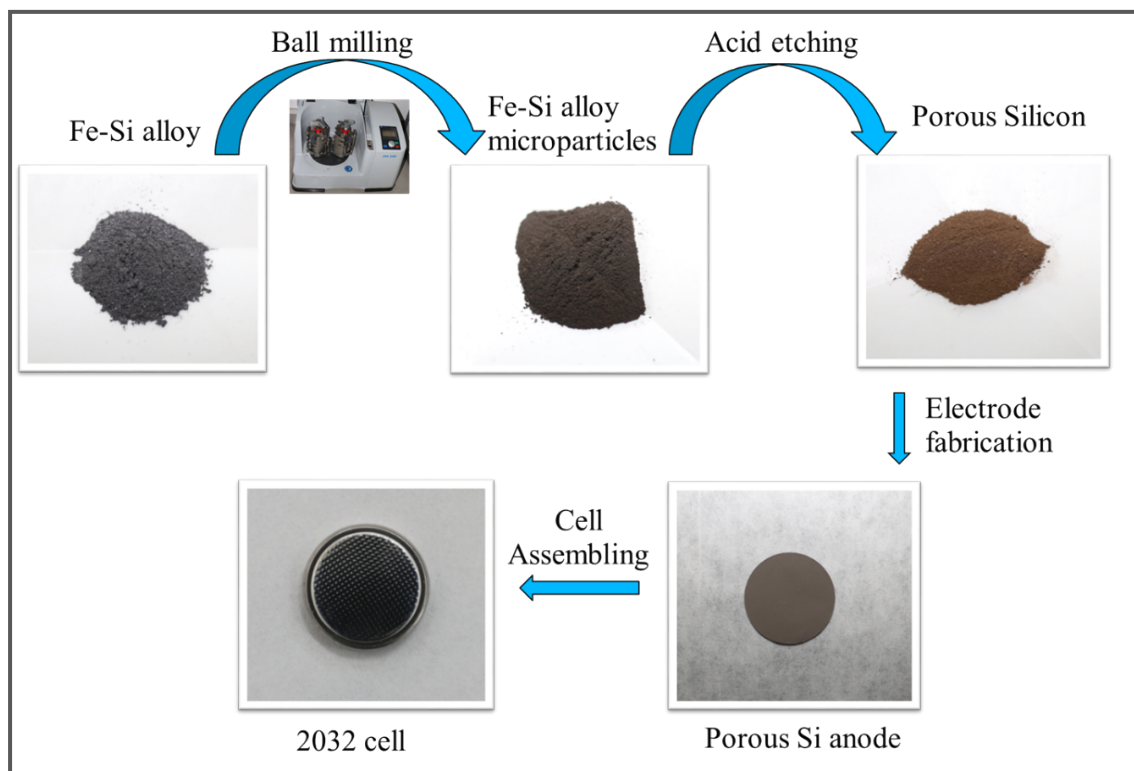


Figure S1. Schematic diagram of the synthesis and morphology of micro-sized porous Si as anode in LIBs.

