1 Rational Design of Well-Dispersed Ultrafine CoS₂ Nanocrystals in Micro-

- 2 Mesoporous Carbon Spheres with Synergistic Effect for High-Performance
- 3 Lithium-Sulfur Batteries
- 4
- 5 Zhanshuang Jin, ^{a, b} Ming Zhao, ^a Tianning Lin, ^a Bingqiu Liu, ^a Qi Zhang, ^a Lingyu
- 6 Zhang, ^a Lihua Chen, ^c Lu Li, ^a, * Zhongmin Su, ^a, ^b Chungang Wang ^a, *
- 7
- 8 ^a Department of Chemistry, Northeast Normal University 5268 Renmin Street,
- 9 Changchun, Jilin 130024, P. R. China
- ^b Department of Chemistry, Faculty of Science, Yanbian University, Yanji, Jilin,
 133002, China
- 12 ^c Shandong Key Laboratory of Biochemical Analysis; College of Chemistry and
- 13 Molecular Engineering, Qingdao University of Science and Technology, Qingdao
- 14 266042, PR China
- 15 *Correspondence: E-mail: lil106@nenu.edu.cn; wangcg925@nenu.edu.cn
- 16
- 17

18 Experimental Section

19 Materials: Polyacrylic acid (PAA) was purchased from Sigma-Aldrich (USA). Zinc

20 oxide (ZnO), isopropyl alcohol (IPA), aqueous ammonia solution, ethylene glycol,

- 21 thiocarbamide, cobaltous acetate, cobaltous chloride hexahydrate (CoCl₂·6H₂O,
- 22 99.8%), anhydrous ethanol and sulfur were obtained from Sinopharm Chemical
- 23 Reagent Beijing Co., Ltd and used without further purification. Deionized water was
- 24 used in all experiments.

25 Synthesis of PAA-Zn NSs: In a 2 L conical flask, a PAA aqueous solution (0.2 g mL-

26 1 , 3 mL) and 0.12 g ZnO were added in deionized water (0.6 L) and ultrasonically

27 dispersed for 30 min. After that, isopropyl alcohol (1.2 L) was dripped to the flask

28 under magnetic stirring to obtain the PAA-Zn nanospheres suspension.

29 Synthesis of Co(OH)₂/PAA-Zn NSs: 1 mL of $NH_3 \cdot H_2O$ (2 M) solution was added

- 30 into the obtained 1.8 L PAA-Zn nanospheres suspension under magnetic stirring. In
- 31 succession, 2 mL of $CoCl_2 \cdot 6H_2O$ (60 mg) solution was injected dropwise into the

solution at room temperature for 4 h to obtain the Co(OH)₂/PAA-Zn NSs. The
 obtained Co(OH)₂/PAA-Zn NSs were centrifuged and washed several times by
 isopropyl alcohol and finally dried at 50 °C for 24 h for further experiment.

Synthesis of uCoS₂@MMC NSs, MMC NSs and large-grained CoS₂: The 4 Co(OH)₂/PAA-Zn NSs were annealed from room temperature to 700 °C at a heating 5 rate of 2 °C min⁻¹ and then maintained at 700 °C for 4 h under an argon atmosphere to 6 obtain the uCo@MMC materials. The as-obtained uCo@MMC hybrid material and 7 sublimed sulfur (2:1, weight ratio) were well mixed and annealed under an argon flow 8 at 300 °C for 12 h to obtain the uCoS₂@MMC composites. After washing in HCl 9 aqueous solution, the as-synthesized uCoS2@MMC NSs were converted into MMC 10 NSs. 5 mL of water solution containing 0.4 g of thiocarbamide and 0.025 g of 11 cobaltous acetate was added into the 10 mL of ethylene glycol, and transferred to a 12 Teflon autoclave and maintained at 120 °C for 10 h and then 200 °C for another 10 h. 13 The solution was then filtered and the product was washed six times with 14 alcohol/distilled water and dried at 60 °C for 12 h to yield large-grained CoS₂. 15

16 Synthesis of S/MMC, S/uCoS₂@MMC NSs and S/CoS₂/Super P: The prepared 30 17 mg MMC (uCoS₂@MMC) was mixed with 70 mg sulfur, milling for 30 min and 18 sealed in the glass tube. Then the tube is heated at 155 °C for 12 h. All obtained 19 products were immersed in 30 mL ethanol solution at room temperature for 15 min to 20 eliminate the possible sulfur particles attached on the surface of the S/MMC, and 21 S/CoS₂@MMC composites. The S/CoS₂/Super P was obtained by milling CoS₂ (3 22 mg), Super P (27 mg) and sulfur (60 mg), named as S/CoS₂.

1 Adsorption simulation experiment

2 The Li₂S₆ solution is prepared by mixing Li₂S and sulfur at the molar ratio of 1:5 in a 3 mixed solution of DOL and DME (1:1, volume ratio) followed by magnetic stirring 4 for 20 h at 80 °C. Then, 20 mg Super P (MMC or uCoS₂@MMC) power are added 5 into as prepared Li₂S₆ (5 mL, 2 mmol L⁻¹) solution, respectively. The CoS₂ (2 mg) and 6 Super P (18 mg) are added into as prepared Li₂S₆.

