## **Electronic Supplementary Information**

# Engineering of multi-shelled SnO<sub>2</sub> hollow microspheres for highly stable lithiumion batteries

Jian Zhang,<sup>a</sup> HaoRen,<sup>b</sup> Jiangyan Wang,<sup>c</sup> Jian Qi,<sup>c</sup> RanboYu,<sup>b</sup> Dan Wang<sup>c\*</sup> and Yunling Liu<sup>a\*</sup>

<sup>a</sup> State Key Laboratory of Inorganic Synthesis & Preparative Chemistry, Jilin University, 2699 Qianjin Street, Changchun 130012, P. R. China. \*E-mail: yunling@jlu.edu.cn

<sup>b</sup> Department of Physical Chemistry, School of Metallurgical and Ecological Engineering, University of Science and Technology Beijing, No. 30, Xueyuan Road, Haidian District, Beijing 100083, P. R. China.

<sup>c</sup> National Key Laboratory of Biochemical Engineering, Institute of Process Engineering, Chinese Academy of Sciences, No. 1 Beierjie, Zhongguancun, Beijing 100190, P. R. China. \*Email: danwang@ipe.ac.cn

### **Experimental Section**

#### **Material Synthesis:**

Preparation of multi-shelled SnO<sub>2</sub> hollow spheres: All reagents were analytical grade and purchased from Beijing Chemical Co. Ltd., and used without further purification.

As reported in our previous work, Tin (IV) chloride pentahydrate (SnCl<sub>4</sub>·5H<sub>2</sub>O) was used as the metal precursor. The typical synthetic procedure for quadruple-shelled SnO<sub>2</sub> hollow microspheres is as follows: carbonaceous microspheres (CMSs) were synthesized through the emulsion polymerization reaction of sucrose under the hydrothermal conditions as described elsewhere. Alkali-treated carbonaceous microspheres (ATCMSs) were prepared by immersing CMSs in a 0.05M NaOH solution for 3 h. 0.6 g of ATCMSs was dispersed in 30 mL of 1.2 M tin (IV) chloride solution with the aid of ultrasonication for 20 min. After ultrasonic dispersion, the resulting suspension was aged for 4 h at room temperature, then filtered, washed with water and dried at 80 °C for 12 h. The resultant Sn<sup>4+</sup> infused microspheres were heated to 500 °C in air at the rate of 1 °C min<sup>-1</sup>, and kept at 500 °C for 2 h. The quadrupleshelled SnO<sub>2</sub> hollow microspheres were collected as white powders.

Single-shelled, double-shelled, and triple-shelled  $SnO_2$  hollow microspheres were synthesized by changing the concentration of tin (IV) chloride solution (0.1 M, 0.2 M, and 0.5 M, respectively) and using the same thermal processing procedure described above.

Tin(II) chloride dihydrate was used as the metal precursor in the synthetic procedure for core-shelled  $SnO_2$  hollow microspheres. 0.6 g of CMSs without treated were

dispersed in 60 mL 0.05 M Tin(II) chloride dihydrate aqueous and ethanol mixture solution (V/V = 1:2) with the aid of ultrasonication for 20 min. After ultrasonic dispersion, the resulting suspension was aged for 6 h at room temperature, filtered, washed with water and dried at 80 °C for 12 h. The resultant Sn<sup>2+</sup> infused microspheres were heated to 500 °C in air at the rate of 10 °C min<sup>-1</sup>, and kept at 500 °C for 2 h. Coreshelled SnO<sub>2</sub> hollow microspheres were collected as white powders.

#### Materials characterization:

Scanning electron microscopy (SEM) images were obtained using a JSM-6700 microscope operated at 5.0 kV. Transmission electron microscopy (TEM) images were taken using a FEI Tecnai G<sup>2</sup> F20 s-twin D573 field emission transmission electron microscope with an accelerating voltage of 200 kV. The powder X-ray diffraction (XRD) data were collected on a Rigaku D/Max 2550 X-ray diffractometer using Cu K $\alpha$  radiation ( $\lambda = 1.5418$  Å) operated at 200 mA and 50 kV. The nitrogen adsorption-desorption isotherms were measured at 77 K via Micromeritics Tristar 2420 analyzer. Samples were degassed under vacuum at 200 °C overnight. Thermogravimetric (TG) analyses were performed on TGA Q500 V20.10 Build 36 thermogravimetric analyzer in the temperature range 35-700 °C under air flow with the heating rate of 5 °C min<sup>-1</sup>.

