Electronic Supporting Information

Defective MOF Architecture Threaded by Interlaced Carbon Nanotubes for High-Cycling Lithium-Sulfur Batteries

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Fig. S 1 SEM morphologies of (a) and (b) UiO-66, (c) and (d) UC-2, (e) and (f) UC-5
Fig. S 2 (a)-(c) SEM and (d) TEM photographs of UC-3 composite.
Table S 1 BET characteristics of CNTs, Uio-66, UC series and S@UC hybrid series and their pore volume and average pore diameters (except CNTs) derived from their 77K N\textsubscript{2} isotherms based on the nonlocal density function theory (NLDFT).

| Samples   | $S_{\text{BET}}/(\text{m}^2\cdot\text{g}^{-1})$ | $V_{\text{total}}/(\text{cm}^3\cdot\text{g}^{-1})$ | $D_{\text{average}}/\text{(nm)}$ |
|-----------|---------------------------------|---------------------------------|---------------------------------|
| CNTs      | 278                             | 0.72                            | 12.3                            |
| Uio-66    | 1157                            | 0.43                            | 1.08                            |
| UC-2      | 976                             | 0.47                            | 1.33                            |
| UC-3      | 863                             | 0.56                            | 1.59                            |
| UC-5      | 738                             | 0.53                            | 1.64                            |
| S@UC-2    | 17.13                           | 0.058                           | 1.77                            |
| S@UC-3    | 15.36                           | 0.031                           | 1.85                            |
| S@UC-5    | 6.62                            | 0.012                           | 4.54                            |

(Note that all data of CNTs are obtained from its BET characteristics)
Fig. S 3 XRD patterns of Uio-66, S@UC series and sulfur.
Fig. S 4 C 1s and O 1s XPS spectra of (a) and (b) Uio-66, (c) and (d) w/o-UC-3 and (e) and (f) S@UC-3, respectively.
Table S 2 Data obtained from the quantitative analysis for C 1s and O 1s spectra of w/o-UC-3 and UC-3.

| Spectrum | Bond     | Binding energy (eV) | Content (%) |
|----------|----------|---------------------|-------------|
|          | w/o-UC-3 | UC-3    | w/o-UC-3 | UC-3 |
| C 1s     | C-C      | 287.74  | 284.75  | 68.27% | 67.37% |
|          | C-O      | 285.62  | 285.64  | 19.01% | 18.61% |
|          | C=O      | 286.74  | 286.72  | 4.81%  | 4.78%  |
|          | O=C-O    | 289.46  | 289.64  | 7.91%  | 9.24%  |
| O 1s     | O-Zr     | 530.8   | 530.96  | 7.68%  | 7.93%  |
|          | Zr-O-C   | 532     | 532.06  | 29.09% | 24.49% |
|          | O-C      | 532.8   | 532.82  | 57.00% | 58.34% |
|          | O=C      | 533.76  | 533.92  | 6.24%  | 9.24%  |
Fig. S 5 Galvanostatic charge-discharge profiles of (a) S@CNTs, (b) S@UC-2 and (c) S@UC-5 as the electrode at 0.5 A·g⁻¹
Fig. S 6 The disassemble cell pictures of (a) S@UC-3 electrode and (b) S@CNTs electrode after 300 cycles, conducted and obtained in the Ar gas filled glove box (O₂, H₂O<0.1 ppm). The SEM images of (c)-(e) fresh and (f)-(h) cycled S@UC-3 electrode after 300 cycles cleaned by the DOL/DME (1:1) solvent.
**Fig. S 7** Cycling performance of the S@CNTs, S@Uio-66 and S@UC-3 electrodes at the current density of 0.1 A·g⁻¹.
Fig. S 8 Atomic unit model configurations of the intact Uio-66 (top view and side view)
Fig. S 9 Atomic unit model configurations of (a) intact Uio-66 and (b)-(d) defective Uio-66 with one, two and three linker loss (denoted as D₁-Uio-66, D₂-Uio-66 and D₃-Uio-66). Gray, red, white and light blue spheres represent C, O, H and Zr atoms, respectively.
### Table S 3 Performance comparisons of the representative MOFs-based sulfur electrodes (1C=1675 mA·g⁻¹).

