

Unveiling the Reaction Mechanism of Sb₂S₃-Co₉S₈/NC Anode for High-Performance Lithium-Ion Batteries

Guanxia Ke^a #, Xiaochao Wu^a #, Huanhui Chen^{a, b} #, Wanqing Li^a, Shuang Fan^a, Hongwei Mi^a *,
Yongliang Li^a, Qianling Zhang^a, Chuanxin He^a, Xiangzhong Ren^a *

^a*College of Chemistry and Environmental Engineering, International Joint Research Center for Molecular Science, Shenzhen University, Shenzhen, Guangdong 518060, P.R. China*

^b*Shenzhen Engineering Laboratory of Flexible Transparent Conductive Films, School of Materials Science and Engineering, Harbin Institute of Technology, Shenzhen 518055, P.R. China*

Corresponding author:

Xiangzhong Ren, E-mail: renxz@szu.edu.cn, Tel/Fax: +86-755-26558134

Hongwei Mi, E-mail: milia807@szu.edu.cn, Tel/Fax: +86-755-26538657

These authors contributed equally to this work and should be considered as co-first authors.

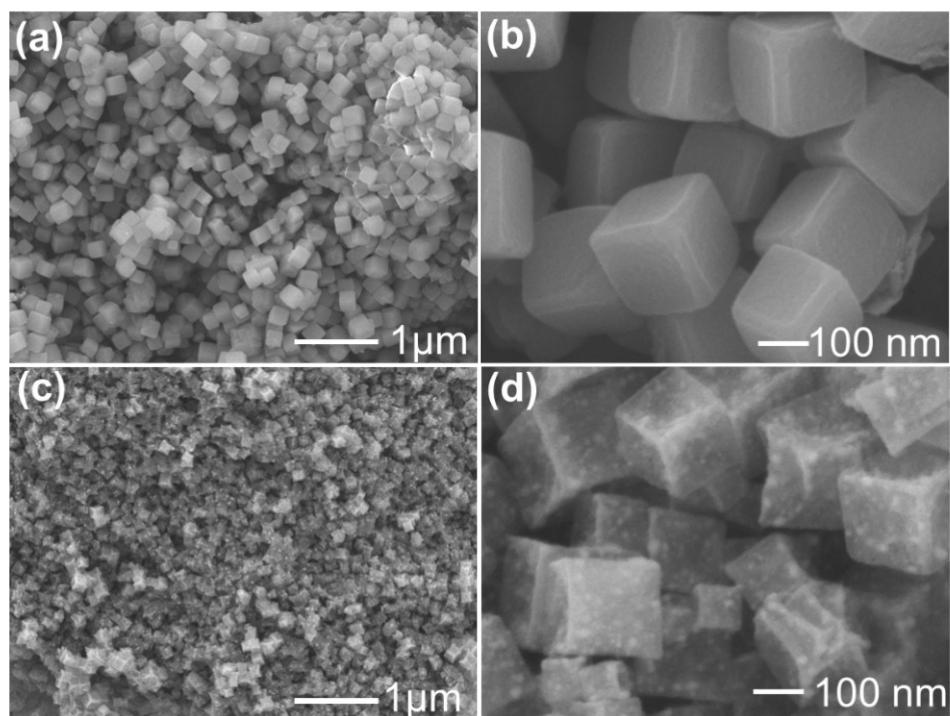


Fig. S1. SEM images of (a-b) the ZIF-67sample and (c-d) the Co/NC sample.

