Electronic Supplementary Information

Surface-Dominated Potassium Storage Enabled by Single-Atomic Sulfur for High-Performance K-Ion Battery Anode

Guo-Zhan Yang^a, Yan-Fei Chen^a, Bao-Qi Feng^a, Chen-Xin Ye^a, Xue-Bin Ye^a, Hongchang Jin^b, En Zhou^b, Xian Zeng^a, Ze-Lin Zheng^a, Xue-Ling Chen^a, De-Shan Bin^{* a}, and An-Min Cao^{* c}

a. College of Chemistry and Materials Science, and Guangdong Provincial Key Laboratory of Functional Supramolecular Coordination Materials and Applications, Jinan University, Guangzhou 510632, P.R. China. E-mail: bindeshan@jnu.edu.cn.
b. Hefei National Laboratory for Physical Sciences at the Microscale, and Department of Applied Chemistry, University of Science and Technology of China, Hefei 230026 (P. R. China)

c. CAS Key Laboratory of Molecular Nanostructure and Nanotechnology, and Beijing National Laboratory for Molecular Sciences, Institute of Chemistry, Chinese Academy of Sciences (CAS), Beijing 100190 (P. R. China). University of Chinese Academy of Sciences, Beijing 100049 (P. R. China). E-mail: anmin_cao@iccas.ac.cn



Figure S1. Scheme of the synthesis route for the three-shelled hollow resin nanoparticles and the hollow carbon nanoparticles.



Figure S2. TEM images of three-shelled hollow 3-AF resin nanospheres (3S-AFs).



Figure S3. TEM images of single-atomic sulfur bonded to the hollow carbon

nanospheres (ASHCs).



Figure S4. Element mapping of ASHCs, there are C, S, O, N elements. The scale bar is 200 nm.



Figure S5. XPS spectrogram of the ASHCs.



Figure S6. TEM of HCs obtained at 450 °C carbonization.



Figure S7. TEM of S₈/HCs.



Figure S8. The pore size distribution of ASHCs, HCs and S_8 /HCs. The pore volumes for ASHCs (0.18 cm³ g⁻¹) are much larger than HCs (0.06 cm³ g⁻¹), and S_8 /HCs (0.016 cm³ g⁻¹).



Figure S9. Raman spectrum of ASHCs and HCs. The formation of amorphous carbon could also be confirmed by Raman spectrum, which showed typical peaks of D band (1366 cm⁻¹) and G band (1553 cm⁻¹). The Raman spectrum showed obvious signal of the C-S at 403 cm⁻¹ for ASHCs and no visible signal for S-S bond was observed.



Figure S10. TOF-SIM spectrums of the ASHCs sample.



Figure S11. The electronic conductivity for ASHCs and S_8/HCs .



Figure S12. The initial charge/discharge profiles of ASHCs at 0.03A g^{-1} .



Figure S13. The charge/discharge profiles at different current densities.



Figure S14. Rate performance of representative high-capacity anodes for KIBs¹⁻⁸.



Figure S15. The comparison of electrochemical performance for the ASHCs annodes prepared with PVDF binder and CMC/SBR binder. (a) The charge/discharge profiles for the first cycle at 0.05 A g^{-1} (b) The cyclability at 0.15A g^{-1} .



Figure S16. (a) SEM image of ASHCs electrode before potassiation; (b) SEM image of ASHCs electrode after potassiation at 0.09 A g^{-1} .



Figure S17. TEM image of ASHCs after rate performance test at different current density of 0.05, 0.2, 0.4, 0.8, 1.0, 1.5A g⁻¹. Every C rate repeated 5 cycles.



Figure S18. CV curves of ASHCs at 0.2-1 mVs⁻¹. More details to show how the data was analysed: The relationship of peak current (*i*) and the scan rate (*v*) was expressed by Equation (1), which could also be written as Equation (2)^{9,10}:

$$i = av^b \tag{1}$$

 $\log i = b \log v + \log a \tag{2}$

The value of *b* would highly related to the K^+ storage behaviors. Generally, *b*=0.5 suggested the diffusion-limited process, and *b*=1 suggests capacitive-controlled one.

Moreover, to quantify the contribution of diffusion and capacitance, Equation (3) is introduced:

$$i(v) = k_1 v + k_2 v^{1/2} \tag{3}$$

Equation (3) could also be written as Equation (4):

$$i(v)/v^{1/2} = k_1 v^{1/2} + k_2 \tag{4}$$

In Equation (3), v is the scan rates, k_1 and k_2 were constants. k_1v and $k_2v^{1/2}$ reflected as the capacitive-controlled contribution and diffusion-controlled contribution, respectively. Based on Equation (4), we were able to determine the value of k_1 and calculated the capacitive and diffusion contribution.



