

## Supporting Information

# Bio-mimetic ant-nest electrode structures for high sulfur ratio lithium-sulfur batteries

*Guo Ai<sup>†,‡</sup>, Yiling Dai<sup>†</sup>, Wenfeng Mao<sup>†,§</sup>, Hui Zhao<sup>†</sup>, Yanbao Fu<sup>†</sup>, Xiangyun Song<sup>†</sup>, Yunfei En<sup>‡</sup>,*

*Vincent S. Battaglia<sup>†</sup>, Venkat Srinivasan<sup>†</sup>, Gao Liu<sup>†\*</sup>*

<sup>†</sup>Energy Storage and Distributed Resources Division, Energy Technologies Area, Lawrence Berkeley National Laboratory, Berkeley, California 94720, United States

<sup>‡</sup>Science and Technology on Reliability Physics and Application of Electronic Component Laboratory, No. 5 Electronic Research Institute of the Ministry of Industry and Information Technology, Guangzhou 510610, China

<sup>§</sup>Guangzhou Automobile Group Co., Ltd., Guangzhou 511434, China

\* Corresponding author: Gao Liu Tel.: +1-510-486-7207; Email: gliu@lbl.gov

## Materials

The sulfur powder is purchased from U.S. Research Nanomaterials, Inc. CNT and NaCl is purchased from Sigma-Aldrich Inc. Poly(9,9-dioctylfluorene-co-fluorenone-co-methylbenzoic ester) (PFM) is synthesized according to previous work<sup>1</sup>. The chlorobenzene (Sigma-Aldrich Inc.) is used as the solvent for PFM. The electrolyte for cell testing is composed of 1 M lithium salt bis(trifluoromethanesulfonyl)imide (LiTFSI) dissolved in 1,3-dioxolane/1,2-dimethoxyethane/(n-methyl-(n-butyl) pyrrolidiniumbis(trifluoromethanesulfonyl)imide (DOL/DME/PyR14TFSI, 3:3:2 in volume), and 1 wt% LiNO<sub>3</sub>, all purchased from Sigma-Aldrich.

## Cathode fabrication

The PFM is dissolved in chlorobenzene at 5 wt% ratio. Sulfur powder and CNT are added into the binder-solvent solution after the binder is dissolved. For the regular CNT-S electrode, the weight ratio of these three components is: 50% sulfur, 10% PFM, 40% CNT. For the CNT-nest-S electrode, the NaCl particles are first ball-milled into micro-sized particles and then added to the slurry for ball-milling. The composition of the nest structure electrode is 50% sulfur, 10% PFM, 40% CNT for the 50%S electrode; 80% sulfur, 4% PFM, 16% CNT for the 80%S-CNT-nest-S electrode; and 85% sulfur, 3% PFM, 12% CNT for the 85%S-CNT-nest-S electrode. The mixture is combined using the ball-milling method overnight to obtain uniform slurry. The laminate is then made by coating the slurry on a 30- $\mu\text{m}$ -thick battery-grade nickel current collector with a Mitutoyo doctor blade and an Elcometer motorized film applicator. Mass loading of sulfur is 1.5-3.0  $\text{mg}\cdot\text{cm}^{-2}$ . After the laminate is fully dried, the salt is removed by immersing in di-ionized water. All the laminates are further dried in a vacuum oven at 50 °C overnight before making cells.

### **Cell assembly and testing**

Li-S batteries are tested with 2325-type coin cells (National Research Council Canada). The cells are assembled in an argon-filled glove box with oxygen content less than 0.1 ppm. The size of the sulfur electrode is 1/2-inch OD, and the size of the counter electrode lithium metal disk is 11/16-inch OD. The Li foil is purchased from FMC-Lithium Co. The separator used is polypropylene film (Celgar 2400). Galvanostatic cycling tests are performed on a Maccor series 4000 cell tester (Maccor, Inc., Tulsa, OK). The voltage window for cell test is 1.7–2.7 V. The cells are cycled at C/10 for 2 cycles before any other test.