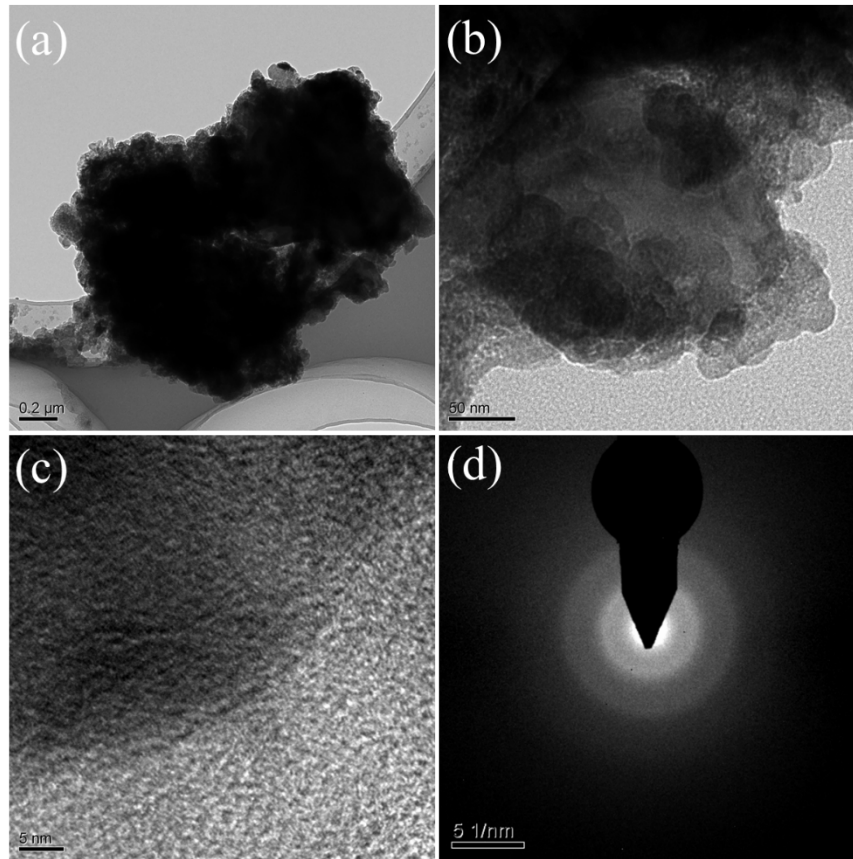


Figure S2. (a) and (b) are the TEM images of the porous Si material after 100 fully charge/discharge cycles at a current density of  $500 \text{ mA g}^{-1}$ . (c) the high-resolution TEM images, and (d) the selected area electron diffraction (SAED) of the porous Si materials after 100 cycles.

Table S1. Comparison of electrochemical performance of porous Si anodes without coating carbon in this work and in literature

Si anodes	Si source	Particle size	Initial Coulombic efficiency	Capacity retention	Rate performance	Ref.
Micro-sized porous silicon	Fe-Si alloy	0.5-5 $\mu\text{m}$	88.1%	1250 mAh g <sup>-1</sup> after 100 cycles at 500 mA g <sup>-1</sup>	558 mAh g <sup>-1</sup> at 5 A g <sup>-1</sup>	this work
Nanocrystalline silicon	SiCl <sub>4</sub>	several tens to about 100 nm	84.7%	1180 mAh g <sup>-1</sup> after 500 cycles at 3 A g <sup>-1</sup>	N/A	1
Mesoporous SiNW	metallurgical -Si	Nano size	52.9%	remains almost 2111 mAh g <sup>-1</sup> over 50 cycles at 0.2C	400 mAh g <sup>-1</sup> at 4C	2
Si nanorods	Al-Si ingot	200 nm in thickness	90%	600 mAh g <sup>-1</sup> at 300 mA g <sup>-1</sup> over 200 cycles	N/A	3
Nano-silicon	SiCl <sub>4</sub> and RSiCl <sub>3</sub> (R=H, C8H17)	5 nm	90%	71% capacity retention over 40 cycles	N/A	4
Nanoporous silicon	Mg <sub>2</sub> Si	15 nm	88%	64% capacity retention over 85 cycles at 360 mA g <sup>-1</sup>	1000 mAh g <sup>-1</sup> at 36 A g <sup>-1</sup>	5
Nest-like silicon nanospheres	NaSi	90-110 nm	N/A	35.9% capacity retention over 50 cycles at 2000 mA g <sup>-1</sup>	N/A	6
Nano-silicon	silica sol	80 nm	74%	89% capacity retention over 40 cycles at 0.36 A g <sup>-1</sup>	350 mAh g <sup>-1</sup> at 18 A g <sup>-1</sup>	7
Silicon nanosheets	sand	~5 nm	~70%	NA	N/A	8
Porous silicon	metallurgical Si	19 nm	N/A	retained 1400 mAh g <sup>-1</sup> at a current rate of 0.2C for 160 cycles.	N/A	9

