Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.
This journal is © The Royal Society of Chemistry 2018

Supporting Information

Dual Carbon-protected Metal Sulfides and Their Application to Sodium-ion Battery Anodes

Xinxin Zhu,[a] Dan Liu,*[bc] Dong Zheng,[c] Gongwei Wang,[c] Xingkang Huang,[c] Joshua Harris,[c] Deyu Qu*[b] and Deyang Qu*[c]

[a]School of Materials Science and Engineering, Wuhan University of Technology, 122 Luoshi Road, Wuhan 430070, P. R. China

[b]Department of Chemistry, School of Chemistry, Chemical Engineering and Life Sciences, Wuhan University of Technology, 122 Luoshi Road, Wuhan 430070, P. R. China

[c]Department of Mechanical Engineering, College of Engineering and Applied Science, University of Wisconsin-Milwaukee, 3200 N. Cramer Street, Milwaukee, WI 53211, USA

Correspong author Email: daniellliu@whut.edu.cn (Dan Liu), deyuquwuhan@163.com (Deyu Qu), qud@uwm.edu (Deyang Qu)

Table S1 The recipes for synthesis of various composites (MS@NC@G).

Products	Precursor	Solution A	Solution B	GO suspension ($6\ mg\ mL^{-1}$)
MnS@NC@G	$Mn(DDTC)_2$/GO	$MnCl_2\cdot 6H_2O$ (0.198 g; 1 mmol) in 25 mL of ethanol	$NaDDTC\cdot 3H_2O$ (0.45 g; 2 mmol) in 25 mL of ethanol	5 mL
$Fe_{1-x}S$@NC@G	$Fe(DDTC)_3$/GO	$FeCl_3\cdot 6H_2O$ (0.270 g; 1 mmol) in 25 mL of ethanol	$NaDDTC\cdot 3H_2O$ (0.676 g; 3 mmol) in 25 mL of ethanol	5 mL
Co_9S_8@NC@G	$Co(DDTC)_2$/GO	$CoCl_2\cdot 6H_2O$ (0.238 g; 1 mmol) in 25 mL of ethanol	$NaDDTC\cdot 3H_2O$ (0.45 g; 2 mmol) in 25 mL of ethanol	5 mL
Ni_3S_2@NC@G	$Ni(DDTC)_2$/GO	$NiCl_2\cdot 6H_2O$ (0.238 g; 1 mmol) in 25 mL of ethanol	$NaDDTC\cdot 3H_2O$ (0.45 g; 2 mmol) in 25 mL of ethanol	5 mL
ZnS@NC@G	$Zn(DDTC)_2$/GO	$ZnCl_2$ (0.136 g; 1 mmol) in 25 mL of ethanol	$NaDDTC\cdot 3H_2O$ (0.45 g; 2 mmol) in 25 mL of ethanol	5 mL
Cu_2S@NC@G	$Cu(DDTC)_2$/GO	$CuCl_2\cdot 2H_2O$ (0.17 g, 1 mmol) in 25 mL of ethanol	$NaDDTC\cdot 3H_2O$ (0.45 g; 2 mmol) in 25 mL of ethanol	5 mL

