

Supplementary Information for

Solvothermal synthesis and electrochemical properties of S-doped Bi₂Se₃ hierarchical microstructure assembled by stacked nanosheets

Fangxin Mao,^{a, b ‡} Jing Guo,^{b ‡} Shaohua Zhang,^c Fan Yang,^b Qiao Sun,^a Jianmin Ma,^{b*} and Zhen Li^{a*}

^a Center for Molecular Imaging and Nuclear Medicine, School for Radiological and Interdisciplinary Sciences (RAD-X), Soochow University; Collaborative Innovation Center of Radiation Medicine of Jiangsu Higher Education Institutions, Suzhou, 215123, China. Email :zhenli@suda.edu.cn

^b Key Laboratory for Micro-/Nano-Optoelectronic Devices of the Ministry of Education, School of Physics and Electronics, Hunan University, Changsha 410082, P. R. China. nanoelechem@hnu.edu.cn

^c Institute for Superconducting & Electronic Materials, The University of Wollongong, NSW 2500, Australia.

[‡]F. X. Mao and J. Guo make equal contributions to the manuscript.

Materials synthesis

S-doped Bi₂Se₃ hierarchical microstructures were synthesized from bismuth trichloride and selenium powder in the presence of mercaptoethanol by a solvothermal method. In a typical synthesis, 0.5 mmol Bismuth trichloride was dissolved in a mixture of 0.5 mL mercaptoethanol and 15 mL ethanediamine, and 0.5 mmol selenium was dissolved in another mixture with the same amount of mercaptoethanol and ethanediamine. Two solutions were mixed together under drastic magnetic stirring, and then 0.35 mmol EDTA (ethylenediamine tetraacetic acid disodium salt) was added and stirred for another 5 min. The mixture solution was transferred into a Teflon-lined stainless steel autoclave with a capacity of 50 mL. The autoclave was sealed and heated at 120 °C for 24 h in an electric furnace, and then cooled naturally to room temperature. The product was collected and washed with absolute ethanol and distilled water for several times, and dried at 60 °C in a vacuum drying chamber. The evolution of sample morphology was investigated by characterization of samples prepared at ambient temperature without solvothermal treatment, and solvothermally treated at 120 °C for 1 h, 3 h, and 12 h. To investigate the impacts of S-doping or addition of EDTA on the morphology and crystalline structure of samples, similar reactions were conducted without mercaptoethanol or EDTA under the same conditions, and the resultant product was purified by the same way.

Materials characterization

The morphology of samples was characterized by scanning electron microscope (SEM; Hitachi S-4800, Japan) and Transmission Electron Microscope (TEM; Tecnai G2 spirit BioTwin). Their crystal structures were characterized by powder X-ray diffraction (XRD; Model D8 Advance, Bruker, Germany) with Cu K α 1 radiation (40 KV, 40 mA). Raman spectra were recorded on a micro-Raman spectroscopy. The elemental

components and their contents were quantitative analyzed with ICP-OES (inductively coupled plasma optical emission spectroscopy). The elemental mapping was determined by scanning transmission electron microscopy X-ray energy dispersive spectrometry (STEM-XEDS). X-ray photoelectron spectroscopy was measured to further investigate the composition of products. Their Brunauer-Emmett-Teller (BET) surface area was determined using a Micromeritics model ASAP 2020M+C physical and chemical adsorption analyzer.

Electrochemical evaluation

CR2032 coin cells were assembled in a glove box filled with argon and were used for characterizing the electrochemical performance of S-doped Bi₂Se₃ hierarchical microstructure. The lithium metal serves as the counter and reference electrodes. The working electrode paste was prepared by mixing the active material, conductive agent (super-P) and binder PVDF (poly (vinyl difluoride)) with a weight ratio of 8: 1: 1, the resultant slurry was deposited onto the pure Cu foam with a thickness of 15 μ m, and then cut into round shape with a radius of 0.8 cm. Celgard polypropylene membrane was used as a separator. LiPF₆ solution was used as electrolyte prepared by dissolving 1 M LiPF₆ in EC (ethylene carbonate)/ DMC (dimethyl carbonate)/ DEC (diethyl carbonate) with a weight ratio of 1: 1: 1.

To evaluate the performance of cells, CV (cyclic voltammograms) was measured with the Arbin battery test system in a voltage range of 0.01-3.0 V. Charge-discharge cycles and rate performance were carried on a Land CT2001A battery test system with current densities of 50 mA g⁻¹ and 50, 100, 250, 500 mA g⁻¹ between the voltage of 0.01- 3.0 V.

Table. S1 Comparison of electrochemical performance of Bi₂Se₃ nanostructures from current work as anode of lithium ion batteries with literature reports.

