

Supporting Information for

A Ternary Hybrid Material for High Performance Lithium-Sulfur Battery

Qi Fan,^{1,2} Wen Liu,¹ Zhe Weng,¹ Yueming Sun,² Hailiang Wang^{1*}

¹Department of Chemistry and Energy Sciences Institute, Yale University, CT 06511, United States

²School of Chemistry and Chemical Engineering, Southeast University, Nanjing, Jiangsu, 211189, China

Correspondence to: hailiang.wang@yale.edu

Preparation of mildly oxidized CNTs. CNTs were oxidized by a modified Hummers method. Multi-wall CNTs (CNano Tech. Ltd.) were purified by calcinations at 400 °C for 1 h and washed with 10 wt% HCl to remove metal residues. 1g of purified CNTs were dispersed into 23 ml of concentrated H₂SO₄ and the mixture was stirred at room temperature overnight. Next, the solution was heated to 40 °C in an oil bath. 350 mg of NaNO₃ was added, followed by the slow addition of 1 g of KMnO₄ while keeping the reaction temperature below 45°C. The solution was kept at 40°C under stirring for 30 min. 3 ml of water was added into the flask, followed by another 3 ml after 5 minutes. After another 5 minutes, 40 ml of water was added. 15 minutes later, the flask was removed from the oil bath and 140 ml of water and 10 ml of 30% H₂O₂ were added to end the reaction. Oxidized CNTs were collected, repetitively washed with 5 wt% HCl solution and then water, and finally lyophilized to acquire the mildly oxidized CNTs (Fig. S8).

Preparation of Li₂S₆ solution. Polysulfide solution was prepared by dissolving stoichiometric amounts of Li₂S and sulfur in DOL at 80 °C for 10 hours.

Polysulfide adsorption study. Test solutions were prepared by mixing 20 μl of 0.3 M Li₂S₆ in DOL, 1 ml of DOL and 1 ml of DME. 5 mg of CNT/NiFe₂O₄, CNT/NiFe₂O₄-2 or CNTs was added to each solution. The solutions were vigorously stirred for 20 min. All procedures were completed in an Ar-filled glove box. To further test whether the host materials can still effectively trap polysulfides after the long-term cycling tests, the cycled cathodes of CNT/NiFe₂O₄-S, CNT/NiFe₂O₄-S-2 and CNT-S with absorbed electrolyte were each directly soaked in 4 mL of DOL/DME (1:1, vol) mixed solvent for 24 hours. All procedures were completed in an Ar-filled glove box.

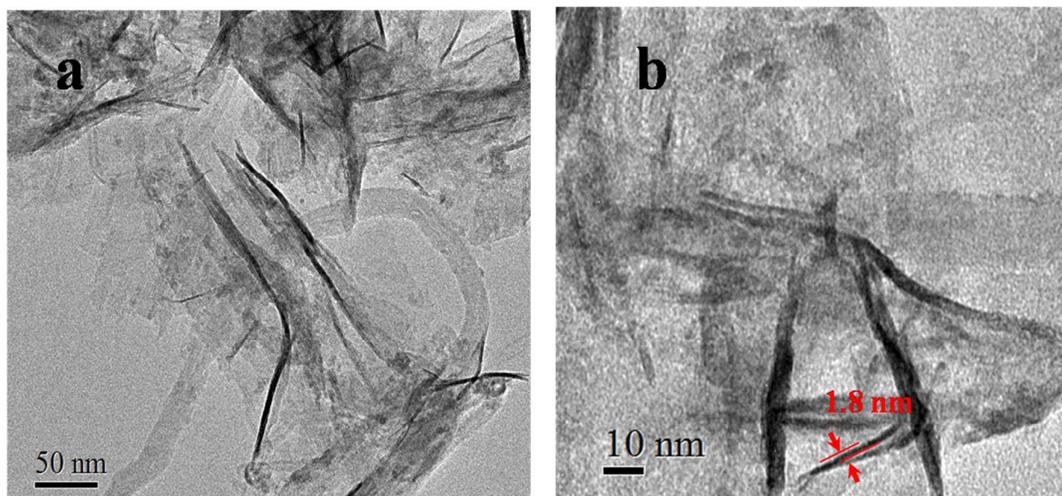


Fig. S1 TEM images of NiFe₂O₄ nanosheets grown on CNTs.

