Supporting Information

Ball-in-Ball SnO_2/SnS@Void@C as Anode for Enhanced Electrochemical Performances of Li/Na Ion Batteries

Rongguan Lv[a], Bin Xie[b], Xiaoyu Wu[b*], Haiyan Yu[a], Qinahui Wu[c*], Fang Guo[d], Ming Chen[b*]

a College of Chemistry and Chemical Engineering, Yangzhou Polytechnic Institute, Yangzhou 225127, Jiangsu, P. R. China

b School of Chemistry and Chemical Engineering, Yangzhou University, Yangzhou 225002, Jiangsu, P. R. China

c Laboratory of Advanced Functional Materials of Nanjing, Nanjing Xiaozhuang University, Nanjing 211171, Jiangsu, P. R. China

d School of Chemistry and Chemical Engineering, Yancheng Institute of Technology Yancheng 224051, Jiangsu, P. R. China

* Corresponding Authors
E-mail address: wuxiaoyu1116@163.com (X. Wu); 1017241434@qq.com (Q. Wu); chenming@yzu.edu.cn (M. Chen).

1. Experimental Section

1.1 Materials

$Na_2[Sn(OH)_6]$, urea, resorcinol, formaldehyde, $NH_3 \cdot H_2O$, ethanol, NaOH, and polyvinylidene difluoride (PVDF) were analytical grade and purchased from Shanghai Chemical Corp. All commercially available chemicals and solvents were reagent grade and used as received.

1.2 Materials characterization

Field-emission scanning electron microscopy (FESEM) images were obtained from Hitachi S-4800 (Japan). The Philips TECNAI-12 apparatus was used for transmission electron microscopy (TEM). High-resolution TEM (HRTEM) and high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) were performed on FEI Tecnai G2 F30 STWIN (USA) operating at 300 kV. On D8 advance superspeed powder diffractometer(Bruker), X-ray diffraction (XRD) data were collected using a graphite monochromator and Cu K radiation (λ= 0.1541 nm). Thermo Escalab 250 equipment was used to acquire X-ray photoelectron spectroscopy (XPS) using Al Ka radiation (hv = 1486.6 eV). After samples were dried at 100 ℃ for 6 hours, surface areas and pore size distributions were measured using the BET technique in an automated surface area and porosity analyzer (ASAP 2020, HD88) at -196 ℃.

1.3 Electrochemical measurement

The anode electrodes were made by dispersing SnO_2/SnS@Void@C in n-

methyl-2-pyrrolidone (NMP) at a mass ratio of 8:1:1 with acetylene black, 15% polyvinylidene fluoride (PVDF) binder, and stirring at room temperature for 24 h. The slurry is then evenly applied to the surface of the copper foil and dried at 80 ℃ for 8 h. Each sample had a mass loading of 0.79 ~ 1.23 mg cm^{-2}. The CR 2032 button battery pack with circular lithium and sodium metal sheets as reference electrodes installed in a high purity argon glovebox (Vacuum Co., Ltd.). 1 M $LiPF_6$ in EC/DMC/EMC (volume ratio 1:1:1) and 1 M $NaPF_6$ in DOI/DME (volume ratio 1:1) as the battery electrolyte with Celgard 2400 polypropylene as the diaphragm. Cyclic voltammetry (CV) is performed using an electrochemical workstation (CHI660 E, Chenghua, CHN) with a scanning rate of 0.1 mV s^{-1} and a voltage range of 0.001 V to 3.0 V. To verify rate performances and cycling performances, galvanostatic charge and discharge cycling of the cells were performed using battery test equipment (CT-3008W, Xinwei, CHN) at various voltages ranging from 0.01-3 V (vs. Li^+/Li) and 0.01-3 V (vs. Na^+/Na).