### **Electrochemical measurements:**

The electrochemical behavior of the prepared multi-shelled  $SnO_2$  hollow microsphere samples was carried out using CR2032 coin-type cells with lithium metal as the counter and reference electrodes at room temperature. The electrolyte was 1 M LiPF<sub>6</sub> mixed in a 1:1 volume ratio with ethylene carbonate and diethyl carbonate. The working electrode was fabricated by compressing a mixture of the active materials, conductive material (carbon black), and binder (sodium carboxymethyl cellulose, NaCMC) in a weight ratio of  $SnO_2$ /carbon black/NaCMC = 7:2:1 onto a copper foil current collector. The active material loading in each electrode disc (around 15 mm in diameter) is about 1-2 mg, corresponding to approximately 1 mg cm<sup>-2</sup>. The cells were assembled in an argon-filled glove box with the concentrations of moisture and oxygen below 1 ppm.

The electrode capacity was measured by a galvanostatic discharge-charge method with different voltage windows 0.005-3 V at 100 mA  $g^{-1}$  with a Landdt-5 V, 5 mA battery test system.

Cyclic voltammogram curves were examined between 0.005-3.0 V (vs.  $Li^+/Li$ ) at a constant scan rate of 2 mV s<sup>-1</sup>. Electrochemical impedance spectroscopy (EIS) tests were carried out over the frequency ranging from 0.1 to 105 Hz with an Ac amplify voltage of 10 mV.

Morphology	Adsorption condition	Calcination process
	Tin (IV) chloride aqueous	
Single-shelled SnO <sub>2</sub> -HMS	solution 0.1 M, RT, 4 h	1 °C/min, 500 °C, 2 h
	Tin (IV) chloride aqueous	
Double-shelled SnO <sub>2</sub> -HMS	solution 0.2 M, RT, 4 h	1 °C/min, 500 °C, 2 h
	Tin(II) chloride dehydrate	
Core-shelled SnO <sub>2</sub> -HMS	aqueous and ethanol mixture	10 °C/min, 500 °C, 2 h
	solution (V/V=1:2) 0.05 M, RT, 6 h	
	Tin (IV) chloride aqueous	
Triple-shelled SnO <sub>2</sub> -HMS	solution 0.5 M, RT, 4 h	1 °C/min, 500 °C, 2 h
	Tin (IV) chloride aqueous	
Quadruple-shelled SnO <sub>2</sub> -HMS	solution 1.2 M, RT, 4 h	1 °C/min, 500 °C, 2 h

**Table S1.** Synthesis method and calcination processes of multi-shelled  $SnO_2$  hollow microspheres (HMS).

**Table S2.** Summary of parameters of the as-prepared multi-shelled  $SnO_2$  HMS according to nitrogen adsorption-desorption isotherm.

Structures	Specific Surface Area (m <sup>2</sup> g <sup>-1)</sup>	Pore volume (cm <sup>3</sup> g <sup>-1</sup> )
Single-shelled SnO <sub>2</sub> -HMS	37	0.22
Double-shelled SnO <sub>2</sub> -HMS	43	0.24
Core-shelled SnO <sub>2</sub> -HMS	55	0.31
Triple-shelled SnO <sub>2</sub> -HMS	50	0.36
Quadruple-shelled SnO <sub>2</sub> -HMS	62	0.28