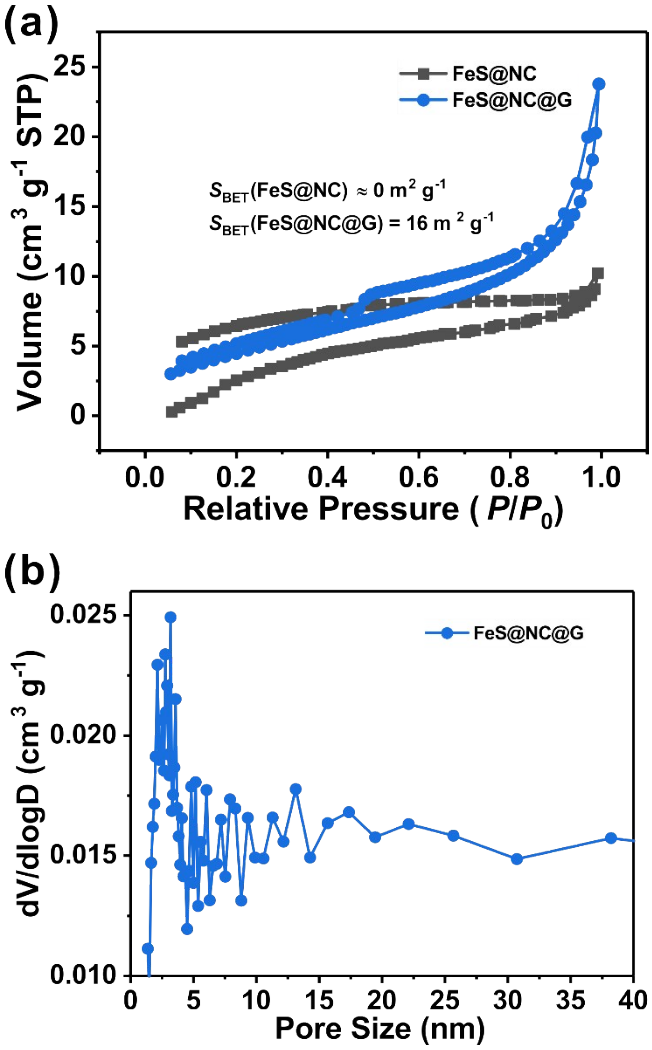

Figure S1 (a) Nitrogen sorption isotherms of FeS@NC and FeS@NC@G composites. (b) The corresponding BJH pore size distribution of FeS@NC@G composite.

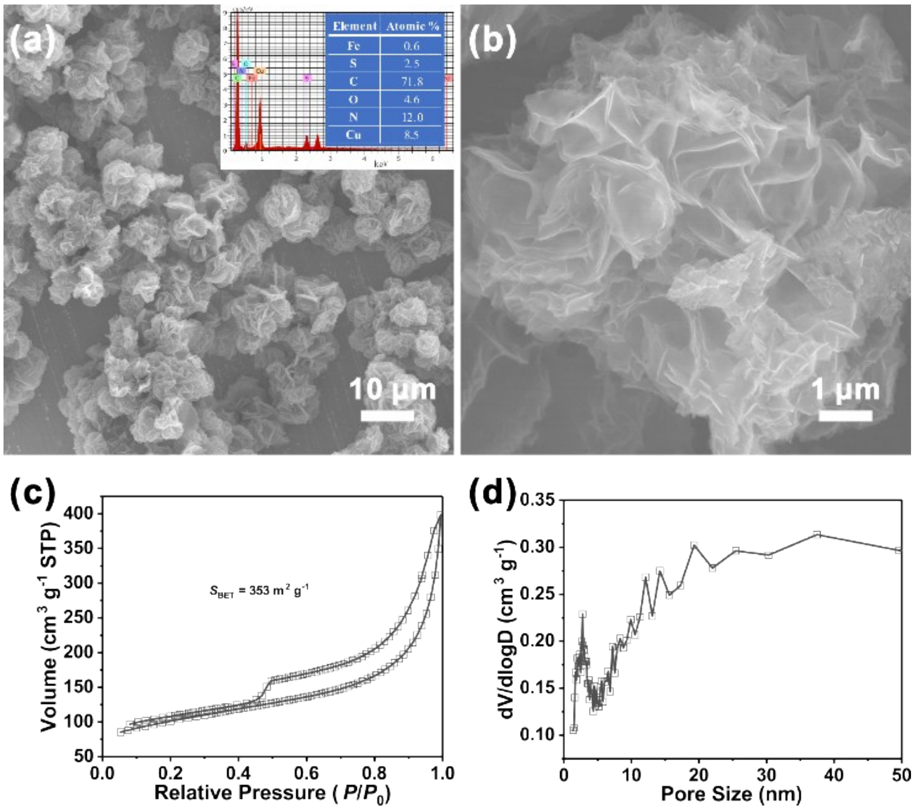

Figure S2 Characterization of porous carbon that was obtained by removing $Fe_{1-x}S$ component in $Fe_{1-x}S$@NC composite with aqua regia: (a, b) SEM images; (b) nitrogen sorption isotherm; (c) BJH pore size distribution curve.