Structure	Performance	Ref.
S-doped Bi ₂ Se ₃ hierarchical microspheres assembled from nanosheets	238.9/109.4 mAh g ⁻¹ after 30/100 cycles	Present work
Bi ₂ Se ₃ rectangular/self-assembled nanosheets	34 mAh g ⁻¹ after 50 cycles	1
Bi ₂ Se ₃ rectangular hierarchical microrods	55 mAh g ⁻¹ after 49 cycles	2
Bi ₂ Se ₃ stacking / individual nanosheets	45/30 mAh g ⁻¹ after 50 cycles	3
Bi ₂ Se _{3-x} S _x nanoflowers/Bi ₂ Se ₃ nanoplates	235.1/123.4 mAh g ⁻¹ after 30 cycles	4
In-doped Bi ₂ Se ₃ hierarchical nanostructures	160.3 mAh g ⁻¹ after 50	5

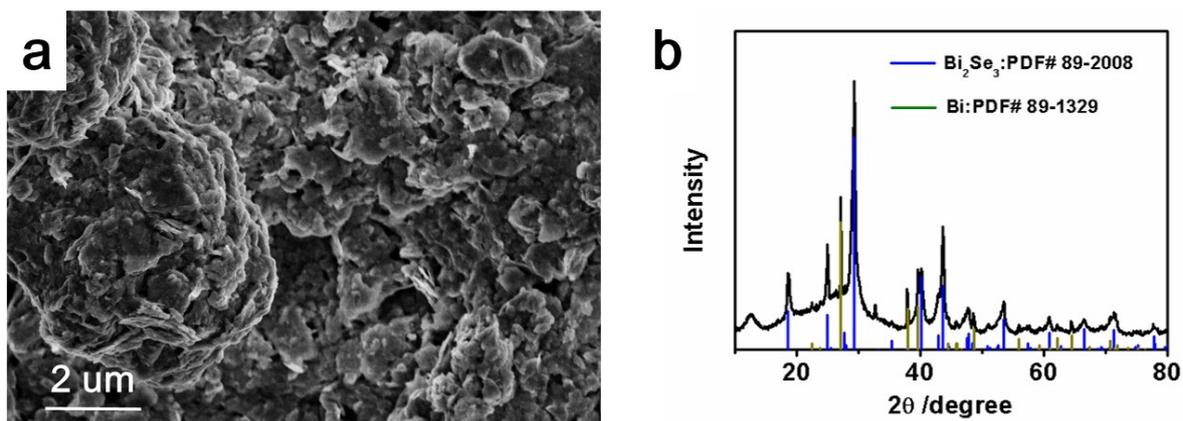


Fig. S1 (a) SEM image and (b) XRD of Bi₂Se₃ synthesized without mercaptoethanol.

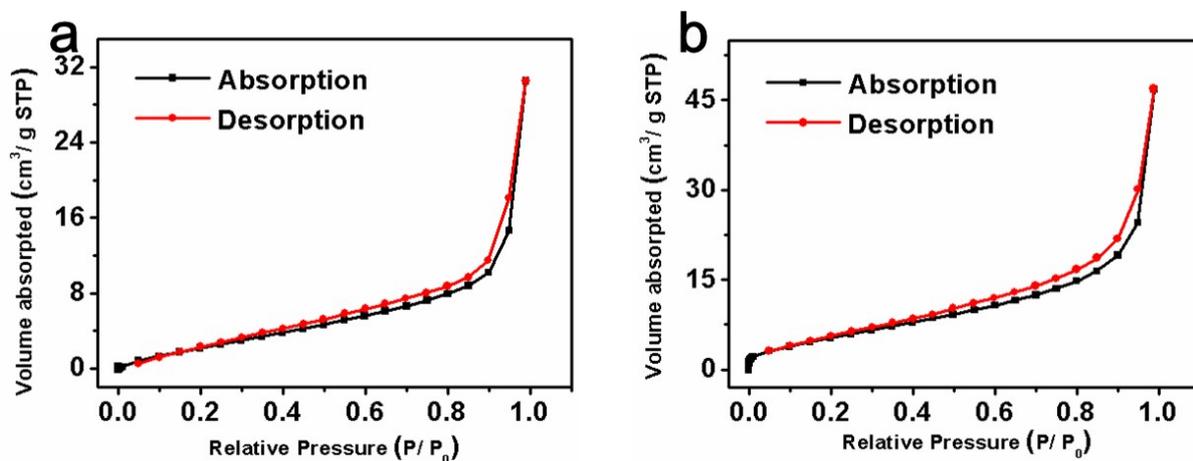


Fig. S2 Specific surface area of (a) S-doped Bi₂Se₃; (b) undoped sample

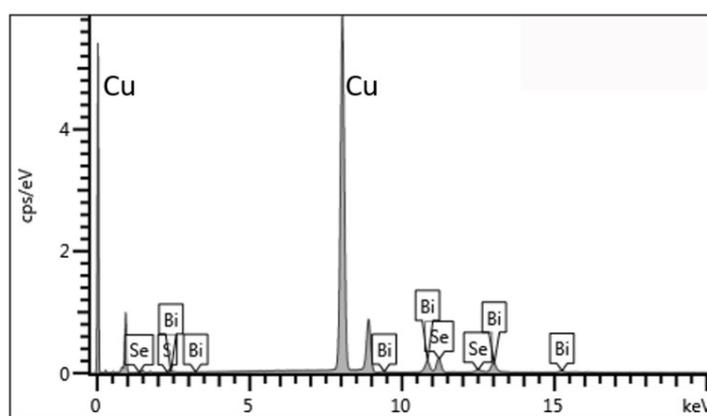


Fig. S3 EDS of the electoral district for face scanning for S-doped Bi₂Se₃ hierarchical microsphere under STEM.