Figure S19. The capacity contribution of the single-atomic sulfur species in ASHCs at $0.03A \text{ g}^{-1}$ at the second cycle. The content of sulfur was quantified to be 32.0 wt% by the element analysis (EA), Accordingly, the capacity contribution of the single-atomic sulfur species in ASHCs could be estimated by the equation:

$$C_{\text{sulfur}} = (C_{\text{ASHCs}} - 0.68 * C_{\text{HCs}})/0.32$$

Where C_{sulfur} is the capacity for the single-atomic sulfur species, C_{ASHCs} is the capacity for the ASHCs composite, C_{HCs} is the capacity for the HCs. We collected the data points at different voltages from ASHCs and HCs, calculated the capacity contribution of the single-atomic sulfur species, and then prepared the charge/discharge profile for the single-atomic sulfur species.

Table S1. The comparisons of specific surface area (SSA) of S-free carbon host and the S/C composite reported in the literatures.

Materials	SSA (S-free)/m ² g ⁻¹	SSA (with S)/m ² g ⁻¹	References
Carbon confined S ₂₋₄	308	8.5	ACS Nano 2019, 13, 2536-2543
SAC-350	228	27	Energy Storage Materials, 2020, 27, 426-434
SPOF	33.1	28.9	J. Energy Chem., 2021, 62, 645-652
SHCS	355.8	8.3	Adv.Mater. 2019, 31, 1900429
MOF-C/S/PDAc	628.5	97.8	Adv. Energy Mater. 2020, 10, 2000931
S-MCS-600	1525.2	1006.7	Electrochim. Acta., 2017, 241, 63-72
S-NC	432	56	Energy Storage Materials, 2020, 27, 212- 225
ASHCs	52.9	268	This work

Anodes	Reversible Capacity	ICE	References
SHCS	581 mAh g ⁻¹ at 0.025 A g ⁻¹	51.4%	Adv. Mater. 2019, 32, 1900429
SNHC	~300 mAh g ⁻¹ at 0.1 A g ⁻¹	~36.6%	Adv. Energy Mater. 2019, 9, 1901379
SPOF	557 mAh g ⁻¹ at 0.05 A g ⁻¹	73.2%	J. Energy Chem. 2021, 62, 645-652
S-PAN	610 mAh g ⁻¹ at 0.05 A g ⁻¹	64.8%	ACS Nano 2021, 15, 18419-18428
NSCN ₃₀	408 mAh g ⁻¹ at 0.05 A g ⁻¹	33.0%	J. Energy Chem. 2022, 66, 195-204
S/N-PHCs	461 mAh g ⁻¹ at 0.1 A g ⁻¹	67.7%	Chem. Eng. J. 2021, 409, 127383
SHC-3	365 mAh g ⁻¹ at 0.05 A g ⁻¹	51.3%	J. Energy Chem. 2022, 68, 688-698
SO-SC	~435 mAh g ⁻¹ at 0.1 A g ⁻¹	58.1%	Electrochim. Acta. 367 (2021) 137526
ASHCs	686 mAh g ⁻¹ at 0.03A g ⁻¹ 651 mAh g ⁻¹ at 0.05A g ⁻¹ 616 mAh g ⁻¹ at 0.15 A g ⁻¹	68.4% (0.05A g ⁻¹)	This work

Table S2. The reversible capacity of reported S/C composite in KIB anode.

Notes: All the specific capacities were calculated based on the mass of S/C composite; all the capacities are from the initial cycles. ICE is initial coulombic efficiency.

Materials	S2p3/2 (eV)	S2p3/2 (eV)	References
Elemental sulfur (S ₈)	164.0	165.2	This work
Elemental sulfur (S ₈)	164.0	165.2	ACS Energy Lett. 2016, 1, 431-437
CNT confined 1D long-chain S	164.1	165.2	J. Am. Chem. Soc. 2015, 137, 2215- 2218
Confined and covalent $S_x(x \ge 2)$	163.9	165.3	Electrochim. Acta 2019, 293, 191-198
Confined $S_x (x=2-4)$	163.7	164.8	J. Am. Chem. Soc. 2012, 134, 18510- 18513
Confined and covalent $S_x(x \ge 2)$	163.7	/	Adv. Mater. 2019, 31, 1900429
Single-atomic S (C-S-C)	163.4	164.5	This work

Table S3. The binding energy for S2p for the different sulfur species from different S/C composites.

Notes: It has been reported that the formation of S-C bond would make the binding energy of S2p shifts to the lower binding energy¹¹. From Table S3, we could also find that with the increase of the length of chain S_x , the binding energy of S2p became lower. Accordingly, the single-atomic S in ASHCs has the lowest binding energy due to its shortest S chain (C-S₁-C).

