# Preparation of ZnS@N-doped-carbon composites via a ZnS-amine

## precursor vacuum pyrolysis route

Wen-Hua Liao,<sup>a, b</sup> Qian-Qian Hu,<sup>b</sup> Min Cheng,<sup>a, b</sup> Xiao-Hui Wu,<sup>a</sup> Guang-Hao Zhan,<sup>b, d</sup> Rui-Bo Yan,<sup>a,b</sup>

Jian-Rong Li,<sup>c\*</sup> Xiao-Ying Huang<sup>b\*</sup>



Fig.S1. EDS spectrum of ZnS@NC-H



Fig. S2. XRD of Exp-ZnS(*ba*) pyrolysis at 600 °C in Ar atmosphere (left) and in N<sub>2</sub> atmosphere during TG test (right).



Fig. S3. SEM image of (a-c) ZnS@NC-L, (d-f) ZnS@NC-M, (g-h)ZnS@NC-H.



Fig. S4. N<sub>2</sub> adsorption desorption isotherm of ZnS@NC-*M* and ZnS@NC-*H*.



Fig. S5. XPS spectra of ZnS@NC-*L* (a, d, g, j), ZnS@NC-*M* (b, e, h, k) and ZnS@NC-*H* (c, f, i, l).



Fig. S6. XPS spectra of three types of nitrogen atoms of ZnS@NC-L



Fig. S7. XRD of Exp-ZnS(ba) vacuum pyrolysis at 400 and 800 °C.



Fig. S8. TGA curves of preparation procedures of (a) Exp-ZnS(ha), (b) $\text{Exp-ZnS}(en)_{0.5}$ and (c)  $\text{Exp-ZnS}(pda)_{0.5}$  by reflux method.



Fig. S9. The EIS plots of ZnS@NC-L, ZnS@NC-M and ZnS@NC-H.



Fig. S10. Long cycling performances of bare ZnS at a current density of 0.1 A g<sup>-1</sup>.



Fig. S11. Initial three cycle CV curves of bare ZnS at a scan rate of 0.2 mV s<sup>-1</sup> between 0.05 and 3.0 V vs Li/Li<sup>+</sup>.

Sample	C wt%	N wt%	H wt%	
ZnS(ba) prepared by the	26.17	7.70	5.88	
reflux method				
ZnS( <i>ba</i> ) pyrolysis at 600 °C	0.31	<0.3	< 0.3	
of Ar atmosphere				
ZnS( <i>ba</i> ) pyrolysis at 400 °C	3.69	0.56	0.39	
by vacuum pyrolysis				
ZnS( <i>ba</i> ) pyrolysis at 800 °C	12.32	2.10	<0.3	
by vacuum pyrolysis				

Table S1. Elemental analysis results of different materials.

### Preparation of ZnS(*ba*) pyrolysis at 400 ℃ and 800 ℃ by vacuum pyrolysis:

The obtained ZnS(ba) is encapsulated in a quartz glass tube after being evacuated. Then, the ZnS@NC materials are obtained by pyrolysis of ZnS(ba) at 400 and 800 °C for 2 h with the heating rate of 2 °C min<sup>-1</sup>, respectively.

Materials	Method	Additional carbon source	Additional nitrogen source	Ref.
ZnS@NC	ZnS-amine, Vacuum pyrolysis			This literature
ZnS@C nanoparticles anchored on 3D N-doped carbon foam	Annealing in $N_2$	MA sponge	MA sponge	1
ZnS@N.f-MWCNTs@rGO	Hydrothermal method	Pre-prepared N-doped functionalized multiwall carbon nanotubes and reduced graphene oxide	Pre-prepared N-doped functionalized multiwall carbon nanotubes	2
Mesoporous ZnS@N-doped carbon composites	In-situ sulfuration, Carbonization in $N_2$	Methionine	Methionine	3
N-doped carbon coating mesoporous ZnS nanospheres	Dopamine polymerization, Thermal treatment in Ar	Polydopamine	Polydopamine	4
ZnO/ZnS@N-C	Nitrogen-rich MOF, Annealing in Ar	CNT		5
ZnS quantum dots@multilayered N-doped carbon matrix	Nitrogen-rich MOF, Vacuum pyrolysis, Sulfuration			6
ZnS/N-doped carbonaceous fibers	Pyrolyzed in N <sub>2</sub>	Aspergillus niger	Aspergillus niger	7
ZnS nanoparticles wrapped in N-doped mesoporous carbon nanosheets	Nitrogen-rich MOF, Annealing in N <sub>2</sub> , Sulfuration			8
ZnS-N/C nanocomposites	Nitrogen-rich MOF, Annealing in N2			9

#### Table S2. Different synthesis strategy of ZnS/NC materials.

#### Referene

- X. Ma, X. Xiong, P. Zou, W. Liu, F. Wang, L. Liang, Y. Liu, C. Yuan and Z. Lin, General and scalable fabrication of core-shell metal sulfides@C anchored on 3D N-doped foam toward flexible sodium ion batteries, *Small*, 2019, **15**, 1903259.
- M. W. Khan, X. Zuo, Q. Yang, H. Tang, K. M. U. Rehman, M. Wu and G. Li, Quantum dot embedded N-doped functionalized multiwall carbon nanotubes boost the short-circuit current of Ru(ii) based dye-sensitized solar cells, *Nanoscale*, 2020, **12**, 1046-1060.
- J. Zhu, Z. Chen, L. Jia, Y. Lu, X. Wei, X. Wang, W. D. Wu, N. Han, Y. Li and Z. Wu, Solvent-free nanocasting toward universal synthesis of ordered mesoporous transition metal sulfide@N-doped carbon composites for electrochemical applications, *Nano Res.*, 2019, **12**, 2250-2258.
- W. Ji, L. Hu, X. Hu, Y. Ding and Z. Wen, Nitrogen-doped carbon coating mesoporous ZnS nanospheres as high-performance anode material of sodium-ion batteries, *Mater. Today Commun.*, 2019, **19**, 396-401.
- 5. C. Guo, Q. Wang, J. He, C. Wu, K. Xie, Y. Liu, W. Zhang, H. Cheng, H. Hu and C. Wang, Rational

design of unique ZnO/ZnS@N-C heterostructures for high performance lithium-ion batteries, *J. Phys. Chem. Lett.*, 2020, **11**, 905-912.

- D. Fang, S. Chen, X. Wang, Y. Bando, D. Golberg and S. Zhang, ZnS quantum dots@multilayered carbon: geological-plate-movement-inspired design for high-energy Li-ion batteries, *J. Mater. Chem. A*, 2018, 6, 8358-8365.
- 7. J. Li, L. Wang, L. Li, C. Lv, I. V. Zatovsky and W. Han, Metal sulfides@carbon microfiber networks for boosting lithium ion/sodium ion storage via a general metal-aspergillus niger bioleaching strategy, *ACS Appl. Mater. Interfaces*, 2019, **11**, 8072-8080.
- 8. Z. B. Zhai, K. J. Huang, X. Wu, H. Hu, Y. Xu and R. M. Chai, Metal-organic framework derived small sized metal sulfide nanoparticles anchored on N-doped carbon plates for high-capacity energy storage, *Dalton Trans.*, 2019, **48**, 4712-4718.
- 9. X. Lin, B. Liu, H. Huang, C. Shi, Y. Liu and Z. Kang, One-step synthesis of ZnS-N/C nanocomposites derived from Zn-based chiral metal-organic frameworks with highly efficient photocatalytic activity for the selective oxidation of cis-cyclooctene, *Inorg. Chem. Front.*, 2018, **5**, 723-731.