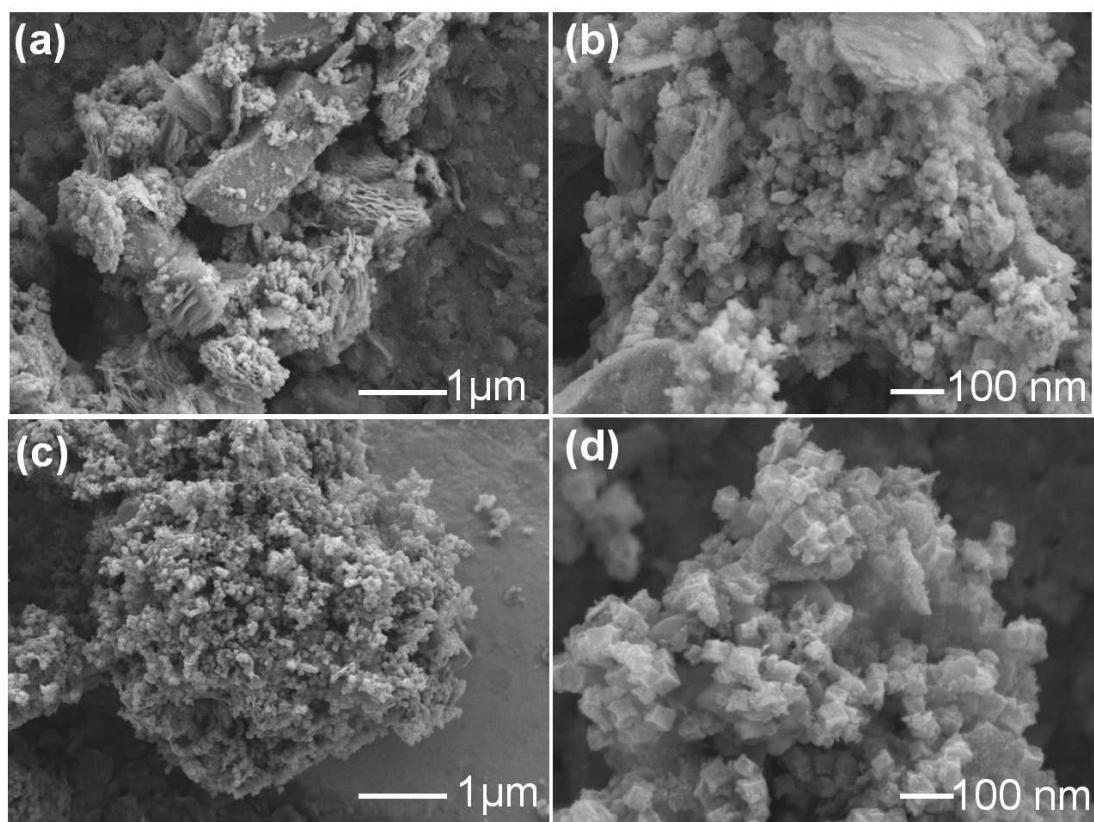


Fig. S2. SEM images of (a-b) the Sb₂S₃ sample and (c-d) the Co₉S₈/NC sample.

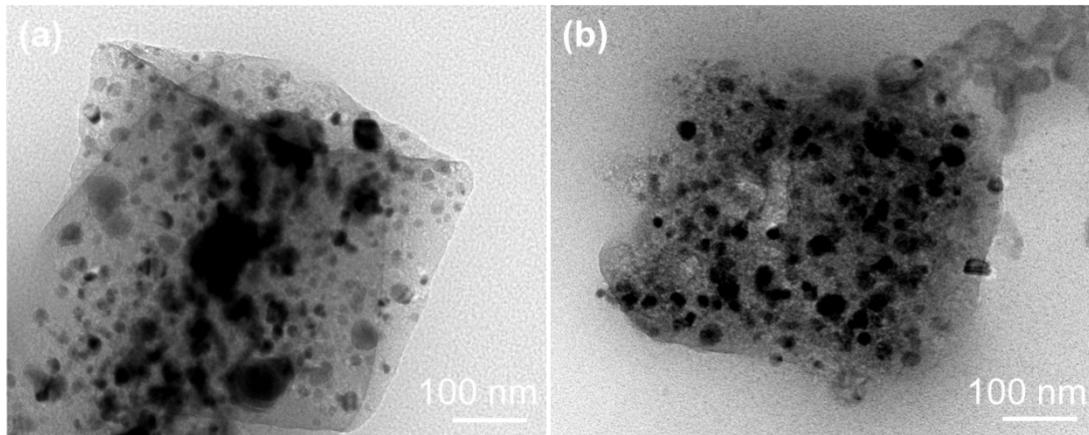


Fig. S3. TEM images of (a) the Co/NC sample and (b) the Co₉S₈/NC sample.