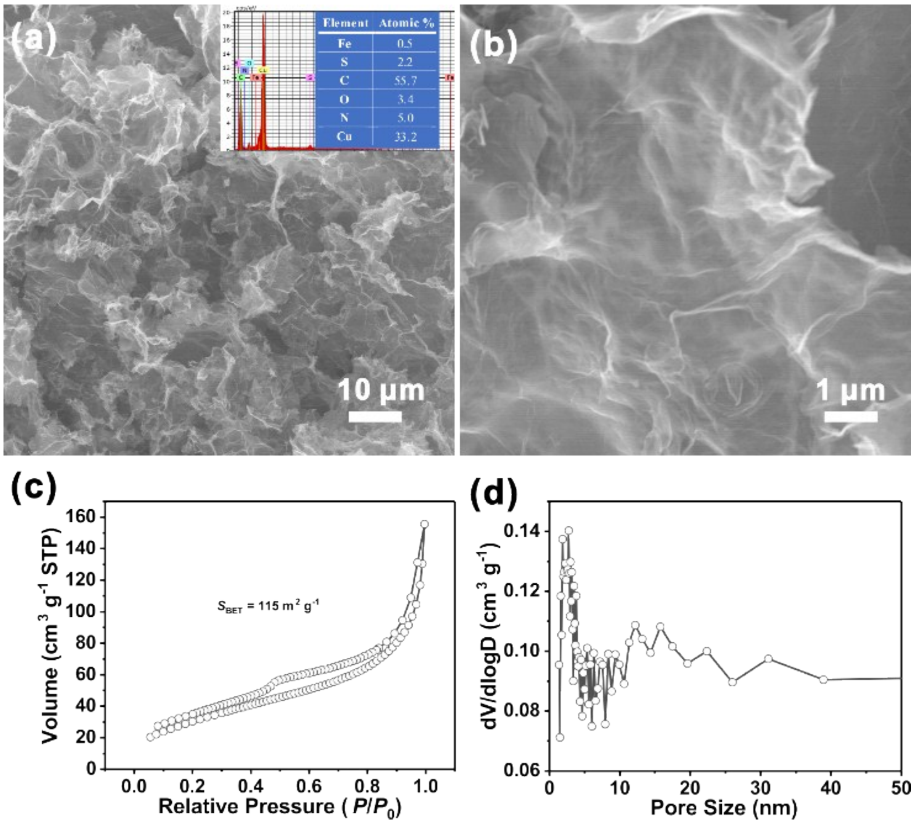

Figure S3 Characterization of porous carbon that was obtained by removing $Fe_{1-x}S$ component in $Fe_{1-x}S$@NC@G composite with aqua regia: (a, b) SEM images; (b) nitrogen sorption isotherm; (c) BJH pore size distribution curve.

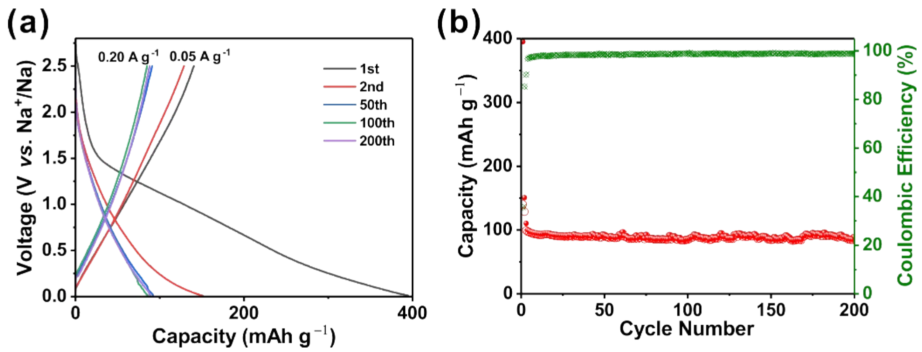

Figure S4 Electrochemical Na storage performance of porous carbon that was obtained by removing $Fe_{1-x}S$ component in $Fe_{1-x}S$@NC@G composite with aqua regia: (a) Representative galvanostatic discharge/charge profiles of the porous carbon at 0.2 A g^{-1} after initial two-cycle activation at 0.05 A g^{-1}; (b) cycling performance of the porous carbon.