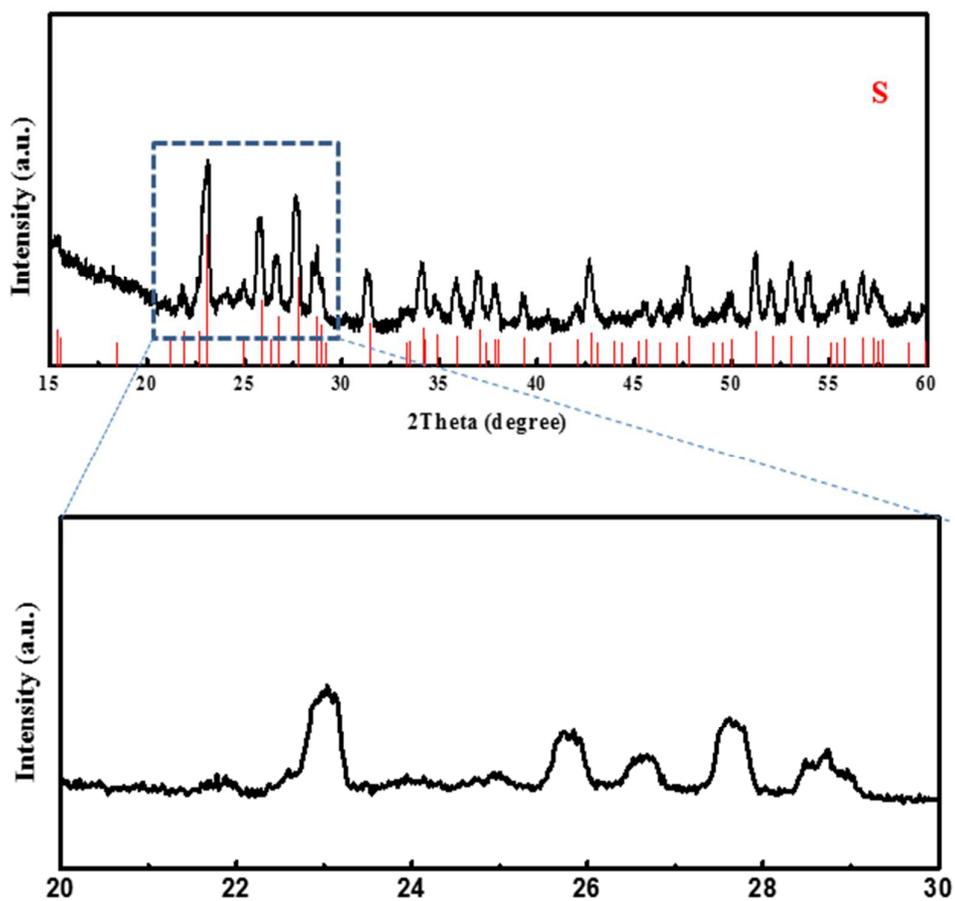


Fig. S2 XRD pattern of the CNT/NiFe₂O₄-S ternary hybrid material.

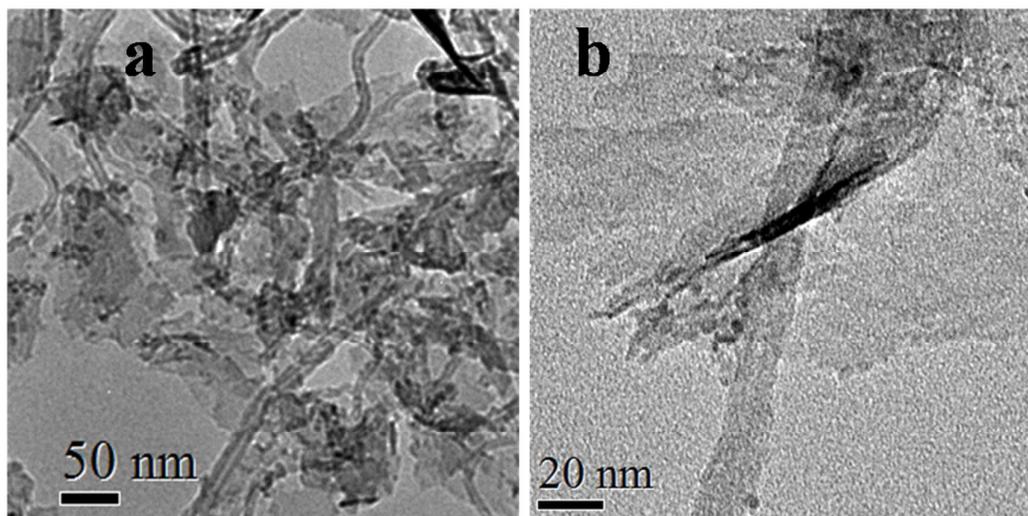


Fig. S3 TEM images of CNT/NiFe₂O₄-S after long-term cycling.