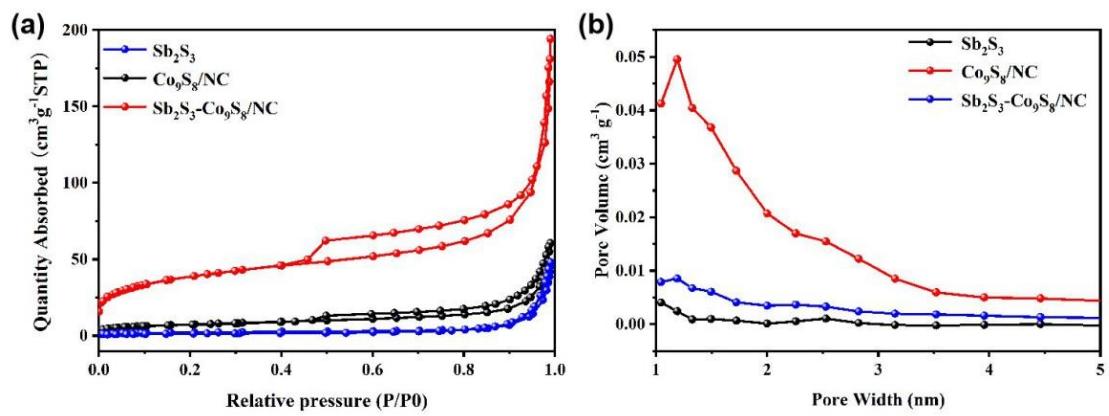


Fig. S4. (a) Nitrogen adsorption–desorption isotherm curves and (b) pore size distributions of Sb₂S₃, Co₉S₈/NC and Sb₂S₃-Co₉S₈/NC samples.

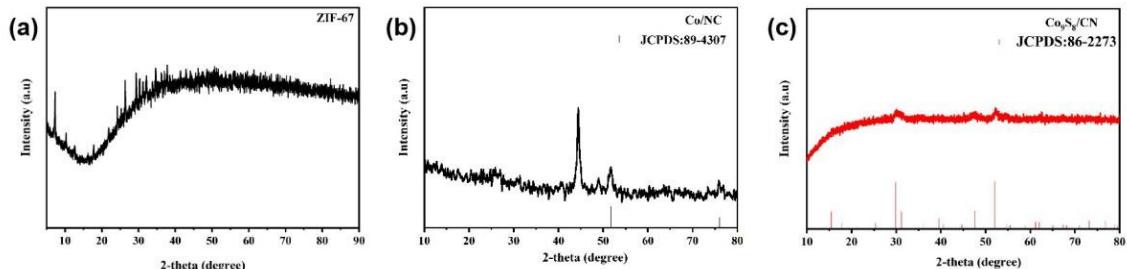


Fig. S5. XRD of (a) ZIF-67 sample, (b) Co/NC sample and (c) Co₉S₈/NC sample.

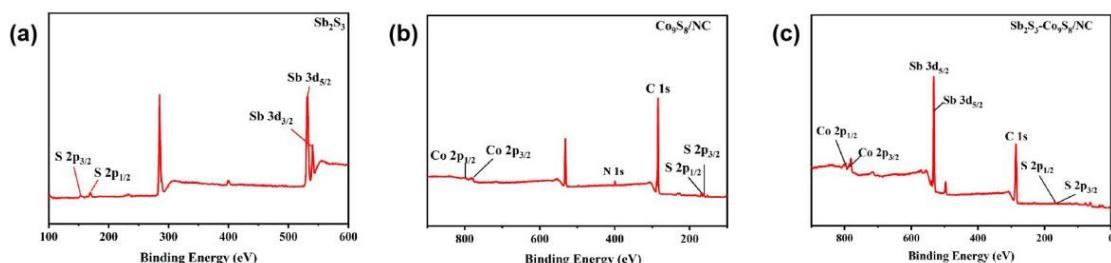


Fig. S6. XPS spectra of (a) the Sb₂S₃, (b) Co₉S₈/NC and (c) Sb₂S₃-Co₉S₈/NC.

