

Supporting Information

Metallic NiSe₂ Nanoarray Towards Ultralong life and Fast Li₂S Oxidation Kinetic of Li-S Batteries

*Maoxu Wang,^a Lishuang Fan,^a Xian Wu,^a Yue Qiu,^a Bin Guan,^a Yan Wang,^a Naiqing Zhang,^{*ab} and Kening Sun,^{*ab}*

^a State Key Laboratory of Urban Water Resource and Environment, School of Chemistry and Chemical Engineering, Harbin Institute of Technology, Harbin, 150001 (China)

^b Academy of Fundamental and Interdisciplinary Sciences, Harbin Institute of Technology, Harbin, 150001 (China)

*Corresponding Author

Naiqing Zhang (znqmww@163.com)

Academy of Fundamental and Interdisciplinary Sciences, Harbin Institute of Technology, Harbin, China

Tel: +451 86412153 Fax: +86-451-86412153

Experiment Section

Synthesis of C@NiSe₂: The Ni-based precursors was firstly prepared via the previous work. In the details, 5.26 g NiSO₄·6H₂O and 1 g K₂S₂O₈ dissolved into 45 mL deionized water and then stirring for 10 min. Then, 3 mL NH₃·H₂O was drop by drop added into the above hybrid solution and keep stirring for 30 seconds. Follow that, the carbon cloth (3.5*4.5 cm²) was added into the mixed solution. After 1 h, taking out the carbon cloth and washed with deionized water. Then the Ni-based precursors on carbon cloth was obtained after drying at room temperature for 6 h. To synthesis of C@NiSe₂, the Ni-based precursors on carbon cloth was drop into the hybrid solution, which contained 38 mg NaBH₄, 39.5 mg Se and 35 mL deionized water. Then, the mixed solution was transferred into a 100 mL Taflon-lined stainless autoclave and keep it in an electricity heat drum wind drying oven at 180 °C lasting for 24 h. When it cooled to room temperature naturally, the as-prepared C@NiSe₂ was taken out and washed with deionized water. After that, the C@NiSe₂ was dried at 70 °C overnight.

Synthesis of C@NiSe₂/S: Firstly, 300 mg sulfur was dissolved into 1 mL CS₂ solution. Then, the C@NiSe₂ (carbon cloth) with a size of 1*1 cm² dipped into above sulfur solution for 5 min. And the C@NiSe₂ (carbon cloth) with sulfur dried at 40 °C for 1 h. After that, the dried C@NiSe₂/ (carbon cloth) with sulfur transferred into a 10 mL Taflon-lined stainless autoclave and keep it in an electricity heat drum wind drying oven at 155 °C lasting for 24 h. After cooling to room temperature naturally, the C@NiSe₂/S (C/S) with the sulfur loading about 5.0 mg cm⁻² was obtained. To obtain the C@NiSe₂/S with a high sulfur loading about 12.0 mg cm⁻², the dipping time increased to the time that waiting for the CS₂ fully volatilize.

Materials characterization. The morphologies of C@NiSe₂ were observed via the SEM (Hitachi, SU8010) and HRTEM (G2 F20FEI Tecnai G2 F20 microscope at 200 kV). The crystal structure of C@NiSe₂ was characterized by XRD (PANalytical X'Pert PRO, monochromated Cu K α radiation 40 mA, 40 kV). And the detailed surface chemical composition and elemental bonding configuration of C@NiSe₂ were determined by XPS analysis with the energy resolution 0.5 eV and the step size 0.1 eV. The UV-vis analysis was used to evaluate the adsorption capability of different anchor materials. The content of NiSe₂ in the C@NiSe₂ sample was verified by TGA analysis (Shimadzu DRG-60).

Electrochemical Measurements. C@NiSe₂/S was used as the electrode without additional conductive additive and insulating binder. Celgard 3501 sheets as the separator and the 2025 coin cells were assembled in a glovebox filled with Ar with the Li metal disc as the counter electrode. The electrolyte was composed of 1 mol/L lithium bis (trifluoromethanesulfonyl) imide (LiTFSI) in a solvent of 1, 3-dioxolane (DOL) and dimethoxymethane (DME) (1:1 ratio by volume) with 2% LiNO₃ addition. The Neware battery test system was used to carry out the charge-discharge performance, and the voltage windows is 1.7-2.8 V. The CV measurements were recorded with a CHI600D electrochemical workstation from 1.7 to 2.8 V. The EIS measurements was investigated by PARSTAT 2273 advanced electrochemical system, and the frequency range from 1 MHz to 1 Hz. In addition, the measurement time is about 24 h after cell assembly.

