Supporting Information

Rational Designed 3D Interconnected Porous Tin Dioxide Cube with Reserved Space for Volume Expansion as Advanced Anode of Lithium-Ion Batteries

Shuyi Kong^{1,2}, Jijian Xu¹, Gaoxin Lin^{1,2}, Shaoning Zhang¹, Wujie Dong^{1,2}*, Jiacheng Wang^{1,2}*, Fuqiang Huang^{1,3}*

¹ State Key Laboratory of High Performance Ceramics and Superfine Microstructure,

Shanghai Institute of Ceramics, Chinese Academy of Sciences, 1295 Dingxi Road,

Shanghai 200050, China

² Center of Materials Science and Optoelectronics Engineering, University of Chinese

Academy of Sciences, 19 Yuquan Road, Beijing 100049, China

³ State Key Laboratory of Rare Earth Materials Chemistry and Applications, College

of Chemistry and Molecular Engineering, Peking University, Beijing 100871, China

Corresponding Author: <u>huangfq@mail.sic.ac.cn</u> (F.Q. Huang);

jiacheng.wang@mail.sic.ac.cn (J.C. Wang);

dongwujie@mail.sic.ac.cn (W.J. Dong).

Experimental Section

Materials synthesis

All chemicals used in this work were commercially available and used without any further purification.

Preparation of pc-SnO₂. The CaSn(OH)₆ cubes were prepared according to the previous report ¹. In a typical procedure, 2.2 mmol CaCl₂ and 2 mmol Na₂SnO₃ were dissolved in 20 mL deionized water, respectively. Then 50 mg PVP was introduced into the CaCl₂ solution with vigorous stirring. The two aqueous solutions were mixed and transferred to a 50 mL Teflon autoclave, which was then heated at 140 °C for 10 h. After naturally cooling, the products were filtered and dried at 80 °C overnight. The resulting CaSn(OH)₆ cubes were calcined at 500 °C for 2 h in air to obtain the CaSnO₃ and 0.5mmol Na₂EDTA were dissolved in the mixed solution of 18 mL ethylene glycol and 18 mL deionized water. Then, this solution was transferred to a 50 mL Teflon autoclave and then heated at 180 °C for 12 h. After naturally cooling, the products were filtered and dried at 80 °C overnight to obtain pc-SnO₂.

Preparation of commercial SnO₂. Commercial SnO₂ comes from Sigma-Aldrich without further purification.

Sample characterization

X-ray diffraction (XRD) patterns were obtained with a Bruker D8 Advance diffractometer operating with Cu Kα radiation. The morphologies of the samples were

observed on a JEOL-JEM 2100F transmission electron microscope (TEM) and a JEOL 7800F field emission scanning electron microscope (FE-SEM). The BET isotherm was obtained at 77 K on an ASAP 2460 system, and the pore size distribution was calculated by the NLDFT method.

Electrochemical measurements

Electrochemical measurements were performed using coin-cells assembled in an argon-filled glove box. The active material powder (70 wt%), acetylene black (20 wt%) and a polyvinylidene fluoride (PVDF) binder (10 wt%) are homogeneously mixed in N-methyl pyrrolidinone (NMP) solvent and then coated uniformly on a copper foil to form the composite electrodes. Pure lithium foil was used as the counter electrode. The electrolyte was consisted of a solution of 1 M LiPF₆ in a 50: 50 w/w mixture of ethylene carbonate and dimethyl carbonate. Galvanostatic cycling was carried out using a Land CT2001C tester (Wuhan, China) between cut-off voltages of 3.0 and 0.01 V at room temperature. Cyclic voltammetry (CV) measurements were used a CHI760e electrochemical workstation with a potential range between 0.01 and 3.0 V at a scan rate of $0.2 \text{ mV} \text{ s}^{-1}$.