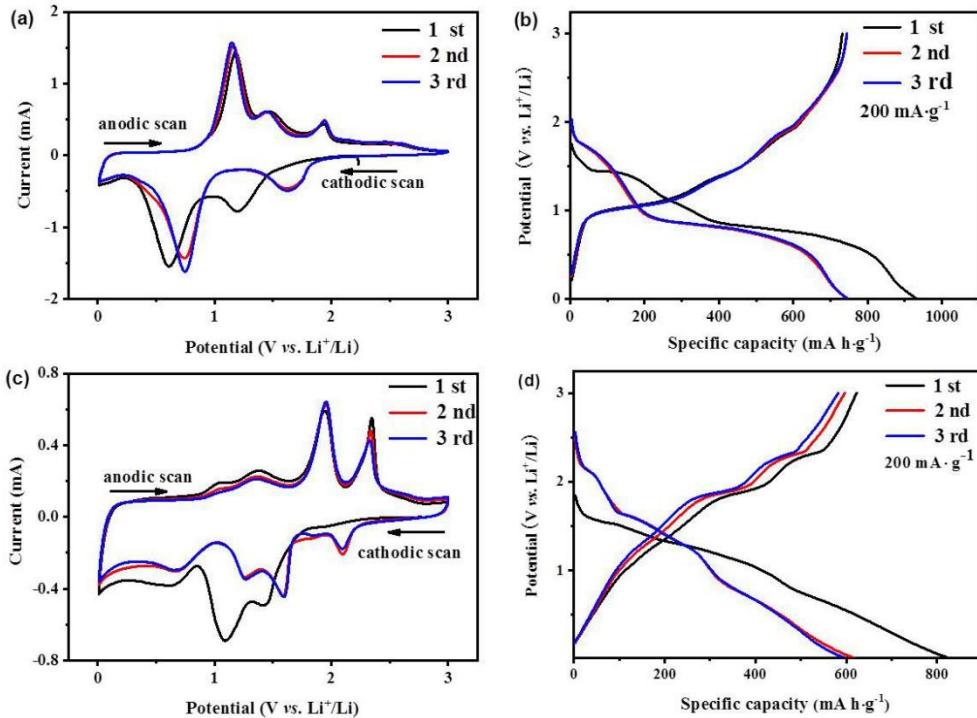


Fig. S7. (a)(c) CV curves of Sb₂S₃ and Co₉S₈/NC in the potential range at 0.01-3 V at 0.2 mV·s⁻¹; (b)(d) the discharge–charge curves of the Sb₂S₃ and Co₉S₈/NC at a current density of 0.2 A·g⁻¹.