Theoretical Computation. The first principle calculations were conducted, using spin-polarized Perdew–Burke–Ernzerhof (PBE) exchange-correlation functional in the framework of CASTEP in Materials Studio of Accelrys Inc. The CI-NEB is applied for computing diffusion, which is an improved algorithm of the traditional NEB method and is more efficient in obtaining the minimum energy path between the given initial and final positions with linear interpolation of the diffusion

coordinates.

Results

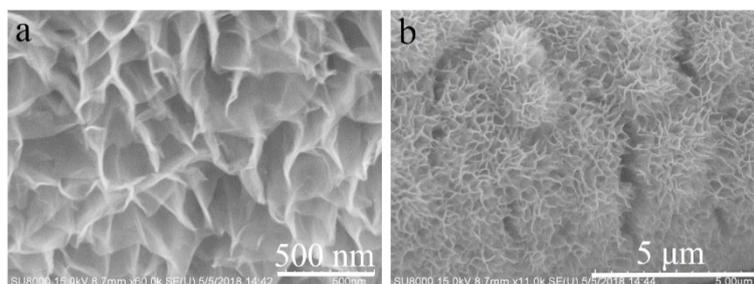


Fig. S1. The SEM images of Ni-based precursors.



Fig. S2. The flexible display of C@NiSe₂.

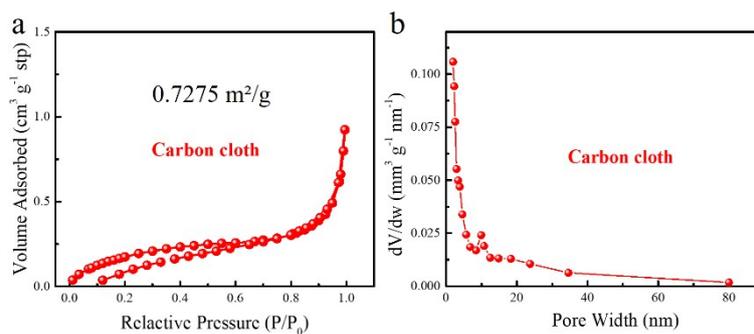


Fig. S3. Nitrogen adsorption–desorption isotherms for carbon cloth. b) The corresponding pore size distribution curve of carbon cloth.

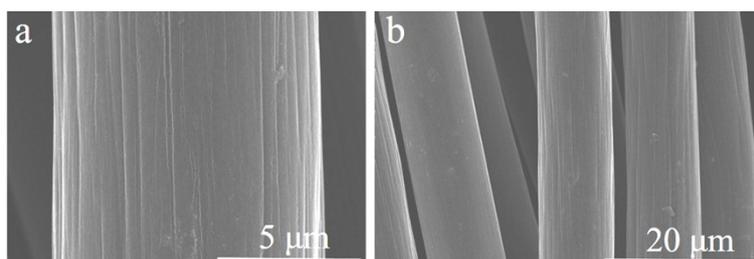


Fig. S4. SEM images of carbon cloth a) 5 μm, b) 20 μm.

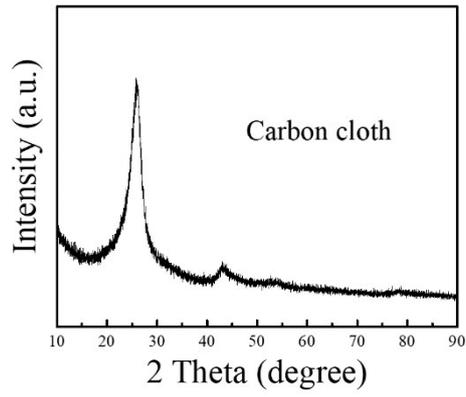


Fig. S5. XRD pattern of carbon cloth.

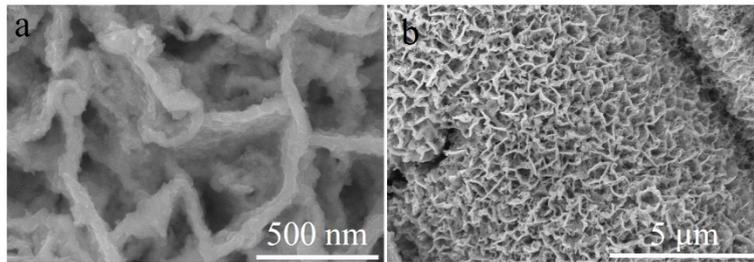


Fig. S6. SEM pictures of C@NiSe₂/S with the sulfur loading of 5.0 mg cm⁻².

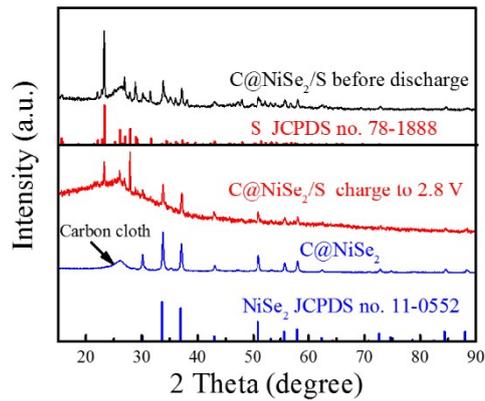


Fig. S7. The ex-situ XRD patterns of C@NiSe₂/S and C@NiSe₂ at different states.