Material	Cycling performance	Rate capacity
SnO ₂ @HPC@NC ²	1100 mA h g ⁻¹ after 100 cycles at 0.1 A g ⁻¹	310 mAh g^{-1} at 5 A g^{-1}
c-SnO ₂ @3D-CNT ³	820.8 mA h g ⁻¹ after 500 cycles at 1A g ⁻¹ .	849.2 mA h g ⁻¹ at 1A g ⁻¹
C@SnO ₂ -rGO-SnO ₂ ⁴	1211 mA h g ⁻¹ after 300 cycles at 0.2 A g ⁻¹	545 mA h g ⁻¹ at 5 A g ⁻¹
p-h-SnO ₂ /GA ⁵	620 mA h g ⁻¹ after 200 cycles at 0.05A g ⁻¹	$\sim 420~mA~h~g^{\text{-1}}$ at 1 A $g^{\text{-1}}$
SnO ₂ @C tube in SnO ₂ @C tube ⁶	774.5 mA h g $^{-1}$ after 450 cycles at 0.2 A g $^{-1}$	338.4 mA h g ⁻¹ at 3 A g ⁻¹
Hollow nanoplate aggregated SnO ₂ nanofibers ⁷	375 mA h g ⁻¹ after 700 cycles at 3 A g ⁻¹	571 mA h g ⁻¹ at 4 A g ⁻¹
SnO ₂ @C q-HNCs ⁸	732 mA h g ⁻¹ after 350 cycles at 0.2A g ⁻¹	545 mA h g ⁻¹ at 3 A g ⁻¹
C@SnO ₂ /Sn@rGO ⁹	601.9 mA h g ⁻¹ after 900 cycles at 1 A g ⁻¹	304.8 mA h g ⁻¹ at 5 A g ⁻¹
non-smooth carbon coating porous SnO ₂ quasi-nanocubes ¹⁰	${\sim}800~mA~h~g^{-1}$ after 200 cycles at 0.2A g^{-1}	479.2 mA h g ⁻¹ at 3 A g ⁻¹
C@SnO ₂ @C ¹¹	712.6 mA h g ⁻¹ after 300 cycles at 0.2 A g ⁻¹	355.5 mA h g ⁻¹ at 3.2 A g ⁻¹
3D interconnected porous tin dioxide cube with reserved space (this work)	723 mA h g ⁻¹ after 300 cycles at 0.2 A g ⁻¹	736 mA h g ⁻¹ at 5 A g ⁻¹ ,

Table S1 The performance of previous works in LIBs



Fig. S1. a) FESEM images of CaSn(OH)₆ (Full image of **Fig. 1b**).



Fig. S2 Grading analysis of a) $CaSn(OH)_6$, b) $CaSnO_3$, and c) SnO_2 . Scale bar = 1 μ m.



Fig. S3. Sn 3d XPS spectrum of porous SnO_2 cube (Al K α radiation, carbon peak at 284.8 eV).



Fig. S4. Elemental mapping images of the SnO₂.



Fig. S5 Rate capability of porous SnO₂ cube electrode.



Fig. S6 cycling performance of porous cubic SnO₂ with different and correct mass loadings..

References

- 1. Z. Lu, J. Liu, Y. Tang and Y. Li, *Inorganic Chemistry Communications*, 2004, **7**, 731-733.
- 2. Y. Hong, W. Mao, Q. Hu, S. Chang, D. Li, J. Zhang, G. Liu and G. Ai, *Journal of Power Sources*, 2019, **428**, 44-52.
- 3. P. Bhattacharya, J. H. Lee, K. K. Kar and H. S. Park, *Chemical Engineering Journal*, 2019, **369**, 422-431.
- 4. W. Yao, S. Wu, L. Zhan and Y. Wang, *Chemical Engineering Journal*, 2019, **361**, 329-341.
- 5. J. Choi, Y. Myung, M. G. Gu and S.-K. Kim, *Journal of Industrial and Engineering Chemistry*, 2019, **71**, 345-350.
- 6. Q. Tian, F. Zhang, L. Yang and P. Chen, *Energy Technology*, 2019, **7**, 1801048.
- 7. J.-S. Park, Y. J. Oh, J. H. Kim and Y. C. Kang, *Mater Charact*, 2020, **161**, 110099.
- 8. Q. Tian, Y. Chen, W. Zhang, J. Chen and L. Yang, *Applied Surface Science*, 2020, **507**, 145189.
- 9. W. Su, Y. Liang and Y. Tang, *Journal of Alloys and Compounds*, 2019, **801**, 402-408.
- 10. Q. Tian, F. Zhang, W. Zhang and L. Yang, *Electrochimica Acta*, 2019, **307**, 393-402.
- 11. B. Cao, Z. Liu, C. Xu, J. Huang, H. Fang and Y. Chen, *Journal of Power Sources*, 2019, **414**, 233-241.