Nano-Si	silica	less than 10 nm	64.5%	650 mAh g <sup>-1</sup> after 55 cycles at 0.045 mA/cm <sup>2</sup>	N/A	10
Hollow silicon nanotube	SiH <sub>4</sub>	wall thickness 60 to 80 nm	75%	73% capacity retention over 400 cycles at 2A g <sup>-1</sup>	1300 mAh g <sup>-1</sup> at 4 A g <sup>-1</sup>	11
Amorphous silicon	Silicon sputtering target	wall thickness was ~200 nm	82%	1730 mAh g <sup>-1</sup> after 200 cycles at 0.42 A g <sup>-1</sup>	1480 mAh g <sup>-1</sup> at 8.4 A g <sup>-1</sup>	12
Micrometer-sized porous silicon	SiO	micrometer-sized	N/A	45% capacity retention after 1000 cycles	N/A	13
Silicon nanowire	C <sub>6</sub> H <sub>8</sub> Si	diameter from 10 to 50 nm	60%	54% capacity retention after 20 cycles relative to the first charging cycle at C/20	N/A	14
Nanoscale hollow porous silicon	silica	120 nm	84%	over 93% capacity retention after 99 cycles at 500 mA g <sup>-1</sup>	over 2000 mAh g <sup>-1</sup> at 4000 mA g <sup>-1</sup>	15

- (1) Lin, N.; Han, Y.; Wang, L.; Zhou, J.; Zhou, J.; Zhu, Y.; Qian, Y. *Angewandte Chemie* **2015**, *54*, 3822.
- (2) Li, X.; Yan, C.; Wang, J.; Graff, A.; Schweizer, S. L.; Sprafke, A.; Schmidt, O. G.; Wehrspohn, R. B. *Advanced Energy Materials* **2015**, *5*, n/a.
- (3) Wang, J.; Meng, X.; Fan, X.; Zhang, W.; Zhang, H.; Wang, C. *ACS Nano* **2015**.
- (4) Kim, H.; Seo, M.; Park, M. H.; Cho, J. *Angewandte Chemie* **2010**, *49*, 2146.
- (5) Liang, J. W.; Li, X. N.; Hou, Z. G.; Guo, C.; Zhu, Y. C.; Qian, Y. T. *Chemical communications* **2015**, *51*, 7230.
- (6) Ma, H.; Cheng, F.; Chen, J. Y.; Zhao, J. Z.; Li, C. S.; Tao, Z. L.; Liang, J. *Advanced materials* **2007**, *19*, 4067.
- (7) Liang, J.; Li, X.; Zhu, Y.; Guo, C.; Qian, Y. *Nano Research* **2014**, *8*, 1497.
- (8) Kim, W. S.; Hwa, Y.; Shin, J. H.; Yang, M.; Sohn, H. J.; Hong, S. H. *Nanoscale* **2014**, *6*, 4297.
- (9) Ge, M.; Lu, Y.; Ercius, P.; Rong, J.; Fang, X.; Mecklenburg, M.; Zhou, C. *Nano letters* **2014**, *14*, 261.
- (10) Liu, X.; Gao, Y.; Jin, R.; Luo, H.; Peng, P.; Liu, Y. *Nano Energy* **2014**, *4*, 31.
- (11) Epur, R.; Hanumantha, P. J.; Datta, M. K.; Hong, D.; Gattu, B.; Kumta, P. N. *Journal of Materials Chemistry A* **2015**, *3*, 11117.

- (12) Zhao, Y.; Peng, L.; Ding, Y.; Yu, G. *Chemical communications* **2014**, *50*, 12959.
- (13) Lu, Z.; Liu, N.; Lee, H.-W.; Zhao, J.; Li, W.; Li, Y.; Cui, Y. *ACS Nano* **2015**, *9*, 2540.
- (14) Chockla, A. M.; Harris, J. T.; Akhavan, V. A.; Bogart, T. D.; Holmberg, V. C.; Steinhagen, C.; Mullins, C. B.; Stevenson, K. J.; Korgel, B. A. *Journal of the American Chemical Society* **2011**, *133*, 20914.
- (15) Chen, D.; Mei, X.; Ji, G.; Lu, M.; Xie, J.; Lu, J.; Lee, J. Y. *Angew. Chem.-Int. Edit.* **2012**, *51*, 2409.