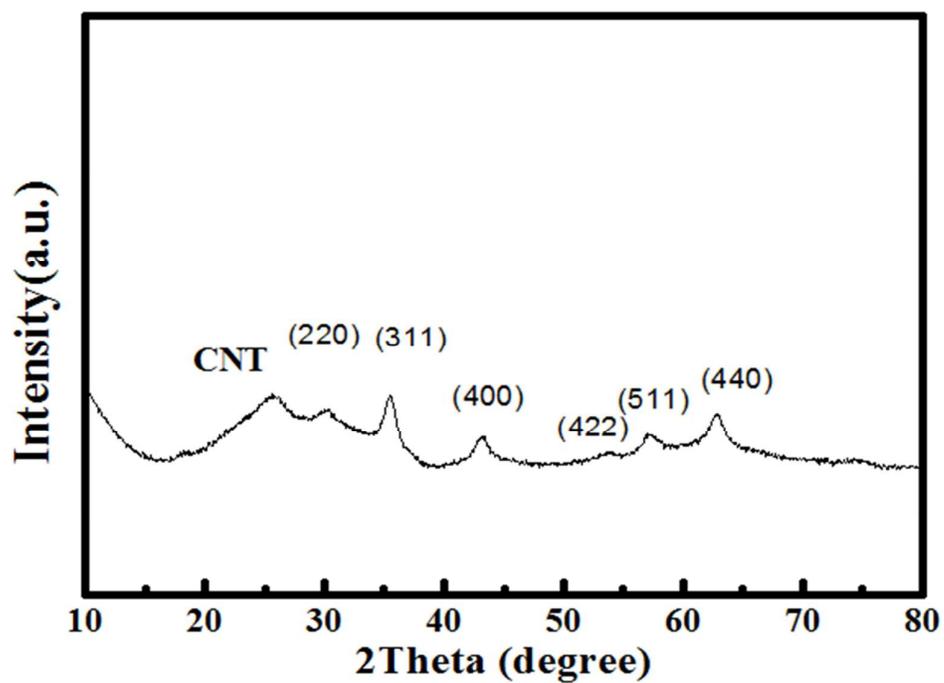


Fig. S4 XRD pattern of the discharged electrode material after hundreds of cycles.

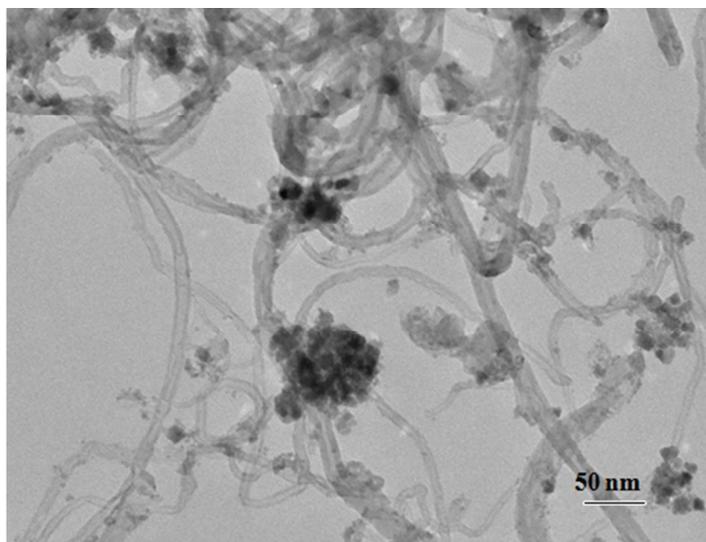


Fig. S5 TEM image of NiFe₂O₄ nanoparticles grown on CNTs.