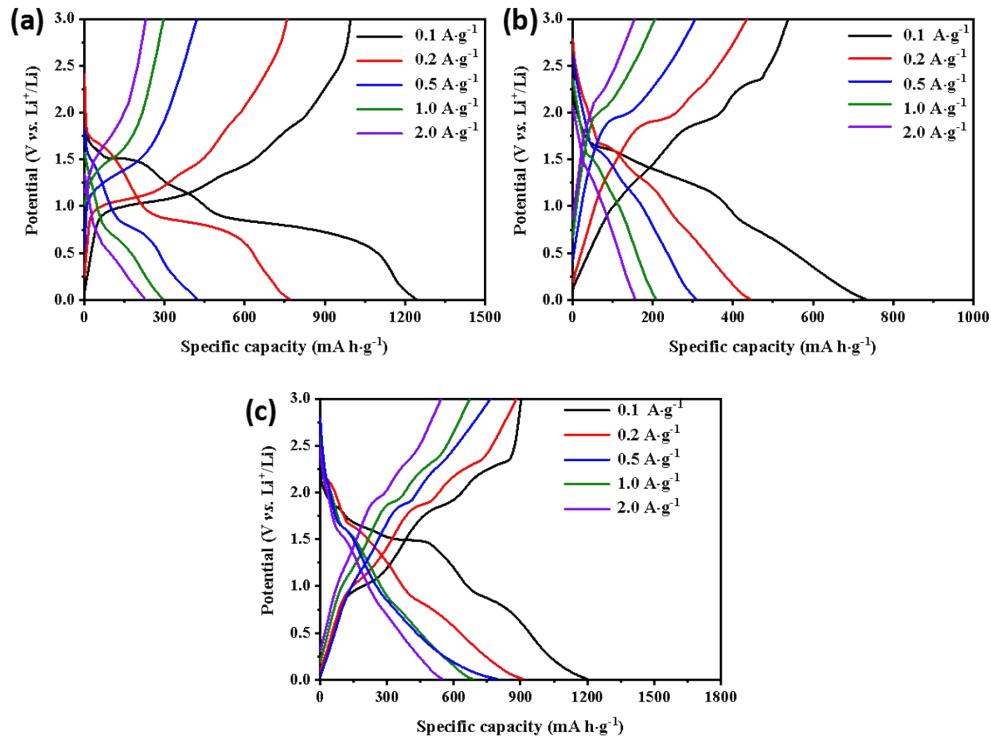


Fig. S8. The Charge / Discharge curves of Sb₂S₃(a), Co₉S₈/NC(b) and Sb₂S₃-Co₉S₈/NC at various rates.

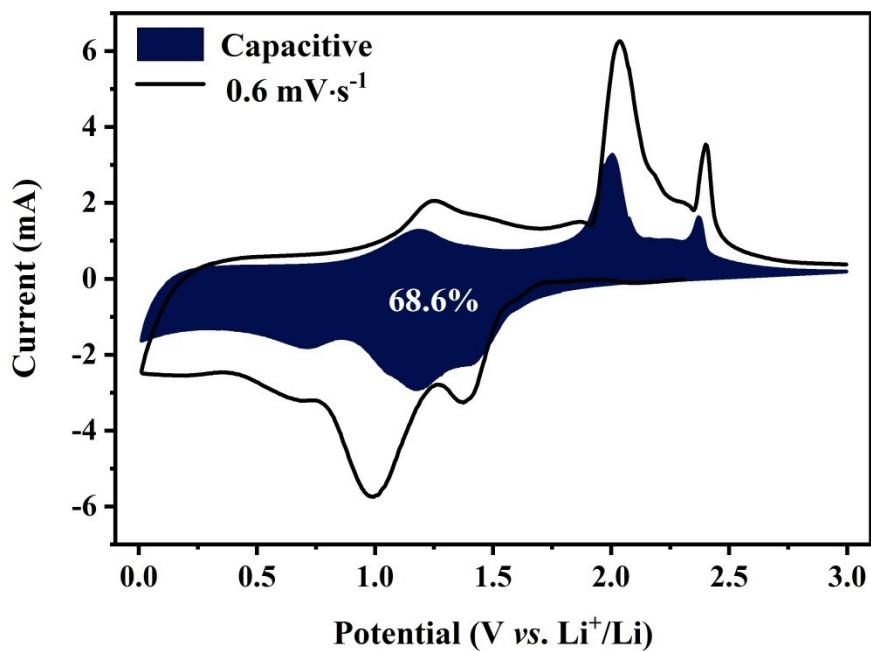


Fig. S9. CV curve with the pseudocapacitive contribution of $\text{Sb}_2\text{S}_3\text{-Co}_9\text{S}_8/\text{NC}$ at $0.6 \text{ mV}\cdot\text{s}^{-1}$.

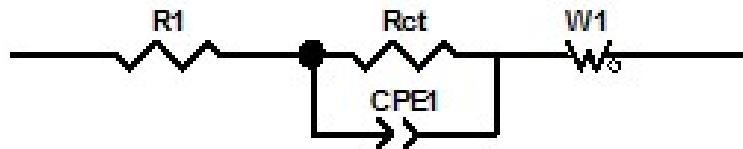


Fig. S10. The equivalent circuit of the samples.