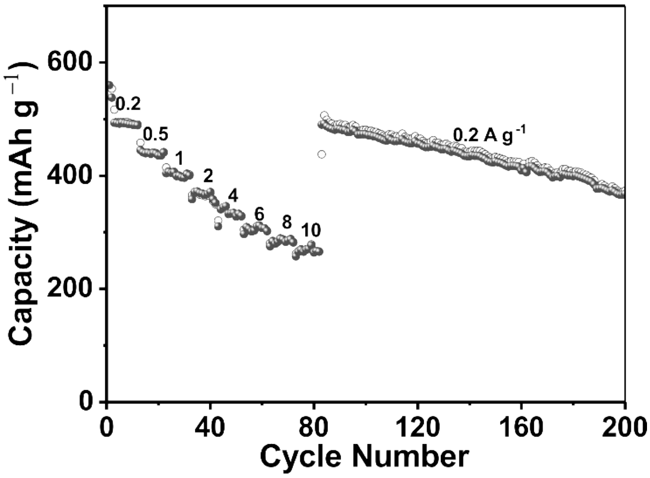

Figure S5 Rate performance of $Fe_{1-x}S$@NC electrode.

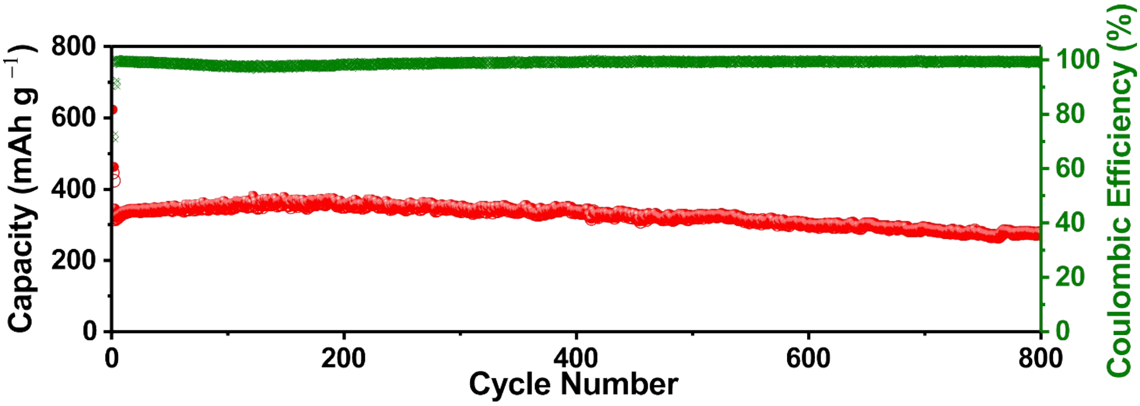

Figure S6 Cycling performance of $Fe_{1-x}S$@NC@G electrode at 1 A g^{-1} in SIB half-cell.

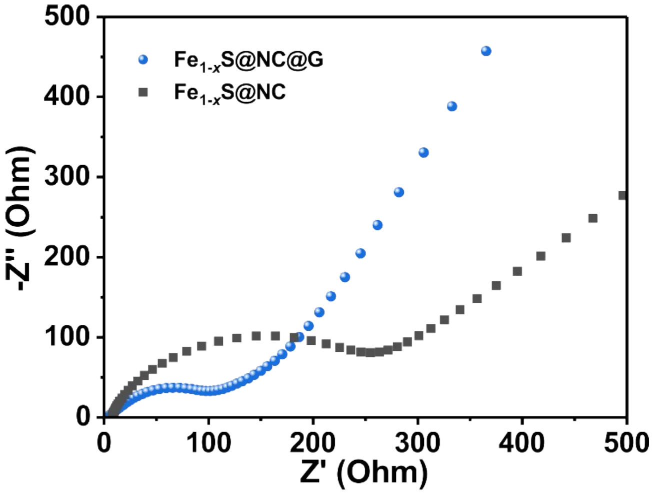

Figure S7 EIS Nyquist plots of $Fe_{1-x}S$@NC@G and $Fe_{1-x}S$@NC electrodes after rate capability testing at desodiated state.