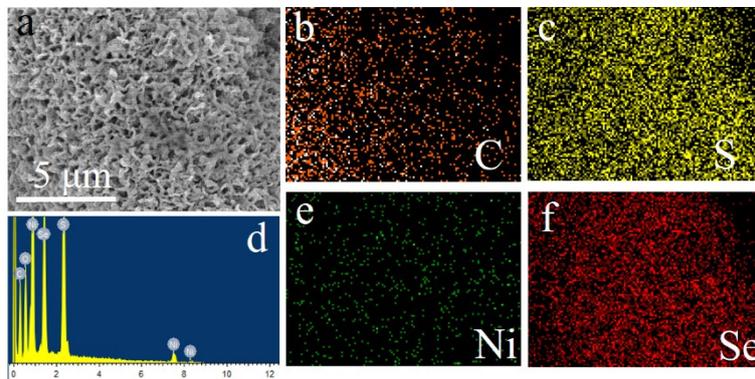


Fig. S8. SEM image and corresponding EDS mapping of C@NiSe₂/S with the sulfur loading of 5.0 mg cm⁻².

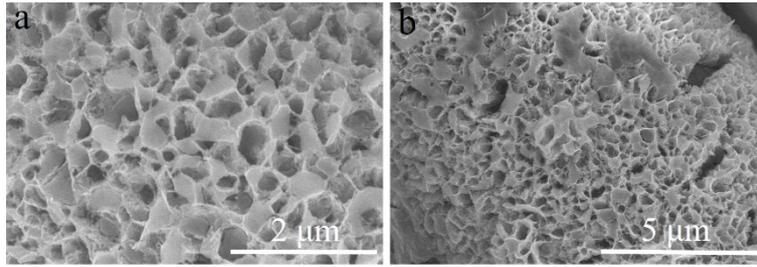


Fig. S9. SEM pictures of C@NiSe₂/S with the sulfur loading of 12.0 mg cm⁻².

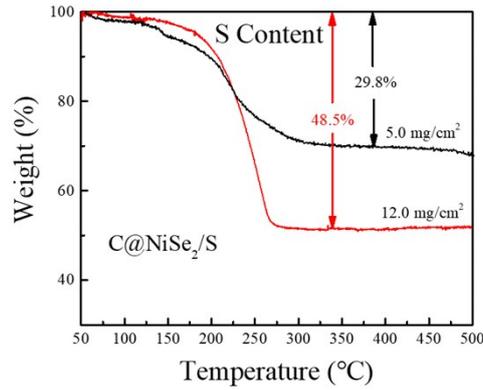


Fig. S10. Thermogravimetric (TG) curves of sulfur cathodes with C@NiSe₂.

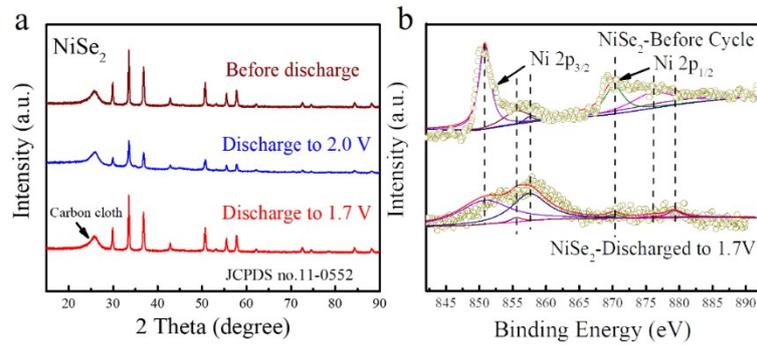


Fig. 11. a) XRD pattern of NiSe₂ at different discharge state. b) The XPS pattern of Ni before discharge and discharge to 1.7 V.

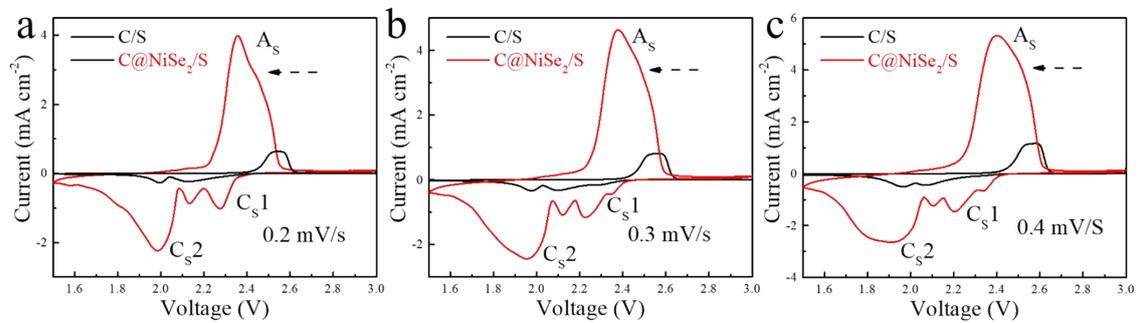


Fig. S12. The CV curves of C@NiSe₂/S with the scanning rate from 0.2 mV/s to 0.4 mV/s.