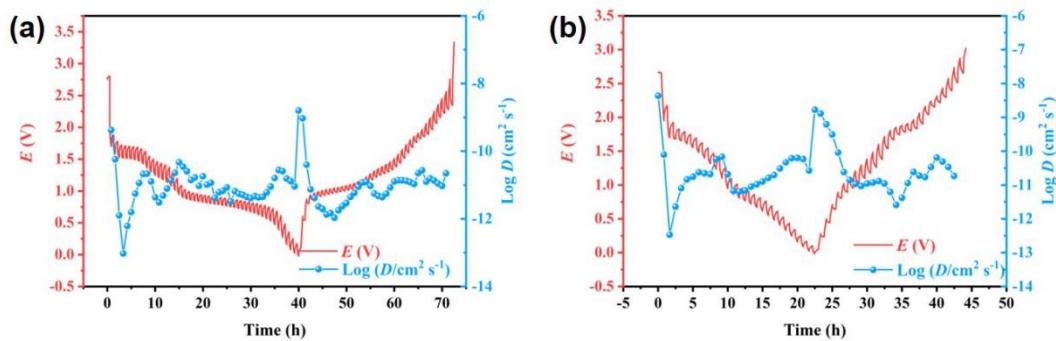


Fig. S11. GITT and DLi^+ curves of (a) Sb_2S_3 electrode and (b) $\text{Co}_9\text{S}_8/\text{NC}$ electrode.

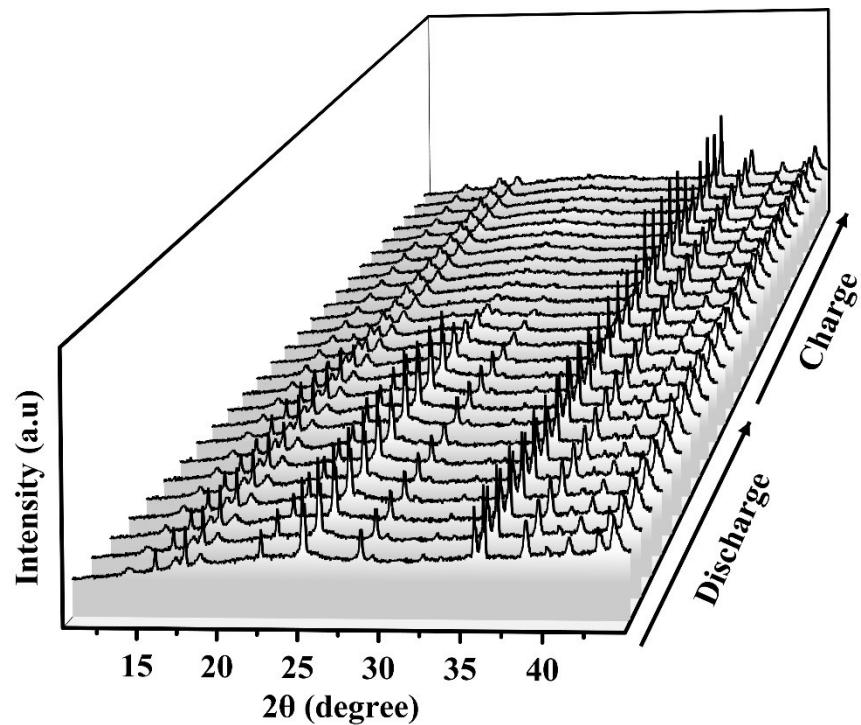


Fig. S12. 3D waterfall chart of Sb₂S₃-Co₉S₈/NC electrodes during the first cycle.