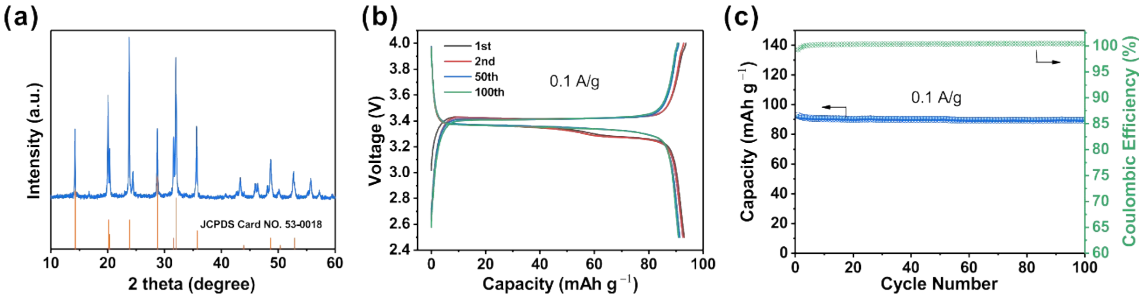

Figure S8 (a) XRD pattern, (b) charge/discharge voltage profiles, and (c) cycling performance at a current density of 0.1 A g^{-1} of home-made $Na_3V_2(PO_4)_2$@C. The $Na_3V_2(PO_4)_2$@C material is prepared according to a modified method reported previously.[1] The detailed procedure is as follow: firstly, citric acid (0.768 g) was dissolved in deionized water (100 mL), and the resultant solution was heated to 80 °C. Then NH_4VO_3 (0.468 g) and NaH_2PO_4 (0.72 g) was added sequentially under continuous stirring. The mixture was held at 80 °C under stirring to evaporate the water and then further dried in an oven at 100 °C. The resulting material was ground into powder and sintered at 750 °C for 12 h (heating ramp: 5 °C min^{-1}) under an argon flow (80 mL min^{-1}) to obtain the final Na_3V_2(PO4)$_3$@C composite.

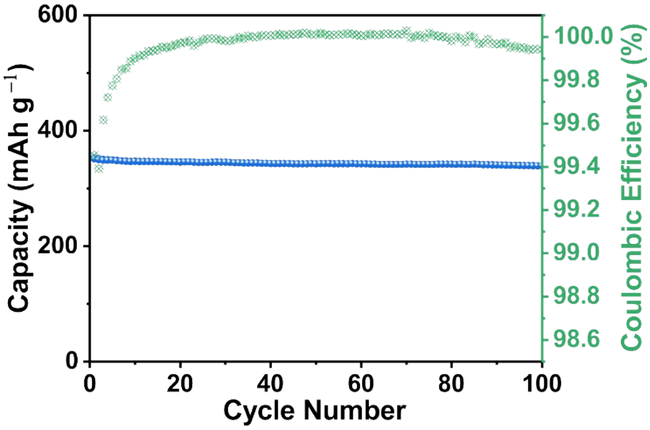

Figure S9 Cycling performance of designed $Fe_{1-x}S$@NC@G //$Na_3V_2(PO_4)_2$@C SIB full cell (capacities are calculated based on the $Fe_{1-x}S$@NC@G anodic material).

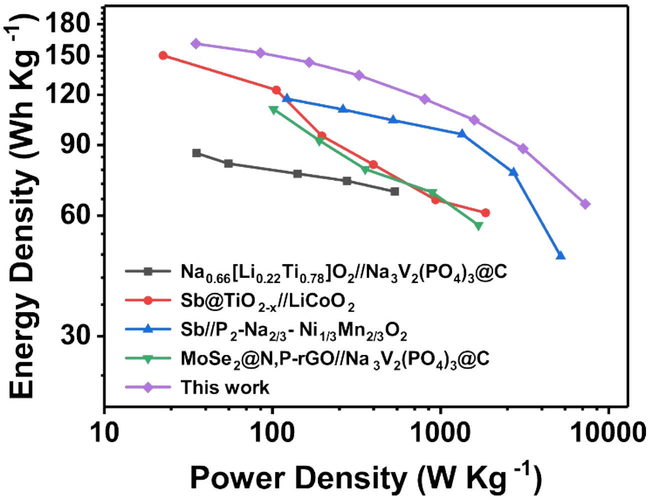

Figure S10 Comparison of full-cell Ragone plots between $Fe_{1-x}S$@NC@G//NVP@C and other reported SIB full-cells including $Na_{0.66}[Li_{0.22}Ti_{0.78}]O_2$//$Na_3V_2(PO_4)_3$@C,[2] Sb@$TiO_{2-x}$//$LiCoO_2$,[3] Sb//P2-$Na_{2/3}$-$Ni_{1/3}Mn_{2/3}O_2$,[4] and $MoSe_2$@N,P-rGO// $Na_3V_2(PO_4)_3$@C.[5]