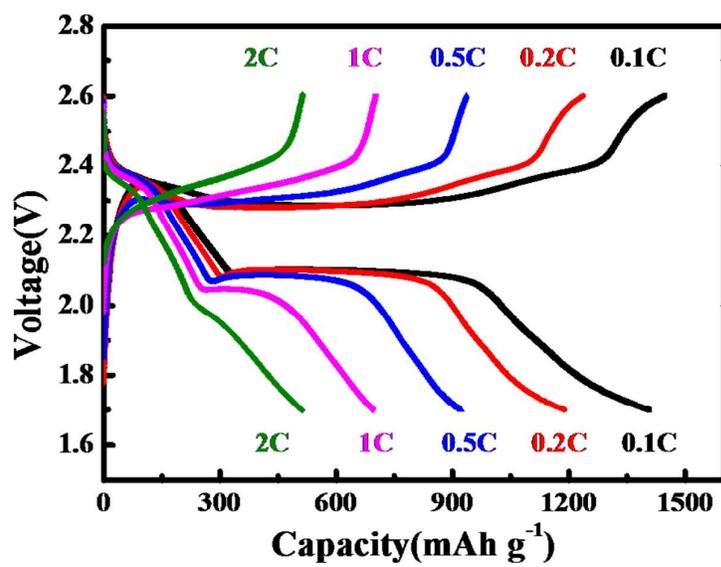


Fig. S6 Charging/discharging voltage profiles of the CNT-S at various C rates from 0.1 to 2 C.

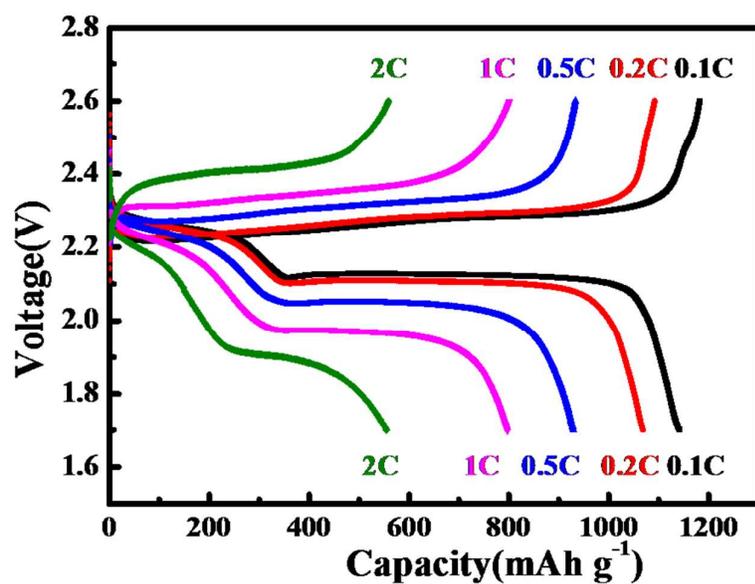


Fig. S7 Charging/discharging voltage profiles of the CNT/NiFe₂O₄-S-2 at various C rates from 0.1 to 2 C.

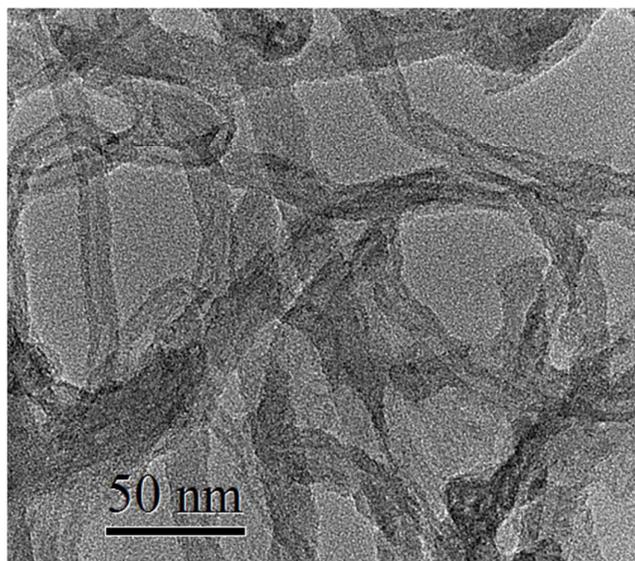


Fig. S8 TEM image of the mildly oxidized CNTs.