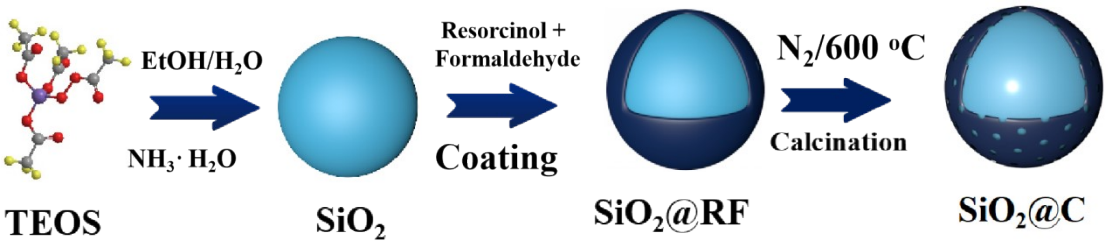

Figure S1 Schematic illustration for synthesizing SiO_2@C

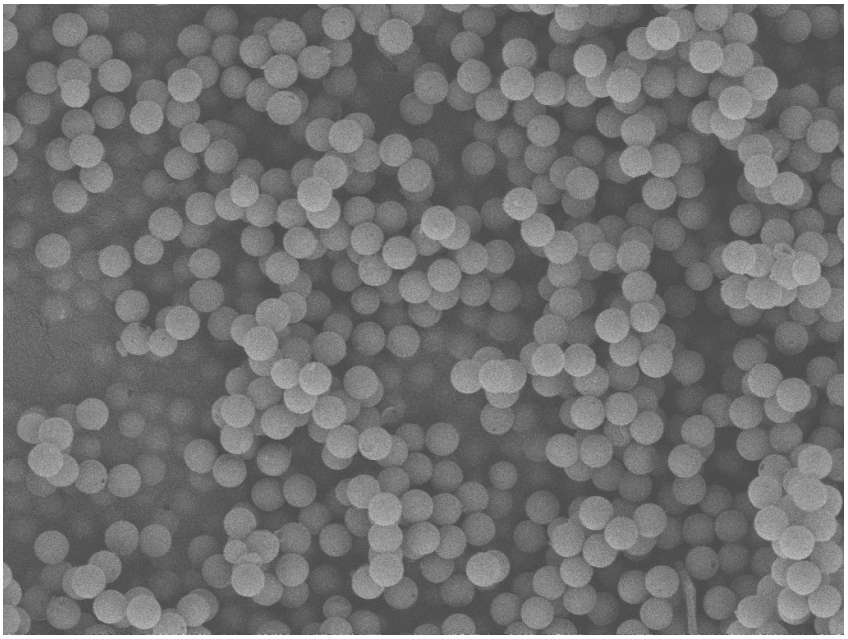

Figure S2 SEM images of SiO_2@C

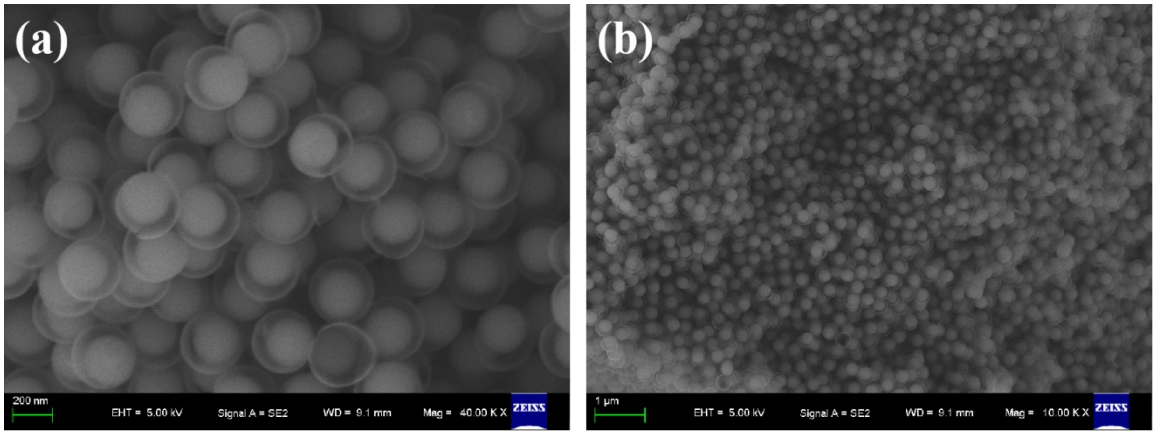

Figure S3 SEM images of SnO_2/SnS@Void@C