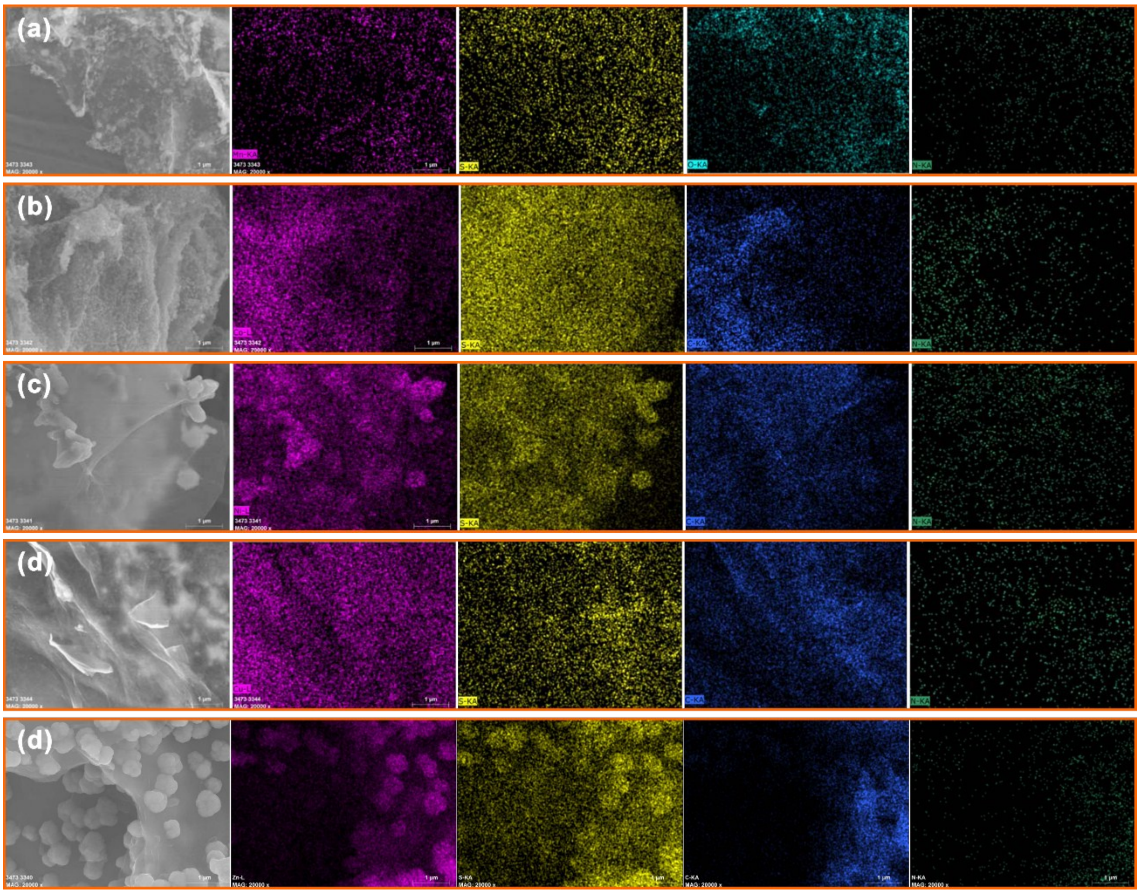

Figure S11 SEM images and the corresponding elemental mapping images of (a) MnS@NC@G, (b) Co_9S_8@NC@G, (c) Ni_3S_2@NC@G, (d) Cu_2S@NC@G, and (e) ZnS@NC@G.