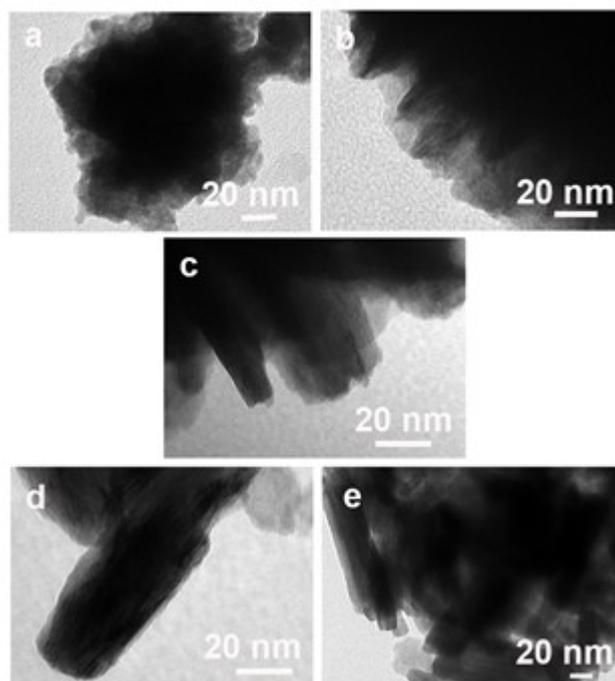


Fig. S4 (a-e) TEM images of samples prepared at ambient temperature, and at 120°C for 1h, 3h, 12h, and 24h, and prepared in the absence of EDTA.

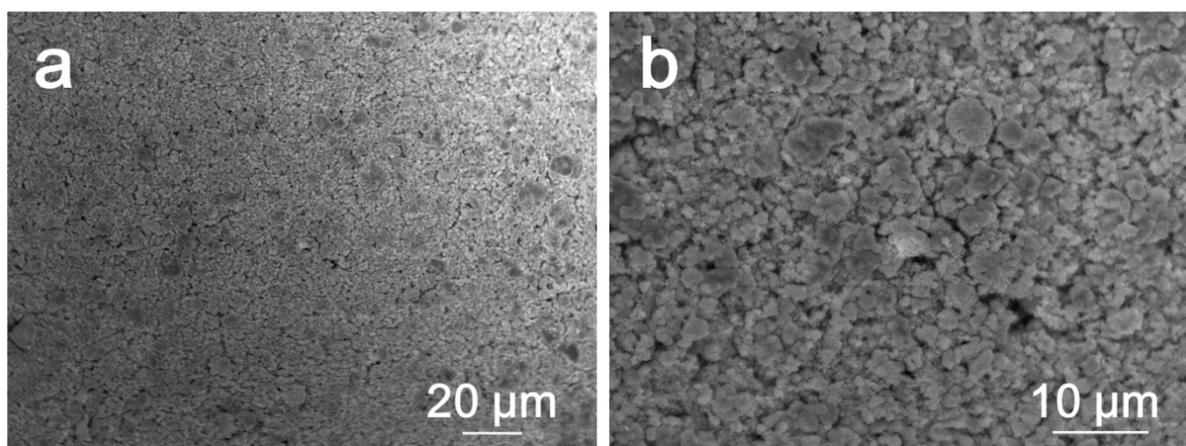


Fig. S5 SEM of the electrode material after tested 100 charging-discharging cycles: (a) low and (b) high magnification.

1. Z. Ali, C. Cao, J. Li, Y. Wang, T. Cao, M. Tanveer, M. Tahir, F. Idrees and F. K. Butt, *J. Power Sources*, 2013, 229, 216-222.
2. H. Xu, G. Chen, R. Jin, J. Pei, Y. Wang and D. Chen, *Crystengcomm*, 2013, 15, 1618-1625.
3. H. Xu, G. Chen, R. Jin, D. Chen, Y. Wang and J. Pei, *RSC Adv.*, 2014, 4, 8922-8929.
4. R. Jin, J. Liu, Y. Xu, G. Li, G. Chen and L. Yang, *J. Mater. Chem. A.*, 2013, 1, 10942-10950.
5. G. Han, Z.-G. Chen, D. Ye, L. Yang, L. Wang, J. Drennan and J. Zou, *J. Mater. Chem. A.*, 2014, 2, 7109-7116.