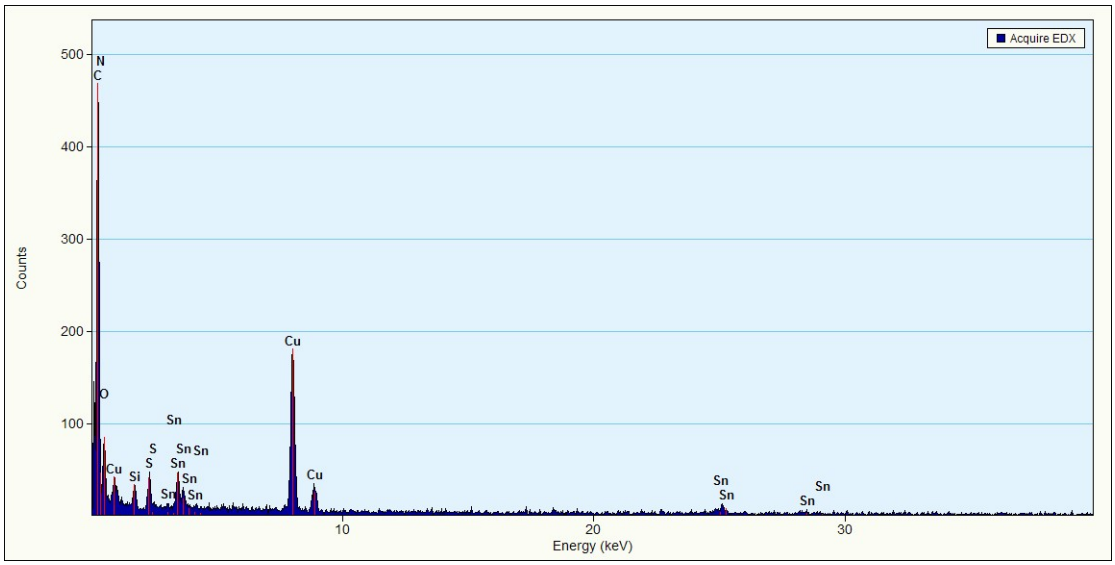

Figure S4 EDX pattern of SnO_2/SnS@Void@C

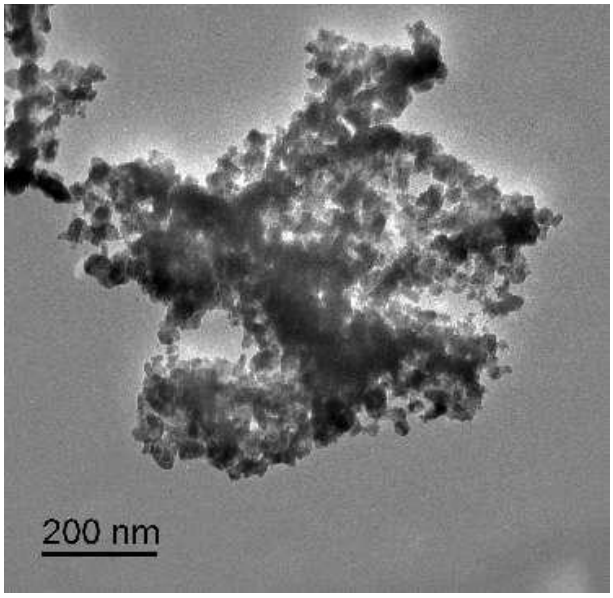

Figure S5 TEM image of pure SnO_2

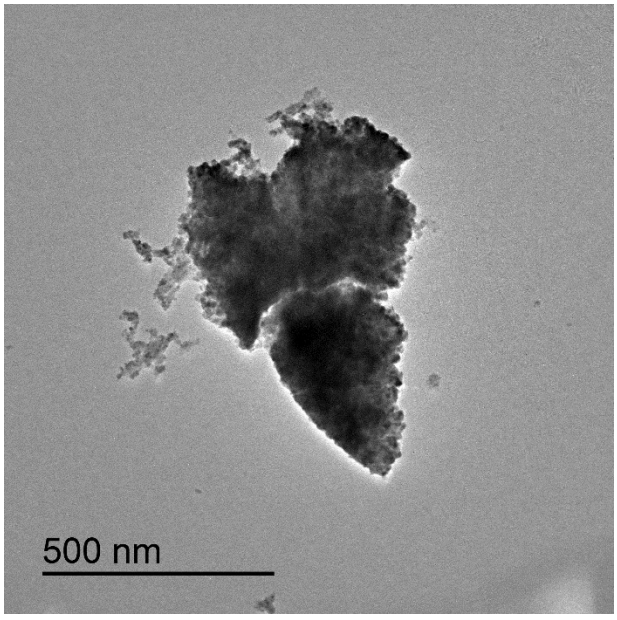

Figure S6 TEM image of pure SnS.