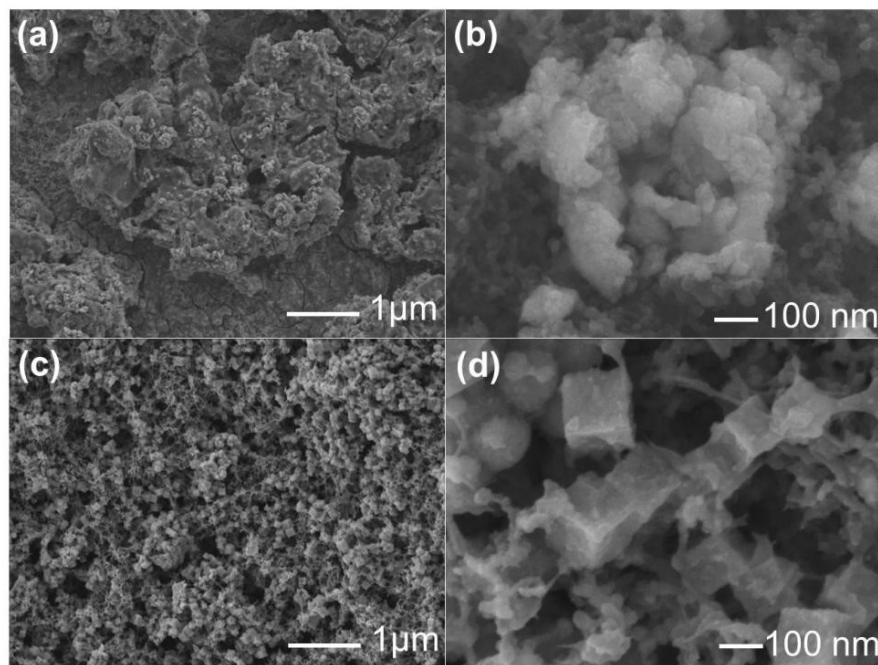


Fig. S13. SEM images of Sb₂S₃ (a, b) and Sb₂S₃-Co₉S₈/NC (c, d) at different magnifications after 100 cycles.

Table S1. Element content for $\text{Sb}_2\text{S}_3\text{-Co}_9\text{S}_8/\text{NC}$ obtained from ICP analysis.

Mass(g)	Element	Elemental content ($\text{mg}\cdot\text{L}^{-1}$)	Weight (%)
0.0344	Co	6.37	18.52
0.0344	S	6.43	18.68
0.0344	Sb	3.07	8.92

Table. S2. Comparison of the electrochemical lithium storage performance of the $\text{Sb}_2\text{S}_3\text{-Co}_9\text{S}_8/\text{NC}$ electrodes with the literature data.

Materials	Current density ($\text{mA}\cdot\text{g}^{-1}$)	cycle number (cycles)	Reversible Capacity ($\text{mA h}\cdot\text{g}^{-1}$)	reference
$\text{Sb}_2\text{S}_3\text{-Co}_9\text{S}_8/\text{NC-2}$	2000	900	616	This work
$\text{Sb}_2\text{S}_3/\text{EG-S}$	5000	100	548	1
$\text{Sb}_2\text{S}_3/\text{CS}$	200	200	566	2
$\text{Co}_9\text{S}_8@\text{MoS}_2$	1000	300	1048	3
$\text{Co}_9\text{S}_8/\text{ZnS}@/\text{NC}$	1000	300	411	4
hollow core–shell $\text{ZnCoS}@\text{Co}_9\text{S}_8/\text{NC}$	2000	400	1095	5
$\text{NiS}_2@\text{CoS}_2@\text{C}@/\text{C}$	1000	100	680	6
$\text{Bi}_2\text{S}_3@\text{Co}_9\text{S}_8$ CHPs	500	800	595	7
$\text{Co}_9\text{S}_8@\text{MPCNF-15}$	200	200	654	8
$\text{Co}_{1-x}\text{S}/\text{NC}@/\text{MoS}_2/\text{C}$	100	150	910	9
$\text{Co}_{1-x}\text{S}/\text{NCS}$	200	100	796	10

CoS ₂ -in-wall-NCSs	200	500	1165	11
Sb ₂ S ₃ hollow microspheres	1000	100	600	12
2D Sb ₂ S ₃	2000	10	750	13