| Cathode                        | Sulfur content in the electrode | Potential range (V) | Maximum capacity (mAh·g⁻¹) | Average fading Rate | Discharge current density (Cycle number) | Ref.  |
|--------------------------------|--------------------------------|---------------------|-----------------------------|---------------------|----------------------------------------|-------|
| S@UC-3                         | ~54%                            | 1.7-2.8             | 1045                        | 0.142%              | 100 mA·g⁻¹ (100)                        |       |
| S@rGO/MIL100(Cr)               | ~41%                            | 1.0-3.0             | 869                         | 0.200%              | 0.1C (100)                             | 1     |
| S@ZIF-8                        | ~30%                            | 1.8-2.8             | 793                         | 0.101%              | 0.5C (300)                             | 2     |
| S@Ni-MOF                       | ~48%                            | 1.5-3.0             | 689                         | 0.094%              | 0.2C (200)                             | 3     |
| S@MOF-525(Cu)                  | ~42%                            | 1.5-3.0             | 1200                        | 0.207%              | 0.2C (200)                             | 4     |
| S@rGO/MIL-100(V)               | ~35%                            | 1.6-3.0             | 849                         | 0.170%              | 0.1C (200)                             | 5     |
| S@HKUST-1/CNTs                 | ~40%                            | 1.7-2.8             | 1263                        | 0.080%              | 0.2C (500)                             | 6     |
| S@nMOF-867                     | —                               | 1.7-2.8             | 907                         | 0.050%              | 835 mA·g⁻¹ (500)                       | 7     |
| S@Cd-MOF                       | ~50%                            | 1.5-2.8             | 1092                        | 0.537%              | 0.1C (50)                              | 8     |

Note that average fading rate is calculated based on the formula:

\[
\left(\frac{C_{\text{Max}} - C_{\text{Ret}}}{C_{\text{Max}}}\right) \times 100\%
\]

C_{\text{Max}} represents the maximum capacity, C_{\text{Ret}} represents the capacity retention after cycling, N represents the cycling numbers.
**Table S 4** Cycling performance comparisons of UC-3 with several representative MOF-derived porous Carbon materials as the sulfur hosts for Li-S batteries

| MOFs             | Cathode     | Sulfur content in the electrode | Potential range (V) | Maximum/Final Capacity (mAh·g⁻¹) | Discharge current density (Cycle number) | Ref.     |
|------------------|-------------|---------------------------------|---------------------|-----------------------------------|------------------------------------------|---------|
| S@UC-3           | ~ 54%       | 1.7-2.8                         |                     | 925/765                           | 500 mA·g⁻¹ (300)                         | This work |
| GS-S/C\text{ZIF8-D} | ~ 38 %     | 1.0-3.0                         | 1117/561            | 168 mA·g⁻¹ (120)                  |                                          | 9       |
| C-S-3            | ~ 22 %      | 1.0-3.0                         | 1655/936            | 335 mA·g⁻¹ (100)                  |                                          | 10      |
| ZIF-8            | S/N3-C      | ~ 46 %                          | 1.0-3.0             | 1500/800                          | 0.1C (100)                               | 11      |
|                  | OCNTA/S     | ~ 56 %                          | 1.7-2.6             | 1037/487                          | 0.2C (1000)                              | 12      |
| S/ZIF-8-NS-C     | ~ 56 %      | 1.7-2.8                         | 887/587             | 0.5C (300)                        |                                          | 13      |
| RGO/C-Co-S       | ~ 50 %      | 1.8-2.6                         | 1218/949            | 300 mA·g⁻¹ (300)                  |                                          | 14      |
| ZIF-67           | NC-800-S60  | ~ 45 %                          | 1.7-2.8             | 1124/511                          | 800 mA·g⁻¹ (400)                         | 15      |
| S@Co-N-GC        | ~ 49 %      | 1.7-2.7                         | 1440/850            | 0.2C (200)                        |                                          | 16      |
| MWCNT@Meso-C/S   | ~ 47 %      | 1.5-3.0                         | 1343/540            | 0.5C (50)                         |                                          | 17      |
| MCP-950/S        | ~ 63 %      | 1.8-2.8                         | 1274/1041           | 0.2C (50)                         |                                          | 18      |
| MOF-5            | MPCM-N-S     | ~ 56 %                          | 1.7-2.8             | 1000/740                          | 0.5C (200)                               | 19      |
| S-Zn-MOF         | ~ 35 %      | 1.7-2.6                         | 1476/609            | 0.2C (200)                        |                                          | 20      |
| GO@Meso-C/S      | ~ 64 %      | 1.8-2.7                         | 1122/825            | 0.2C (100)                        |                                          | 21      |
| Al-MOF           | S/FLHPC     | ~ 46 %                          | 1.5-2.8             | 1100/751                          | 0.5C (200)                               | 22      |
Table S 5 Cycling stability comparisons of UC-3 with several representative polar materials as the sulfur host in Li-S batteries (1C=1675 mA·g⁻¹).