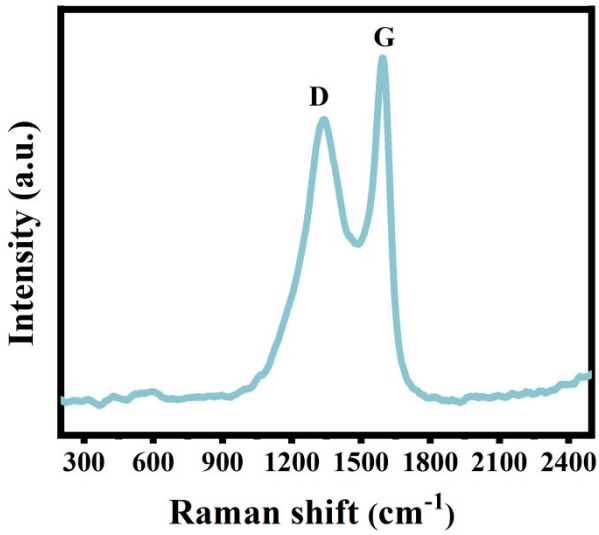

Figure S7 Raman spectrum of SnO_2/SnS@Void@C

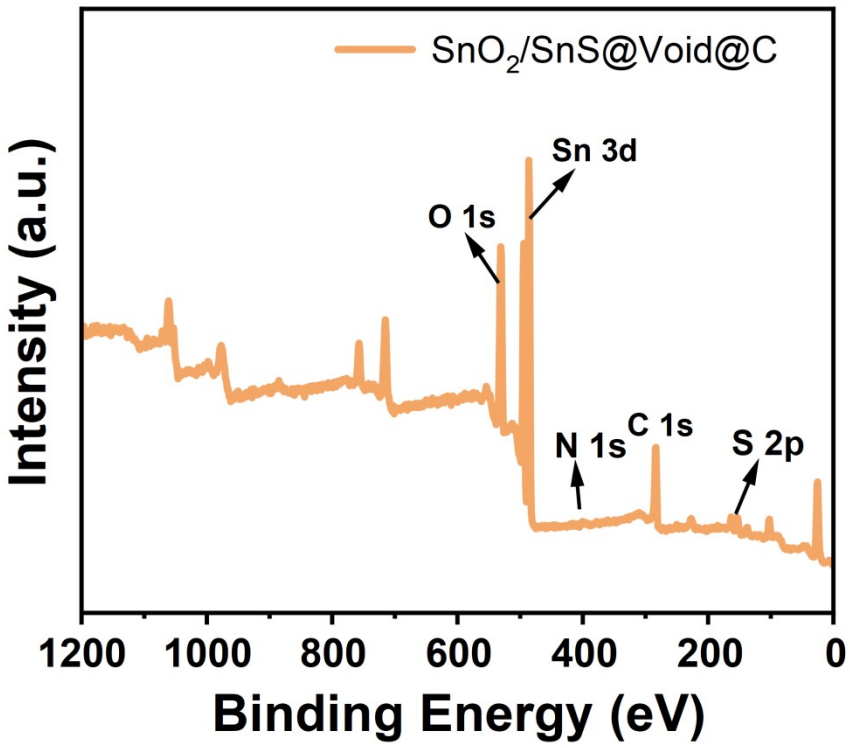

Figure S8 XPS survey spectrum of SnO_2/SnS@Void@C

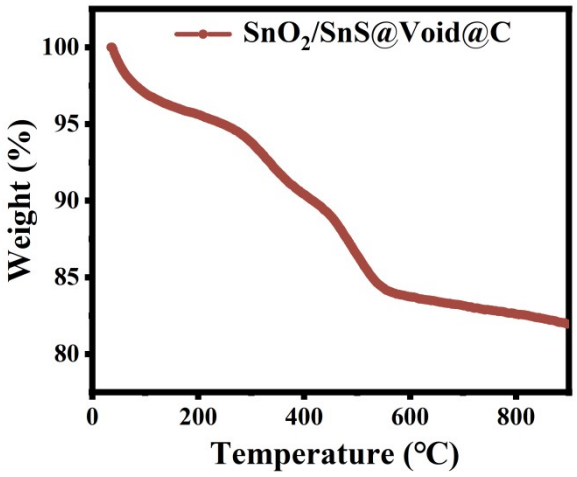