Host Material	Sulfur Loading	Capacity loss per cycle	
		Cycles	Loss (%)
CNT/NiFe ₂ O ₄ nanosheet <i>This work</i>	76 wt%	>500	0.009 (at 1C)
ITO-Carbon Fiber ¹ <i>Ref.1</i>	57 wt%	500	0.036(at 0.2C)
MnO ₂ nanosheet ² <i>Ref. 2</i>	75 wt%	2000	0.036 (at 2C)
TiO ₂ hollow sphere ³ <i>Ref.3</i>	71 wt%	1000	0.033 (at 0.5C)
Ti ₄ O ₇ ⁴ <i>Ref.4</i>	70 wt%	500	0.06 (at 2C)
Amino-functionalized reduced graphene oxide ⁵ <i>Ref.5</i>	60 wt%	350	0.057 (at 0.5C)
Covalently bonded CNT ⁶ <i>Ref.6</i>	83 wt%	500	0.021 (at 0.5C)
Graphene ⁷ <i>Ref.7</i>	70 wt%	300	0.1 (at 1C)
N-Doped Graphene ⁸ <i>Ref.8</i>	60 wt%	700	0.068 (at 1C)
CNT-interpenetrated mesoporous N-doped carbon sphere ⁹ <i>Ref.9</i>	70 wt%	200	0.05 (at 0.2C)
N-Doped Double-Shelled Hollow Carbon Sphere ¹⁰ <i>Ref.10</i>	78 wt%	200	0.19 (at 0.5C)
Ultra-high-surface-area hollow carbon nanosphere ¹¹ <i>Ref.11</i>	67 wt%	500	0.053 (at 1C)
Porous trithiocyanuric acid ¹² <i>Ref.12</i>	63 wt%	450	0.037 (at 0.5C)

Table S1 Comparison of cycling stability of representative S cathode material structures in the literature.

References:

- (1) Pang, Q.; Kundu, D.; Cuisinier, M.; Nazar, L. F. *Nat. commun.* **2014**, *5*, 4759.
- (2) Liang, X.; Hart, C.; Pang, Q.; Garsuch, A.; Weiss, T.; Nazar, L. F. *Nat. commun.* **2015**, *6*, 5682.
- (3) Seh, Z. W.; Li, W.; Cha, J. J.; Zheng, G.; Yang, Y.; McDowell, M. T.; Hsu, P.-C.; Cui, Y. *Nat. commun.* **2013**, *4*, 1331.
- (4) Yao, H.; Zheng, G.; Hsu, P.-C.; Kong, D.; Cha, J. J.; Li, W.; Seh, Z. W.; McDowell, M. T.; Yan, K.; Liang, Z.; Narasimhan, V. K.; Cui, Y. *Nat. commun.*

- 2014**, *5*, 3943.
- (5) Wang, Z.; Dong, Y.; Li, H.; Zhao, Z.; Wu, H. B.; Hao, C.; Liu, S.; Qiu, J.; Lou, X. *W. Nat. commun.* **2014**, *5*, 5002.
 - (6) Wang, L.; Dong, Z.; Wang, D.; Zhang, F.; Jin, J. *Nano Lett.* **2013**, *13*, 6244.
 - (7) Zhou, G.; Pei, S.; Li, L.; Wang, D.-W.; Wang, S.; Huang, K.; Yin, L.-C.; Li, F.; Cheng, H.-M. *Adv. Mater.* **2014**, *26*, 625.
 - (8) Qiu, Y.; Li, W.; Zhao, W.; Li, G.; Hou, Y.; Liu, M.; Zhou, L.; Ye, F.; Li, H.; Wei, Z.; Yang, S.; Duan, W.; Ye, Y.; Guo, J.; Zhang, Y. *Nano Lett.* **2014**, *14*, 4821.
 - (9) Song, J.; Gordin, M. L.; Xu, T.; Chen, S.; Yu, Z.; Sohn, H.; Lu, J.; Ren, Y.; Duan, Y.; Wang, D. *Angew. Chem.* **2015**, *127*, 4399.
 - (10) Zhou, G.; Zhao, Y.; Manthiram, A. *Adv. Ener. Mater.* **2015**, *5*, DOI: 10.1002/aenm. 201402263.
 - (11) Xu, F.; Tang, Z.; Huang, S.; Chen, L.; Liang, Y.; Mai, W.; Zhong, H.; Fu, R.; Wu, D. *Nat. Commun.* **2015**, *6*, 7221.
 - (12) Kim, H.; Lee, J.; Ahn, H.; Kim, O.; Park, M. J. *Nat. Commun.* **2015**, *6*, 7278.