| Polar host material | Sulfur content in the electrode | Fading rate | Discharge current density | Cycle number | Ref. |
|---------------------|--------------------------------|-------------|----------------------------|--------------|------|
| UC-3                | ~ 54 %                         | 0.055%      | 500 mA·g⁻¹                 | 300          | This work |
| TiO₂                | ~ 53 %                         | 0.033 %     | 0.5C                       | 1000         | 23   |
| Ti₄O₇               | ~ 48 %                         | 0.060 %     | 2C                         | 400          | 24   |
| TiO                 | ~ 56 %                         | 0.082 %     | 0.5C                       | 500          | 25   |
| MnO₂                | ~ 56 %                         | 0.028 %     | 0.5C                       | 1500         | 26   |
| VO₂                 | ~ 60 %                         | 0.058 %     | 0.5C                       | 1000         | 27   |
| Nb₂O₅               | ~ 48 %                         | 0.146 %     | 0.5C                       | 200          | 28   |
| TiN                 | ~ 50 %                         | 0.070 %     | 0.5C                       | 500          | 29   |
| VN                  | ~ 56 %                         | 0.094 %     | 1C                         | 200          | 30   |
| TiS₂                | ~ 33% Li₂S                     | 0.058 %     | 0.5C                       | 400          | 31   |
| CoS₂                | ~ 60 %                         | 0.034 %     | 2C                         | 2000         | 32   |
| Co₃S₄               | ~ 53%                          | 0.080 %     | 1C                         | 450          | 33   |
| Co₈S₉               | ~ 60 %                         | 0.045 %     | 0.5C                       | 1500         | 34   |
| WS₂                 | ~ 11 %                         | 0.031 %     | 0.5C                       | 500          | 35   |
| MXene               | ~ 56 %                         | 0.050 %     | 0.5C                       | 650          | 36   |
References:

1. Z. Zhao, S. Wang, R. Liang, Z. Li, Z. Shi and G. Chen, J. Mater. Chem. A, 2014, 2, 13509-13512.

2. J. Zhou, R. Li, X. Fan, Y. Chen, R. Han, W. Li, J. Zheng, B. Wang and X. Li, Energy Environ. Sci., 2014, 7, 2715.

3. J. Zheng, J. Tian, D. Wu, M. Gu, W. Xu, C. Wang, F. Gao, M. H. Engelhard, J.-G. Zhang, J. Liu and J. Xiao, Nano Lett., 2014, 14, 2345-2352.

4. Z. Wang, B. Wang, Y. Yang, Y. Cui, Z. Wang, B. Chen and G. Qian, ACS Appl. Mater. Interfaces, 2015, 7, 20999-21004.

5. Y. Hou, H. Mao and L. Xu, Nano Research, 2017, 10, 344-353.

6. Y. Mao, G. Li, Y. Guo, Z. Li, C. Liang, X. Peng and Z. Lin, Nat. Commun., 2017, 8, 14628.

7. J. H. Park, K. M. Choi, D. K. Lee, B. C. Moon, S. R. Shin, M.-K. Song and J. K. Kang, Sci. Rep-Uk, 2016, 6, 25555.

8. M.-T. Li, Y. Sun, K.-S. Zhao, Z. Wang, X.-L. Wang, Z.-M. Su and H.-M. Xie, ACS Appl. Mater. Interfaces, 2016, 8, 33183-33188.

9. R. Chen, T. Zhao, T. Tian, S. Cao, P. R. Coxon, K. Xi, D. Fairen-Jimenez, R. Vasant Kumar and A. K. Cheetham, APL Mater., 2014, 2, 124109.

10. Z. Li and L. Yin, ACS Appl. Mater. Interfaces, 2015, 7, 4029-4038.

11. X. Li, Q. Sun, J. Liu, B. Xiao, R. Li and X. Sun, J. Power Sources, 2016, 302, 174-179.

12. P. Zuo, H. Zhang, M. He, Q. Li, Y. Ma, C. Du, X. Cheng, H. Huo, Y. Gao and G. Yin, Carbon, 2017, 122, 635-642.

13. Y. Jiang, H. Liu, X. Tan, L. Guo, J. Zhang, S. Liu, Y. Guo, J. Zhang, H. Wang and W. Chu,
14. Z. Li, C. Li, X. Ge, J. Ma, Z. Zhang, Q. Li, C. Wang and L. Yin, *Nano Energy*, 2016, **23**, 15-26.