Morphology	Voltage window	Initial capacity (mAhg <sup>-</sup> <sup>1</sup> )/ Current density (mA g <sup>-</sup> <sup>1</sup> )	Cycling performance Stable capacity (mAhg <sup>-1</sup> )/ Cycling number	References
Hollow spheres	0.005-3V	<1200/100	<150/50cycles	<b>S1</b>
Hollow spheres	0.01-3V	1447/200	151/58cycles	<b>S2</b>
Hollow spheres	0.01-3V	1978/100	477/60cycles	<b>S</b> 3
Hollow spheres	0.005-2.5V	2167/100	601/100cycles	<b>S4</b>
Hollow spheres	0.04-2V	1600/100	380/40cycles	<b>S</b> 5
Hollow spheres	0.005-1.5V	764/100	520/20cycles	<b>S</b> 6
Hollow particles	0-2V	1459/100	52/70cycles	<b>S</b> 7
Core-shelled hollow spheres	0.005-2V	2358/50	>782/30cycles	<b>S8</b>
York-shelled hollow spheres	0.005-1V	1832/625	642/40cycles	<b>S</b> 9
Nano sheets	0.005-3V	——/7 <b>8.</b> 2	559/20cycles	<b>S10</b>
Nanowires	0.01-3V	<1400/391	<100/50cycles	<b>S11</b>
Nanoparticle	0.01-3V	<b>/100</b>	<500/40cycles	<b>S12</b>
Flower-like nanoparticle	0.01-2.5V	736/200	31.4/50cycles	<b>S13</b>
Nanobox	0.01-2V	2242/156.2	570/40cycles	<b>S14</b>
Nanotubes	0.1-2V	1813/100	345/20cycles	S15
Nanotubes	0-2V	1546/180	807/50cycles	<b>S16</b>
Nanorods	0.1-2V	1930/100	<700/20cycles	<b>S17</b>
Nanotubes	0.005-1.5V	1849/100	468/30cycles	<b>S18</b>
Nanoparticle(Sn-MOFs)	0.005-1.5V	/40(1-3cycles)	541/100cycles	<b>S19</b>
		and400(4-100cycles)		
Nanowires	0.05-1.5V	1134/100	<400/50cycles	<b>S20</b>
Microbox	0.005-1.5V	<b>——</b> /200	<200/60cycles	<b>S21</b>
Nanotubes	0.001-1.2V	2002/400	585/50cycles	S22
Nanosheets	0.01-1.2V	<b>——</b> /400	<400/50cycles	<b>S23</b>
Nanospheres	0.01-1.2V	1750/2000	381/250cycles	<b>S24</b>
Mesoporousspheres	0.05-1V	<400/1000	370/50cycles	S25
Single-shelled HMS	0.005-3V	1682/100	500/50cycles	This work
Double-shelled HMS	0.005-3V	1582/100	651/50cycles	This work
Core-shelled HMS	0.005-3V	1781/100	643/50cycles	This work
Triple-shelled HMS	0.005-3V	1927/100	746/50 cycles	This work
Quadruple-shelled HMS	0.005-3V	2025/100	665/50cycles	This work

Table S3. Comparison of the electrochemical performances of  $SnO_2$  nanomaterials.

### **References:**

S1. Y. Chen, Q. Z. Huang, J. Wang, Q. Wang and J. M. Xue, J. Mater. Chem., 2011, 21, 17448-

17453.

- S2. J. S. Cho and Y. C. Kang, *Small*, 2015, **11**, 4673-4681.
- R. Demir-Cakan, Y.-S. Hu, M. Antonietti, J. Maier and M.-M. Titirici, *Chem. Mater.*, 2008, 20, 1227-1229.
- S4. Q. Guo and X. Qin, Journal of Solid State Electrochemistry, 2014, 18, 1031-1039.
- S5. X. Han, X. Han, L. Sun, Q. Liu, W. Xu, L. Li, P. Wang and C. Wang, *CrystEngComm.*, 2015, **17**, 1754-1757.
- S6. P. Wu, N. Du, H. Zhang, J. Yu, Y. Qi and D. Yang, *Nanoscale*, 2011, **3**, 746-750.
- S7. Z. Sun, C. Cao and W.-Q. Han, *RSC Adv.*, 2015, 5, 72825-72829.
- S8. Q. Tian, Y. Tian, Z. Zhang, L. Yang and S.-i. Hirano, J. Mater. Chem. A, 2015, 3, 18036-18044.
- S9. X. Zhang, J. Liang, G. Gao, S. Ding, Z. Yang, W. Yu and B. Q. Li, *Electrochimica Acta*, 2013, 98, 263-267.
- S10. Z. Chen, M. Zhou, Y. Cao, X. Ai, H. Yang and J. Liu, Adv. Energy. Mater., 2012, 2, 95-102.
- S11. D. Deng and J. Y. Lee, *Chem.Mater.*, 2008, **20**, 1841-1846.
- S12. S. Ding, D. Luan, F. Y. C. Boey, J. S. Chen and X. W. Lou, *Chem. Comm.*, 2011, 47, 7155-7157.
- S13. S. Han, B. Jang, T. Kim, S. M. Oh and T. Hyeon, Adv. Funct. Mater., 2005, 15, 1845-1850.
- S14. Y. J. Hong, M. Y. Son and Y. C. Kang, *Adv. Mater.*, 2013, 25, 2279-2283.
- S15. W.-S. Kim, Y.Hwa, H.-C. Kim, J.-H. Choi, H.-J. Sohn and S.-H. Hong, *Nano Res.*, 2014, 7, 1128-1136.
- S16. L. Li, X. Yin, S. Liu, Y. Wang, L. Chen and T. Wang, *Electrochem. Comm.*, 2010, 12, 1383-1386.
- S17. M.-S. Park, G.-X. Wang, Y.-M. Kang, D. Wexler, S.-X. Dou and H.-K. Liu, *Angew. Chem.*, *In. Ed.*, 2007, 46, 750-753.
- S18. C. Wang, Y. Zhou, M. Ge, X. Xu, Z. Zhang and J. Z. Jiang, J. Am. Chem. Soc., 2010, 132, 46-47.
- S19. J. Wang, W. Li, F. Wang, Y. Xia, A. M. Asiri and D. Zhao, *Nanoscale*, 2014, 6, 3217-3222.
- S20. X. Wang, Z. Li, Z. Zhang, Q. Li, E. Guo, C. Wang and L. Yin, *Nanoscale*, 2015, 7, 3604-3613.
- S21. Z. Wang, D. Luan, F. Y. C. Boey and X. W. Lou, J. Am. Chem. Soc., 2011, 133, 4738-4741.
- S22. H. X. Yang, J. F. Qian, Z. X. Chen, X. P. Ai and Y. L. Cao, J. Physical Chem. C, 2007, 111, 14067-14071.
- S23. J. Ye, H. Zhang, R. Yang, X. Li and L. Qi, *Small*, 2010, 6, 296-306.
- S24. L. Zhang, H. B. Wu, B. Liu and X. W. Lou, Energy. Environ. Sci., 2014, 7, 1013-1017.
- S25. B. Zhou, S. Yang, L. Wu, W. Wu, W. Wei, L. Chen, H. Zhang, J. Pan and X. Xiong, *RSC Adv.*, 2015, 5, 49926-49932.
- S26. N. Li and C. R. Martin, J. Electrochem. Soc., 2001, 148, A164-A170.
- S27. S. Panero, G. Savo and B. Scrosati, Electrochem. Solid State Lett., 1999, 2, 365-366.
- S28. J. C. Lytle, H. Yan and N. S. Ergang, J. Mater. Chem. A, 2004, 14, 1616-1622.