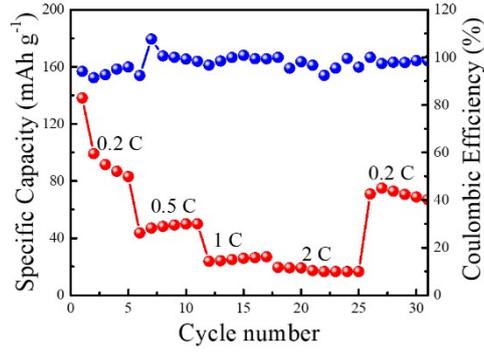


Fig. S13. The rate performance of C@NiSe₂ from 0.2 C to 2 C.

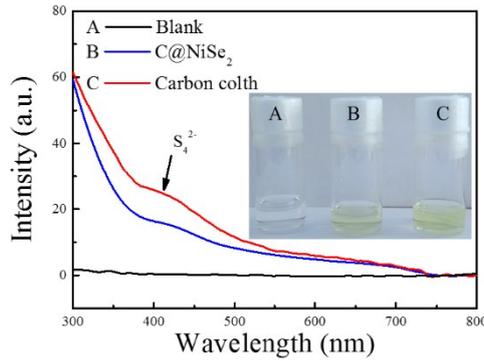


Fig. S14. The DOL/DME solution with cyclized separators of C@NiSe₂/S and C/S, and the corresponding UV-vis spectra.

Table S1. A brief summary of the flexible electrode materials for Li-S batteries

Materials Type	Rate	Sulfur loading (mg/cm ²)	Initial Capacity (mAh/g)	Cycle Number	Cycled Capacity (mAh/g)	Decay Per Cycle	Ref.
C@NiSe ₂	0.2 C	5.0	1250	200	1030	0.089%	This work
	5 C	5.0	620	2000	380	0.019%	
G-NDHCS	0.5 C	3.9	850	200	520	0.194%	AEM ¹
rGO Paper	1 C	1	741	168	592	0.05%	Nano Energy ²
C@WS ₂	0.5 C	1.5	1200	200	1000	0.08%	AEM ³
Polymer	0.5 C	2.1	1050	200	860	0.09%	AM ⁴
ReS ₂	0.5 C	2.0	920	200	800	0.063%	Nano Letters ⁵
MnO ₂	0.2 C	2.4	1000	100	900	0.1%	Nano Energy ⁶
TiO ₂	1 C	1.5-2.0	871	700	608	0.045%	Small ⁷
CC-TiO ₂	0.9 C	4.0	690	500	520	0.05%	EnSM ⁸
TiO/CNF	0.2 C	1.8-2.0	1000	150	800	0.13%	ACSMI ⁹

Reference

1. G. Zhou, Y. Zhao and A. Manthiram, *Advanced Energy Materials*, 2015, **5**, 1402263.
2. C. Wang, X. Wang, Y. Wang, J. Chen, H. Zhou and Y. Huang, *Nano Energy*, 2015, **11**, 678-686.
3. T. Lei, W. Chen, J. Huang, C. Yan, H. Sun, C. Wang, W. Zhang, Y. Li and J. Xiong, *Advanced Energy Materials*, 2017, **7**, 1601843.
4. F. Wu, E. Zhao, D. Gordon, Y. Xiao, C. Hu and G. Yushin, *Advanced materials*, 2016, **28**, 6365-

6371.

5. J. Gao, L. Li, J. Tan, H. Sun, B. Li, J. C. Idrobo, C. V. Singh, T. M. Lu and N. Koratkar, *Nano letters*, 2016, **16**, 3780-3787.
6. H. Xu, L. Qie and A. Manthiram, *Nano Energy*, 2016, **26**, 224-232.
7. T. Lei, Y. Xie, X. Wang, S. Miao, J. Xiong and C. Yan, *Small*, 2017, **13**, 1701013.
8. C. Zha, D. Wu, T. Zhang, J. Wu and H. Chen, *Energy Storage Materials*, 2019, **17**, 118-125.
9. A. Singh and V. Kalra, *ACS applied materials & interfaces*, 2018, **10**, 37937–37947.