15. J. Zhang, M. Huang, B. Xi, K. Mi, A. Yuan and S. Xiong, *Adv. Energy Mater.*, **7**, 1701330-n/a.

16. Y.-J. Li, J.-M. Fan, M.-S. Zheng and Q.-F. Dong, *Energy Environ. Sci.*, 2016, **9**, 1998-2004.

17. W. Bao, Z. Zhang, C. Zhou, Y. Lai and J. Li, *J. Power Sources*, 2014, **248**, 570-576.

18. S. Cai, X. Wang, M. Chen, J. Liu, Q. Lu and S. Wei, *J. Electrochem. Soc.*, 2016, **163**, A2922-A2929.

19. X. Qian, L. Jin, S. Wang, S. Yao, D. Rao, X. Shen, X. Xi and J. Xiang, *RSC Adv.*, 2016, **6**, 94629-94635.

20. P. M. Shanthi, P. J. Hanumantha, B. Gattu, M. Sweeney, M. K. Datta and P. N. Kumta, *Electrochim. Acta*, 2017, **229**, 208-218.

21. W. Bao, Z. Zhang, W. Chen, C. Zhou, Y. Lai and J. Li, *Electrochim. Acta*, 2014, **127**, 342-348.

22. X. Yang, N. Yan, W. Zhou, H. Zhang, X. Li and H. Zhang, *J. Mater. Chem. A*, 2015, **3**, 15314-15323.

23. Z. Wei Seh, W. Li, J. J. Cha, G. Zheng, Y. Yang, M. T. McDowell, P.-C. Hsu and Y. Cui, *Nat. Commun.*, 2013, **4**, 1331.

24. Q. Pang, D. Kundu, M. Cuisinier and L. F. Nazar, *Nat. Commun.*, 2014, **5**, 4759.

25. Z. Li, J. Zhang, B. Guan, D. Wang, L. M. Liu and X. W. Lou, *Nat. Commun.*, 2016, **7**, 13065.

26. X. Wang, G. Li, J. Li, Y. Zhang, A. Wook, A. Yu and Z. Chen, *Energy Environ. Sci.*, 2016, **9**, 25239-25249.
2533-2538.

27. X. Liang, C. Y. Kwok, F. Lodi-Marzano, Q. Pang, M. Cuisinier, H. Huang, C. J. Hart, D. Houtarde, K. Kaup, H. Sommer, T. Brezesinski, J. Janek and L. F. Nazar, *Adv. Energy Mater.*, 2016, *6*, 1501636-n/a.

28. Y. Tao, Y. Wei, Y. Liu, J. Wang, W. Qiao, L. Ling and D. Long, *Energy Environ. Sci.*, 2016, *9*, 3230-3239.

29. Z. Cui, C. Zu, W. Zhou, A. Manthiram and J. B. Goodenough, *Adv. Mater.*, 2016, *28*, 6926-6931.

30. Z. Sun, J. Zhang, L. Yin, G. Hu, R. Fang, H.-M. Cheng and F. Li, *Nat. Commun.*, 2017, *8*, 14627.

31. Z. W. Seh, J. H. Yu, W. Li, P.-C. Hsu, H. Wang, Y. Sun, H. Yao, Q. Zhang and Y. Cui, *Nat. Commun.*, 2014, *5*, 5017.

32. Z. Yuan, H.-J. Peng, T.-Z. Hou, J.-Q. Huang, C.-M. Chen, D.-W. Wang, X.-B. Cheng, F. Wei and Q. Zhang, *Nano Lett.*, 2016, *16*, 519-527.

33. H. Xu and A. Manthiram, *Nano Energy*, 2017, *33*, 124-129.

34. Q. Pang, D. Kundu and L. F. Nazar, *Mater. Horiz.*, 2016, *3*, 130-136.

35. T. Lei, W. Chen, J. Huang, C. Yan, H. Sun, C. Wang, W. Zhang, Y. Li and J. Xiong, *Adv. Energy Mater.*, 2017, *7*, 1601843-n/a.

36. X. Liang, A. Garsuch and L. F. Nazar, *Angew. Chem. Int. Ed.*, 2015, *54*, 3907-3911.