## **Supporting information**

## The $K_{sp}$ gap enabled precipitation transformation reactions from transition metal hydroxides to sulfides for alkali metal ion storage

Qianrui Zhao, <sup>a</sup> Zhiwen Tang, <sup>a</sup> Yuede Pan, <sup>\*a,b</sup> Jingjing Han, <sup>a</sup> Jinbiao Yang, <sup>a</sup> Yongqiang Guo, <sup>a</sup> Xiangqian Lai, <sup>a</sup> Zhewei Yang, <sup>a</sup> Gang Li <sup>\*a</sup>

<sup>a</sup> Institute of Energy Innovation, College of Materials Science and Engineering, Taiyuan University of Technology, Taiyuan 030024, China.

<sup>b</sup> Key Laboratory of Advanced Energy Materials Chemistry (Ministry of Education), College of Chemistry, Nankai University, Tianjin 300071, China.

\*Corresponding authors:

panyuede@tyut.edu.cn (Y. Pan);

ligang02@tyut.edu.cn (G. Li);

Contents: Fig. S1–S5; Table S1



Fig. S1. Scanning electron microscope (SEM) image of  $Cu(OH)_2$  nanowires.



Fig. S2. Thermogravimetric (TG) curve of Cu(OH)<sub>2</sub> nanowires.



Fig. S3. X-ray photoelectron spectroscopy (XPS) curve of the CuS nanomaterial derived from Cu(OH)<sub>2</sub> nanowires.



Fig. S4. CV curve for the fifth cycle of the SIB at a sweep rate of 0.1 mV s<sup>-1</sup>.

Table S1. The chemical reaction equations corresponding to the redox peak of the cyclic voltammetry curves for the alkali metal ion batteries.

		Peak voltage		Podey equation	Drosoc
	-	1 <sup>st</sup> cycle	2 <sup>nd</sup> cycle	Redox equation	Process
reduction peak	SIB	1.91V	1.94	CuS + yNa <sup>+</sup> + ye <sup>-</sup> → Na <sub>y</sub> CuS (y < 0.5) (Irreversible reaction)	R1
		1.41V	1.41	$Na_yCuS + (x-y)Na^+ + (x-y)e^- → Na_xCuS$ $(0.5 < x < 1)$	
		1.11	-	Formation of SEI film	
		0.73V	0.73	$2Na_xCuS + (2-2x)Na^+ + (2-2x)e^- \rightarrow Cu_2S + Na_2S$	R2
		0.41V	0.38	$Cu_2S + 2Na^+ + 2e^- \rightarrow 2Cu + Na_2S$	R3
	LIB	2.03V	2.08	$CuS + yLi^+ + xe^- \rightarrow Li_yCuS$	R1
		1.58V	1.60	$Li_{y}CuS + (x-y)Li^{+} + (x-y)e^{-} \rightarrow Li_{x}CuS$	
		1.20V	1.24	$2Li_xCuS + (2-2x)Li^+ + (2-2x)e^- \rightarrow Cu_2S + Li_2S$	R2
		0.85V	0.85	$Cu_2S + 2Li^+ + 2e^- \rightarrow 2Cu + Li_2S$	R3
	PIB	1.76V	1.95	$CuS + xK^+ + xe^- \rightarrow K_xCuS$	<b>D1</b>
		1.20V	1.41		KI
		0.83	-	Formation of SEI film	
		0.51V	0.51	$K_x$ CuS + (2- $x$ )K <sup>+</sup> + (2- $x$ )e <sup>-</sup> → Cu + $K_2$ S	R3
Oxidation peak	SIB	1.79V	1.79	$2Cu + Na_2S \rightarrow Cu_2S + 2Na^+ + 2e^-$	01
		2.13V	2.13	$Cu_2S + Na_2S \rightarrow 2Na_xCuS + (2-2x)Na^+ + (2-2x)e^-$	02
	LIB	1.87V	1.87	$2Cu + Li_2S \rightarrow Cu_2S + 2Li^+ + 2e^-$	01
		2.06V	2.06	$Cu_2S + Li_2S \rightarrow 2Li_xCuS + (2-2x)Li^+ + (2-2x)e^{-1}$	02
		2.28V	2.28	$Li_xCuS \rightarrow CuS + xLi^+ + xe^-$	03
	PIB	1.44V	1.44	$Cu + K_2S \rightarrow K_xCuS + (2-x)K^+ + (2-x)e^{-x}$	01
		2.00V	2.04	$K_x CuS \rightarrow CuS + xK^+ + xe^-$	O3
		2.39V	2.45		



Fig. S5. Illustration of the peak voltage ranges for CuS storing  $Li^+$ ,  $Na^+$ , or  $K^+$  in literature.<sup>1-7</sup>

## References

- 1. Y. Li, Y. Zhang, Y. Wang, X. Li, Q. Zhang, H. Yan, X. Huang, H. Liu and Y. Zhang, Effect of ether-based electrolyte composition on the lithium storage performance of copper sulfide, *Electrochimica Acta*, 2020, **335**, 135662.
- Y. h. Zhang, L. j. Xu, R. h. Liu, Y. c. Wang, S. h. Luo, Q. Wang and X. Liu, CuS nanoblocks embedded in the three-dimensional porous carbon as composite anode materials for high-performance lithium-ion battery, *Ionics*, 2021, 27, 897-905.
- Y. Hu, L. Zhang, J. Bai, F. Liu, Z. Wang, W. Wu, R. Bradley, L. Li, H. Ruan and S. Guo, Boosting High-Rate Sodium Storage of CuS via a Hollow Spherical Nanostructure and Surface Pseudocapacitive Behavior, ACS Appl. Energy Mater., 2021, 4, 8901-8909.
- 4. D. Yu, M. Li, T. Yu, C. Wang, Y. Zeng, X. Hu, G. Chen, G. Yang and F. Du, Nanotube-assembled pine-needle-like CuS as an effective energy booster for sodium-ion storage, *J. Mater. Chem. A*, 2019, **7**, 10619-10628.
- Y. Xiao, D. Su, X. Wang, S. Wu, L. Zhou, Y. Shi, S. Fang, H.-M. Cheng and F. Li, CuS Microspheres with Tunable Interlayer Space and Micropore as a High-Rate and Long-Life Anode for Sodium-Ion Batteries, *Adv. Energy Mater.*, 2018, 8, 1800930.
- 6. T. G. Nithya C Morphology oriented CuS nanostructures: Superior K-ion storage by surface enhanced pseudocapacitive effects, *Sustain. Energy Fuels*, 2020, **4**, 1-16.
- 7. X. Jia, E. Zhang, X. Yu and B. Lu, Facile Synthesis of Copper Sulfide Nanosheet@Graphene Oxide for the Anode of Potassium-Ion Batteries, *Energy Technol.*, 2019, **8**, 1900987.