Characterization: Transmission electron micrographs were taken by JEOLJEM-7 2100F transmission electron microscope (TEM) under 200 kV accelerating voltage. 8 Scanning electron microscopy (SEM) images were obtained by using an XL30 9 ESEM-FEG field emission scanning electron microscope (FEI Co.). The X-ray 10 photoelectron spectrum (XPS) was performed with an ECSALAB 250 by using non-11 monochromated Al Ka radiation. N2 adsorption-desorption measurements were 12 measured using an intelligent gravimetric analyzer Autosorb-iQ (Quantachrome). The 13 X-ray diffraction (XRD) patterns were obtained on a D8 Focus diffractometer with Cu 14 Ka radiation. The thermogravimetric analysis (TGA) was carried out on a Perkin-15 Elmer TG-7 analyzer heated from room temperature to 800 °C at a ramp rate of 10 °C 16 min⁻¹ in air. The inductively coupled plasma atomic emission spectroscopy (ICP-AES) 17 18 was obtained on Shimadzu, ICPS-8100.

19 Electrochemical Measurements: Electrochemical measurement was conducted 20 using the 2025 foil coin cell. The sulfur composite cathodes were prepared by mixing 21 the selected samples, acetylene black and binder (polyvinylidene fluoride, PVDF) in 22 N-methy-pyrrolidinone (NMP) solvent with a weight ratio of 80:10:10. The mixture

1 was stirred for 12 h, spread on an aluminum foil, and then dried in a vacuum oven at 50 °C to remove the solvent. The obtained film was punched into disks with a 2 diameter of 12 mm. The areal mass loading of sulfur was about 1.0 mg cm⁻², and 20 3 uL of electrolyte was used in the coin cells. To construct high sulfur loading 4 electrodes, we prepared thicker films with a sulfur areal loading of 3.0 mg cm⁻², and 5 55 µL of electrolyte was used in the coin cells. The Li-S batteries were assembled in 6 an argon-filled glovebox with the above-prepared sulfur composite cathodes and 7 lithium metal foil anodes. A solution of 1.0 mol L⁻¹ bis(trifluoro-methane)sulfonamide 8 lithium (LiTFSI) dissolved in a mixed solvent of 1,2-dimethoxyethane (DME) and 9 1,3-dioxolane (DOL) with a 1:1 volume ratio containing $LiNO_3$ (0.1 mol L⁻¹) was 10 used as the electrolyte. The cycling performances of Li-S cells were measured on a 11 Neware Battery Measurement System (Neware, China) at different current densities 12 with a potential window of 1.7-2.8 V vs Li/Li⁺. The CV curves were collected on a 13 CHI760E electrochemical workstation at a scan rate of 0.1 mV s⁻¹ between 1.7 and 14 2.8 V. Electrochemical impedance spectroscopy (EIS) analysis was carried out in the 15 range from 100 kHz to 0.01 Hz. For the symmetric electrochemical cells measurement, 16 90 wt% active material (MMC, uCoS₂@MMC and CoS₂/Super P) and 10 wt% PVDF 17 binder were homogenized in NMP to form a consistent slurry, which was then 18 uniformly coated on aluminum current collector. Each coin cell added 30 µL 19 electrolyte (0.5 mol L⁻¹ Li₂S₆ in DME electrolyte). Cyclic voltammetry (CV) curves 20 were measured at a scan rate of 50 mV s⁻¹ in a potential window of -1.0 to 1.0 V. All 21 22 specific capacity values were obtained based on the mass of elemental sulfur. For the

nucleation of lithium sulfide, the applied Li2S8 electrolyte was prepared by mixing sulfur and Li₂S with a molar ratio of 7:1 in tetraglyme with extra 1.0 mol L⁻¹ LiTFSI under continuous magnetic stirring for 24.0 h. The concentration of $\mathrm{Li}_2 \mathrm{S}_8$ was 2.0 mol[S] L⁻¹. 20 µL of the Li₂S₈ electrolyte was dropped onto the uCoS₂@MMC, CoS_2 /Super P and MMC cathode, while 20 μ L blank electrolyte without Li_2S_8 was added to the anode side. The assembled cells were first galvanostatically discharged at 0.112 mA to 2.06 V and then potentiostatically discharged at 2.05 V for nucleation of Li_2S . The potentiostatic discharge was terminated when the current was below 10^{-5} A.



12 Fig. S1. SEM images of A) MMC and B) CoS_2 .



15 Fig. S2. TGA curve of A) S/uCoS₂@MMC and B) S/MMC under N_2 atmosphere.







Fig. S4. Adsorption capability tests of Super P, CoS₂/Super P, MMC and $uCoS_2@MMC$ in mixed 5 mL DOL/DME solutions of 2 mmol L⁻¹ Li₂S₆.



2 Fig. S5. Co 2p XPS spectra of uCoS₂@MMC before and after interacting with Li₂S₆.





5 Fig. S6. CV curves and onset potentials of redox peaks of A) S/uCoS₂@MMC, B)
6 S/MMC and C) S/CoS₂ cathodes, and corresponding differential CV curves of D)
7 S/uCoS₂@MMC, E) S/MMC and F) S/CoS₂ cathodes.