Figure S9 Thermogravimetric analysis (TGA) curve of SnO_2/SnS@Void@C

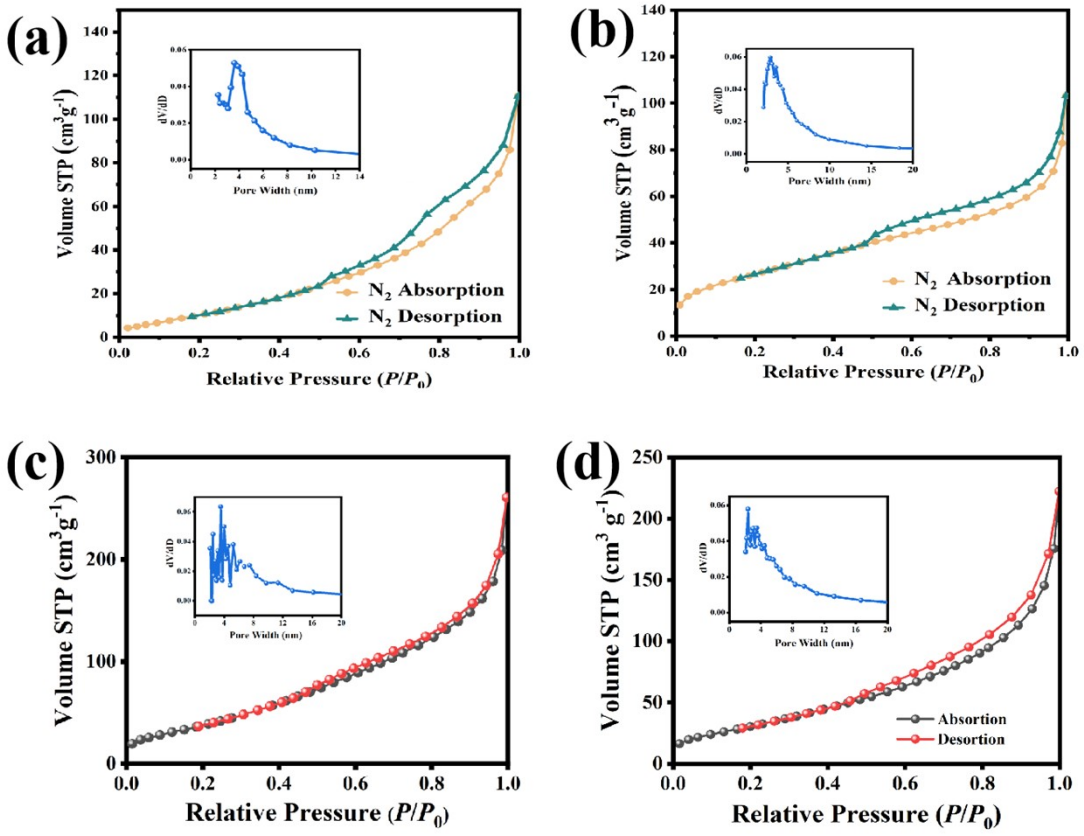

Figure S10 N_2 adsorption−desorption isotherms and corresponding BJH pore-size distribution curses of (a) SnO_2/SnS@Void@C, (b) SnO_2@Void@C, (c) SnO_2 and (d) SnS.