References

- Wang, S.; Cheng, Y.; Xue, H.; Liu, W.; Yi, Z.; Chang, L.; Wang, L. Multifunctional sulfur-mediated strategy enabling fast-charging Sb₂S₃ micro-package anode for lithium-ion storage. *Journal of Materials Chemistry A* **2021**, *9*, 7838-7847.
- Xie, J.; Xia, J.; Yuan, Y.; Liu, L.; Zhang, Y.; Nie, S.; Yan, H. Sb₂S₃ embedded in carbon–silicon oxide nanofibers as high-performance anode materials for lithium-ion and sodium-ion batteries. *Journal Power Sources* **2019**, *435*, 226762.
- Yang, K.; Mei, T.; Chen, Z.; Xiong, M.; Wang, X.; Wang, J.; Li, J.; Yu, L.; Qian, J.; Wang, X. Chinese hydrangea lantern-like Co₉S₈@MoS₂ composites with enhanced lithium-ion battery properties. *Nanoscale* **2020**, *12*, 3435-3442.
- Duan, J.; Wang, Y.; Li, H.; Wei, D.; Wen, F.; Zhang, G.; Liu, P.; Li, L.; Zhang, W.; Chen, Z. Bimetal-organic Framework-derived Co₉S₈/ZnS@NC Heterostructures for Superior Lithium-ion Storage. *Chemistry an-Asian Journal* **2020**, *15*, 1613-1620.
- Aslam, M K.; Shah, S. S.; Li, S.; Chen, C. Kinetically controlled synthesis of MOF nanostructures: single-holed hollow core–shell ZnCoS@Co₉S₈/NC for ultra-high performance lithium-ion batteries. *Journal of Materials Chemistry A* **2018**, *6*, 14083.
- Lin, Y.; Qiu, Z.; Li, D.; Ullah, S.; Hai, Y.; Xin, H.; Liao, W.; Yang, B.; Fan, H.; Xu, J.; Zhu, C. NiS₂@CoS₂ nanocrystals encapsulated in N-doped carbon nanocubes for high performance lithium/sodium ion batteries. *Energy Storage Materials* **2018**, *11*, 67-74.
- Huang, Y.; Hu, X.; Li, J.; Zhang, J.; Cai, D.; Sa, B.; Zhan, H.; Wen, Z. Rational construction of heterostructured core-shell Bi₂S₃@Co₉S₈ complex hollow particles toward high-performance Li- and Na-ion storage. *Energy Storage Materials*, **2020**, *29*, 121-130.
- Zhou, X.; Su, K.; Kang, W.; Cheng, B.; Li, Z.; Jiang, Z. Locking metal sulfide nanoparticles in interconnected porous carbon nanofibers with protective macro-porous skin as freestanding anodes for lithium ion batteries. *Chemical Engineering Journal* **2020**, *397*, 125271.
- Wang, Y.; Xie, W.; Li, D.; Han, P.; Shi, L.; Luo, Y.; Cong, G.; Li, C.; Yu, J.; Zhu, C.; Xu, J. One-pot synthesis of hierarchical Co_{1-x}S/NC@MoS₂/C hollow nanofibers based on one-dimensional metal coordination polymers for enhanced lithium and sodium-ion storage. *Science Bullet* **2020**, *65*, 1460-1469.
- Yang, Z.; Wang, J.; Wu, H.; Kong, F.; Yin, W.; Cheng, H.; Tang, X.; Qian, B.; Tao, S. MOFs derived Co_{1-x}S nanoparticles embedded in N-doped carbon nanosheets with improved electrochemical performance for lithium ion batteries. *Applied Surface Science* **2019**, *479*, 693-699.

11. Fang, L.; Zhang, Y.; Guan, Y.; Zhang, H.; Wang, S.; Wang, Y. CoS₂ nanodots trapped within graphitic structured N-doped carbon spheres with efficient performances for lithium storage. *Journal Materials Chemistry A* **2018**, *6*, 7148-7154.
12. Xie, J.; Liu, L.; Xia, J.; Zhang, Y.; Li, M.; Ouyang, Y.; Nie, S. Wang, X. Template-Free Synthesis of Sb₂S₃Hollow Microspheres as Anode Materials for Lithium-Ion and Sodium-Ion Batteries. *Nano-Micro Letters* **2018**, *10*, 12.
13. Yao, S.; Cui, J.; Deng, Y.; Chong, W.; Kim, J. K. Ultrathin Sb₂S₃ Nanosheet Anodes for Exceptional Pseudocapacitive Contribution to Multi-battery Charge Storage. *Energy Storage Material* **2018**, *20*, 36-45.