Materials	Temperature for initiated S loss	References
S ₈ filled in porous carbon	~160 °C	Nat. Mater. 2009, 8, 500-506
CNT confined 1D long-chain S	~300 °C	Nat. Commun. 2013, 4,2162.
Confined S_x (x=2-4)	~400 °C	ACS Nano 2019, 13, 2536-2543
Confined and covalent $S_x(x \ge 2)$	~400 °C	Adv. Mater. 2019, 31, 1900429
Carbon bonded with chain S_x (x \leq 3)	~420 °C	Energy Storage Materials, 2020, 27, 426-434
Single-atomic S (C-S-C)	~670 °C	This work

Table S4. The comparison of thermal stability of the different sulfur from different S/C composites.

Notes: That the much better thermal stability of ASHCs than that for chain- S_x (x ≥ 2) grafted carbon or carbon-confined small-molecule sulfur composite could be ascribed to the stronger bond energy (272 kJ mol⁻¹) of C-S bond in ASHCs sample than that of S-S (251 kJ mol⁻¹) bond¹².

Supplemental References

(1) An, Y.; Tian, Y.; Ci, L.; Xiong, S.; Feng, J.; Qian, Y., Micron-Sized Nanoporous Antimony with Tunable Porosity for High-Performance Potassium-Ion Batteries, *ACS Nano*, **2018**, *12*, 12932-12940.

(2) Ding, J.; Zhang, H.; Zhou, H.; Feng, J.; Zheng, X.; Zhong, C.; Paek, E.; Hu, W.; Mitlin, D., Sulfur-Grafted Hollow Carbon Spheres for Potassium-Ion Battery Anodes, *Adv. Mater.*, **2019**, *31*, e1900429.

(3) Jin, H.; Wang, H.; Qi, Z.; Bin, D. S.; Zhang, T.; Wan, Y.; Chen, J.; Chuang, C.; Lu, Y. R.; Chan, T. S.; Ju, H.; Cao, A. M.; Yan, W.; Wu, X.; Ji, H.; Wan, L. J., A Black Phosphorus-Graphite Composite Anode for Li-/Na-/K-Ion Batteries, *Angew. Chem. Int. Ed.*, **2020**, *59*, 2318-2322.

(4) Lei, K.; Wang, C.; Liu, L.; Luo, Y.; Mu, C.; Li, F.; Chen, J., A Porous Network of Bismuth Used as the Anode Material for High-Energy-Density Potassium-Ion Batteries, *Angew. Chem. Int. Ed.*, **2018**, *57*, 4687-4691.

(5) Qiu, H.; Zhao, L.; Asif, M.; Huang, X.; Tang, T.; Li, W.; Zhang, T.; Shen, T.; Hou, Y., SnO2 nanoparticles anchored on carbon foam as a freestanding anode for high performance potassium-ion batteries, *Energy Environ. Sci.*, **2020**, *13*, 571-578.

(6) Zhang, W.; Mao, J.; Li, S.; Chen, Z.; Guo, Z., Phosphorus-Based Alloy Materials for Advanced Potassium-Ion Battery Anode, *J. Am. Chem. Soc.*, **2017**, *139*, 3316-3319.

(7) Ge, J.; Fan, L.; Wang, J.; Zhang, Q.; Liu, Z.; Zhang, E.; Liu, Q.; Yu, X.; Lu, B., MoSe2/N-doped carbon as anodes for potassium-ion batteries, *Adv. Energy Mater.*, **2018**, *8*, 1801477.

(8) Fang, K.; Liu, D.; Xiang, X.; Zhu, X.; Tang, H.; Qu, D.; Xie, Z.; Li, J.; Qu, D., Airstable red phosphorus anode for potassium/sodium-ion batteries enabled through dual-protection design, *Nano Energy*, **2020**, *69*, 104451.

(9) Augustyn, V.; Come, J.; Lowe, M. A.; Kim, J. W.; Taberna, P.-L.; Tolbert, S. H.; Abruña, H. D.; Simon, P.; Dunn, B. J. N. m., High-rate electrochemical energy storage through Li⁺ intercalation pseudocapacitance, *Nat. Mater.* **2013**, *12*, 518-522.

(10) Luo, X. X.; Li, W. H.; Liang, H. J.; Zhang, H. X.; Du, K. D.; Wang, X. T.; Liu, X. F.; Zhang, J. P.; Wu, X. L., Covalent Organic Framework with Highly Accessible Carbonyls and pi-Cation Effect for Advanced Potassium-Ion Batteries, *Angew. Chem. Int. Ed.*, **2022**, *61*, e202117661.

(11) Yuan, S.; Bao, J. L.; Wang, L.; Xia, Y.; Truhlar, D. G.; Wang, Y., Graphene-supported nitrogen and boron rich carbon layer for improved performance of lithium–sulfur batteries due to enhanced chemisorption of lithium polysulfides, *Adv. Energy Mater.*, **2016**, *6*, 1501733.

(12) Wei, S.; Ma, L.; Hendrickson, K. E.; Tu, Z.; Archer, L. A., Metal-Sulfur Battery Cathodes Based on PAN-Sulfur Composites, *J. Am. Chem. Soc.*, **2015**, *137*, 12143-12152.