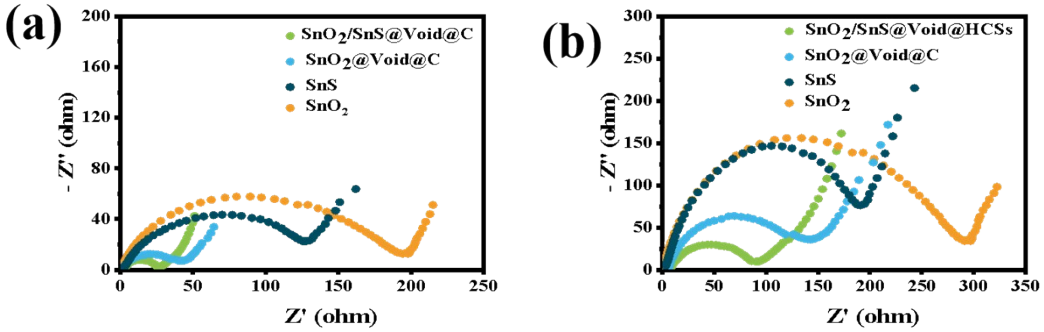

Figure S11 Nyquist plots (a) before cycling and (b) after 50 cycles of SnO_2/SnS@Void@C and pure SnO_2 for LIBs.

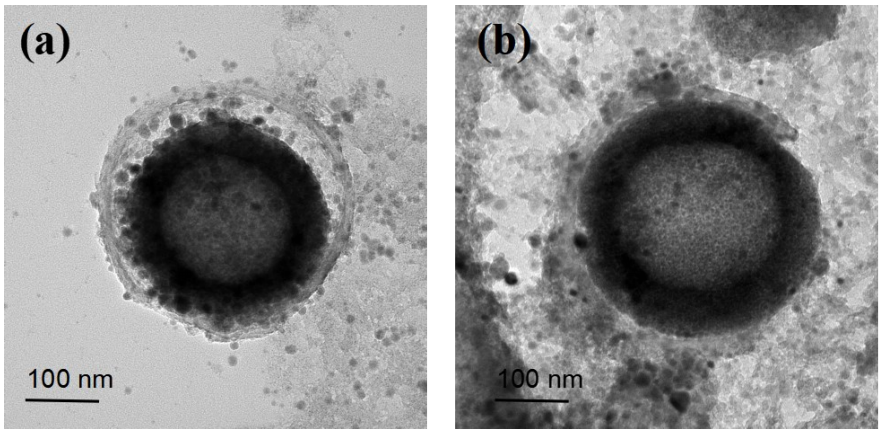

Figure S12 TEM images of SnO_2/SnS@Void@C after 500 cycles for LIBs.