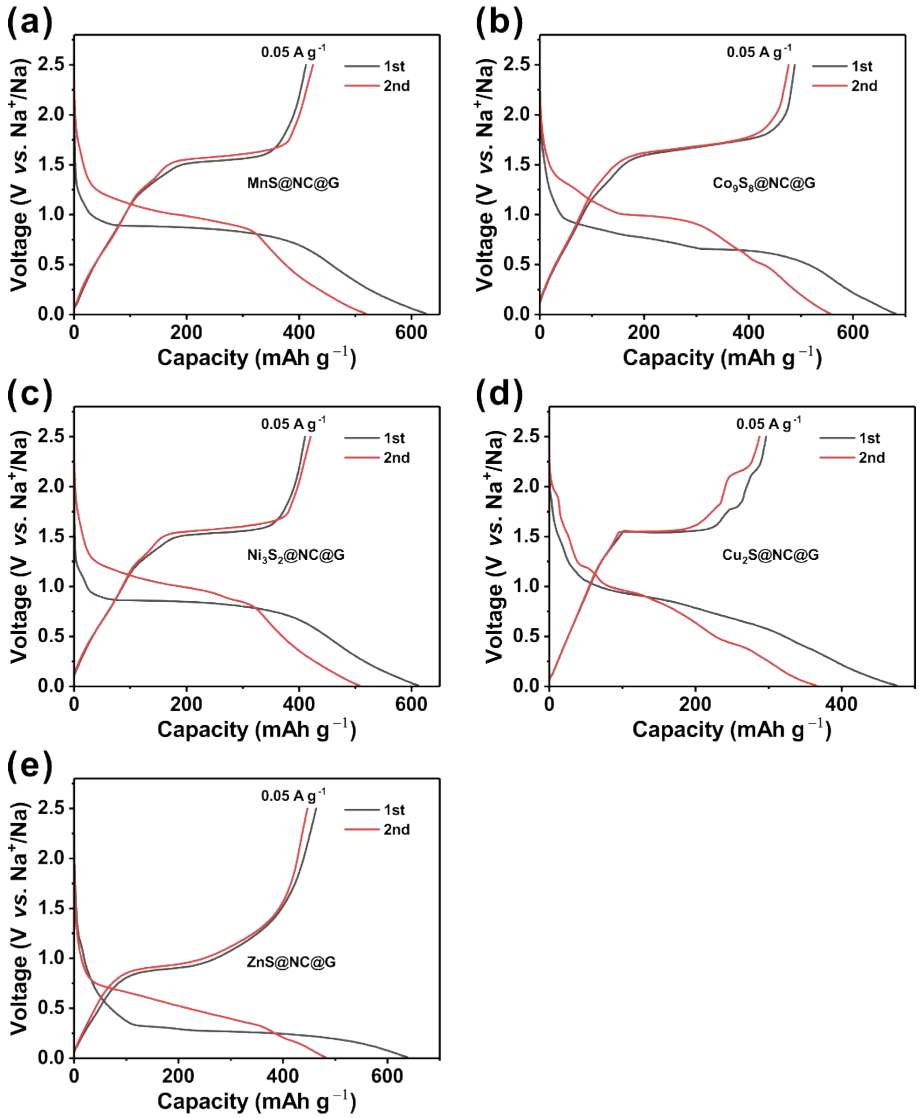

Figure S12 The initial two discharge/charge profiles of (a) MnS@NC@G, (b) Co_9S_8@NC@G, (c) Ni_3S_2@NC@G, (d) Cu_2S@NC@G, and (e) ZnS@NC@G.

References

1 M. J. Aragón, J. Gutiérrez, R. Klee, P. Lavela, R. Alcántara and J. L. Tirado, *J. Electroanal. Chem.*, 2017, **784**, 47-54.

2 Y. Wang, X. Yu, S. Xu, J. Bai, R. Xiao, Y. S. Hu, H. Li, X. Q. Yang, L. Chen and X. Huang, *Nat. Commun.*, 2013, **4**, 2365.

3 N. N. Wang, Z. C. Bai, Y. T. Qian and J. Yang, *Adv. Mater.*, 2016, **28**, 4126-4133.

4 L. Y. Liang, Y. Xu, C. L. Wang, L. Y. Wen, Y. G. Fang, Y. Mi, M. Zhou, H. P. Zhao and Y. Lei, *Energy Environ. Sci.*, 2015, **8**, 2954-2962.

5 F. Niu, J. Yang, N. Wang, D. Zhang, W. Fan, J. Yang and Y. Qian, *Adv. Funct. Mater.*, 2017, 1700522.