Fig. S1. The XRD patterns of multi-shelled SnO<sub>2</sub> hollow microspheres.



**Fig. S2.** (a) TG curve of carbonaceous microspheres with  $Sn^{2+}$  infiltrated under atmosphere at the rate of 5 °C/min, (b) TG curve of carbonaceous microspheres with  $Sn^{4+}$  infiltrated under atmosphere at the rate of 5 °C/min.



Fig. S3. The enlarged TEM image of core-shelled  $SnO_2$  hollow microspheres and porous core inside



Fig. S4. (a) Nitrogen adsorption-desorption isotherm of the as-synthesized multishelled  $SnO_2$  hollow microspheres, (b) Barret-Joyner-Halenda (BJH) pore-size distribution curves of the multi-shelled  $SnO_2$  hollow microspheres according to the nitrogen adsorption-desorption isotherm.



**Fig. S5.** SEM images of the electron film before the test (weight ratio of active materials  $SnO_2$ : carbon black: NaCMC = 7:2:1).



**Fig. S6.** The coulombic efficiency of multi-shelled  $SnO_2$  hollow microspheres at the current rate of 100 mA g<sup>-1</sup> under the voltage range (a) 0.005-3 V and (b) 0.005-1 V



**Fig. S7.** (a-e) TEM images of the single-, double-, core-, triple- and quadruple-shelled  $SnO_2$  hollow microspheres as anode electrodes after 30 cycles, (f) TEM image of quadruple-shelled  $SnO_2$  hollow microspheres as anode electrodes after 50 cycles. All scale bars are 100 nm.



Fig. S8. SEM images of the electron film after 50 cycles.



Fig. S9. Cyclic voltammetry profiles of quadruple-shelled  $SnO_2$  hollow microspheres in the potential range of 0.005-1 V, at a scan rate of 2 mV s<sup>-1</sup>, which are in agreement with other reports.<sup>S26-S28</sup>



**Fig. S10.** (a) Cycling performance of multi-shelled  $SnO_2$  hollow microspheres at the current rate of 100 mA g<sup>-1</sup> under the voltage range from 0.005 to 1 V, (b) Initial charge-discharge voltage profiles of the multi-shelled  $SnO_2$  microspheres.



**Fig. S11**. The TEM images of core-shelled  $SnO_2$  hollow microspheres obtained under different thermal processing procedures ((a) at the rate of 5 °C min<sup>-1</sup> and (b) at the rate of 10 °C min<sup>-1</sup>).



Fig. S12. The SEM images of large-scale multi-shelled  $SnO_2$  hollow microspheres.