11 Fig. S7. Galvanostatic discharge-charge profiles of A) S/MMC and B) S/CoS₂ 12 cathodes at different rates from 0.1 to 2.0 C.



² System number 3 Fig. S8. The cycling performance of the S/uCoS₂@MMC, S/MMC and S/CoS₂ 4 cathodes at 1.0 C

5



9

10

11 Table S1. Performance comparison of $uCoS_2@MMC$ material with other reported 12 sulfur cathodes.

13

Material	Sulfur	Rate	Cycles	Initial	Capacity	References
	content			Capacity	retention	
	(wt%)			$(mAh g^{-1})$	$(mAh g^{-1})$	
CoS2@MCHS	-	0.1 C	100	1230	880	[1]
CoS ₂ /rGO/M	80	0.1 A g ⁻¹	100	1562	884	[2]
WCNTs						
CoS ₂ /RGO	60	0.1 A g ⁻¹	50	1400	640	[3]
CoS ₂ /CP	70.5	0.2 C	200	1239	818	[4]
CoS2@HPGC	60	0.2 C	300	1136	819	[5]
CoS ₂ /rGO	60	0.5 C	100	993	806	[6]
CoS ₂ -NC	68.5	0.5 C	250	1020	702	[7]
CoS2@LRC	70	0.5 A g ⁻¹	400	868	470	[8]
CoS2@NGCNs	64.7	1.0 C	300	674	519	[9]
CoS ₂ -N-C	81.6	1.0 C	500	845	572	[10]
Z-CoS ₂	59	1.0 C	1000	930	440	[11]
CoS ₂	60	2 C	2000	1003	321	[12]
NiO-	73	0.5 C	500	1014	717	[13]
NiCo2O4@C						
TiO ₂ /BaTiO ₃	58	0.5 C	500	898	541	[14]
ZnS-FeS/NC	69	1.0 C	200	933	800	[15]
uCoS2@MMC	65.1	0.1 C	100	1232	988	
		1.0 C	500	932	720	Our work
			1000	932	606	

14

15 16

17 References

18 [1] X. Wang, L. Ma, J. Yang, J. Sun, Mater. Lett., **2019**, 254, 312.

- 1 [2] X. Zhu, Z. Meng, H. Ying, X. Xu, F. Xu, W. Han, Chem. Phys. Lett., 2017, 684, 191.
- 2 [3] B. Qiu, X. Zhao, D. Xia, J. Alloys Compd., 2013, 579, 372.
- 3 [4] Z. Ma, Z. Li, K. Hu, D. Liu, J. Huo, S. Wang, J. Power Sources, 2016, 325, 71.
- 4 [5] G. Ai, Q. Hu, L. Zhang, K. Dai, J. Wang, Z. Xu, Y. Huang, B. Zhang, D. Li, T. Zhang, G. Liu,
- 5 W. Mao, ACS Appl. Mater. Interfaces, **2019**, 11, 33987.
- 6 [6] X. Hong, S. Li, X. Tang, Z. Sun, F. Li, J. Alloys Compd., 2018, 749, 586.
- 7 [7] J. Zhou, N. Lin, W. I. Cai, C. Guo, K. Zhang, J. Zhou, Y. Zhu, Y. Qian, Electrochim. Acta, **2016**, 218, 243.
- 9 [8] J. Zhang, Z. Li, X. W. D. Lou, Angew. Chem. Int. Edit., 2017, 56, 14107.
- 10 [9] S. D. Seo, D. Park, S. Park, D. W. Kim, Adv. Funct. Mater., 2019, 29, 1903712.
- 11 [10] S. Luo, C. Zheng, W. Sun, Y. Wang, J. Ke, Q. Guo, S. Liu, X. Hong, Y. Li, W. Xie,
- 12 Electrochim. Acta, **2018**, 289, 94.
- 13 [11] N. Zhang, Y. Yang, X. Feng, S.-H. Yu, J. Seok, D. A. Muller, H. D. Abruña, J. Mater. Chem.
- 14 A, **2019**, 7, 21128.
- 15 [12] Z. Yuan, H. J. Peng, T. Z. Hou, J. Q. Huang, C. M. Chen, D. W. Wang, X. B. Cheng, F. Wei,
- 16 Q. Zhang, Nano Lett., **2016**, 16, 519.
- [13] L. Hu, C. Dai, H. Liu, Y. Li, B. Shen, Y. Chen, S.-J. Bao, M. Xu, Adv. Energy Mater., 2018,
 8, 1800709.
- 19 [14] H. E. Wang, K. Yin, X. Zhao, N. Qin, Y. Li, Z. Deng, L. Zheng, B. L. Su, Z. Lu, Chem.
- 20 Commun., **2018**, 54, 12250.
- 21 [15] W. Li, Z. Gong, X. Yan, D. Wang, J. Liu, X. Guo, Z. Zhang, G. Li, J. Mater. Chem. A, 2020,
- 8,433.