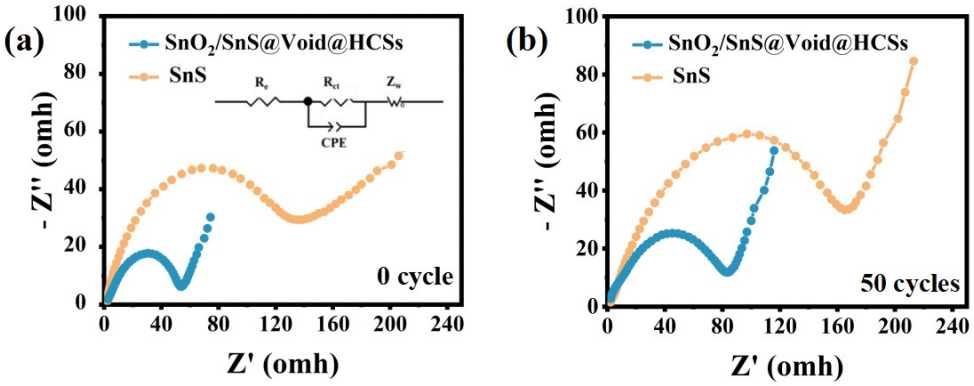

Figure S13 Nyquist plots (a) before cycling and (b) after 50 cycles of SnO_2/SnS@Void@C and pure SnS for SIBs.

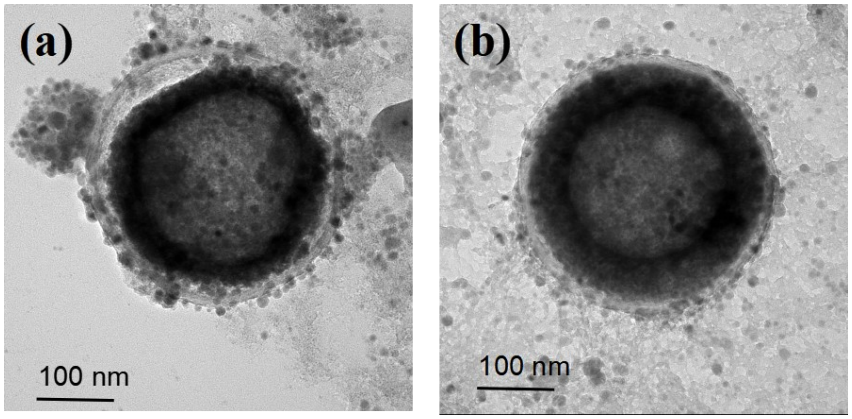

Figure S14 TEM images of SnO_2/SnS@Void@C after 500 cycles for SIBs

Table S1 Comparison of electrochemical performance of SnO_2/SnS@Void@C as anode in LIBs with other Sn based sulfides and oxides in literatures

Sample	Current density (mA g^{-1})	After n th cycle	Capacity (mA h g^{-1})	References
SnO_2/SnS@C	**5000**	**500**	**415**	**This work**
SnO_2 nanotubes	100	30	468	J. Am. Chem. Soc., 2010, 132, 46-47
Nanoparticle(Sn-MOFs)	400	100	541	Nanoscale, 2014, 6, 3217-3222.
Mesoporousspheres	1000	50	370	RSC Adv., 2015, 5, 49926-49932
SnO_2@Cyolk–shell nanospheres	625	100	630	Nanoscale, 2014, 6, 3217
SnO_2/N-Carbon	100	100	750	Nano-Micro Lett. (2018) 10:21
porous SnO_2 /carbon	200	400	1089.5	Electrochimica Acta 307 (2019) 393-402

Table S2 Comparison of electrochemical performance of SnO_2/SnS@Void@C as anode in SIBs with other metal sulfides in literatures

Sample	Current density (mA g^{-1})	After n th cycle	Capacity (mA h g^{-1})	References
SnO_2/SnS@C	**5000**	**500**	**303**	**This work**
MoS_2 S-doped graphene	1000	1000	309	*Adv. Funct. Mater.* **2017,** *27* (40)
Co_9S_8 hollow carbon and rGO	300	500	628	*Adv. Funct. Mater.* **2017,** *27* (38).
NiS_2 nanoparticles	500	300	356.2	*J. Mater. Chem. A* **2018,** *6* (15), 6595-6605
WS_2/MoS_2@carbon	500	250	411.8	*Chem. Eng. J.* **2022,** *443*.
ReS_2@NiS_2	1000	400	220	*Chinese Chemical Letters* **2021,** *32* (11), 3607-3612.
MnS-CoS_2-NC@NC	1000	900	436	*Nano Research* **2022,** *15* (4), 3273-3282