### **Material characterization techniques**

Morphology of the electrode surface is characterized with a JSM-7500F scanning electron microscope at the National Center for Electron Microscopy (NCEM) at Lawrence Berkeley National Laboratory. An energy dispersive X-ray (EDX) spectrometer attached to the SEM (JEOL JSM-7500F) is used to conduct elemental analysis of sulfur and the distribution with an accelerating voltage of 15 kV. Transmission Electron Microscopy (TEM) images is produced by a 200 kilovolt FEI monochromated F20 UT Tecnai. Thermo gravimetric analysis (TGA, TA Instruments Q5000) is used to determine the ratio of the S in the electrode using a heating rate of 10°C/min in N<sub>2</sub>. The cycled Li-S batteries are opened with a cell opener for post-test analysis, and the electrode is washed thoroughly with DOL/DME with a volume ratio of 1:1 inside an argon-filled glove box.

### **Reference**

1. Liu, G.; Xun, S.; Vukmirovic, N.; Song, X.; Olalde-Velasco, P.; Zheng, H.; Battaglia, V. S.; Wang, L.; Yang, W., *Adv. Mater.* 2011, 23, 4679-4683.

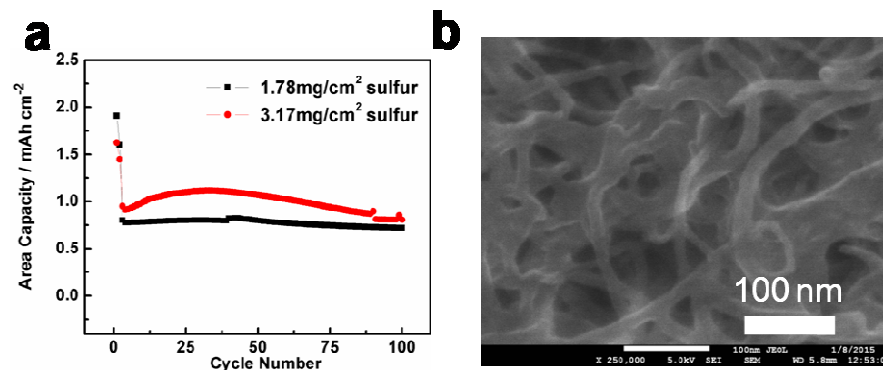


Figure S1. (a) Area capacity of the cycling performance of the CNT-S cells with 1.78 mg·cm<sup>-2</sup> and 3.17 mg·cm<sup>-2</sup> sulfur loading. (b) The SEM top morphology of the fully-discharged CNT-S SEM images.

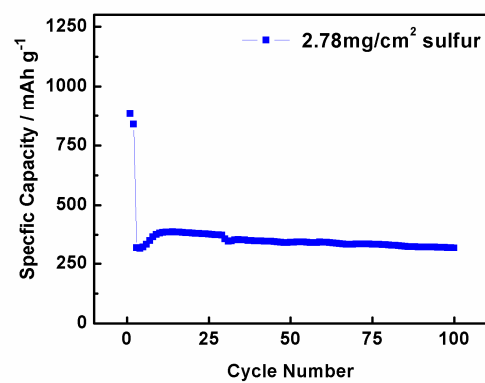


Figure S2. Specific capacity of the cycling performance of the Li-S cells with AB conductive additive and 2.78 mg·cm<sup>-2</sup> sulfur loading.

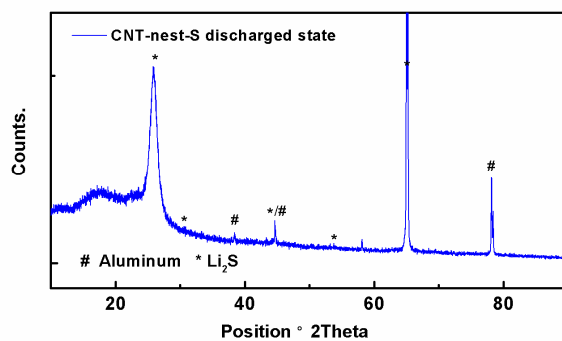


Figure S3. XRD characterization of the cycled CNT-nest-S electrode. Li<sub>2</sub>S (labeled with “\*”) is assigned with PDF# 00-23-0369. And the aluminum current collector (labeled with “#”) is assigned with PDF# 01-085-1327.

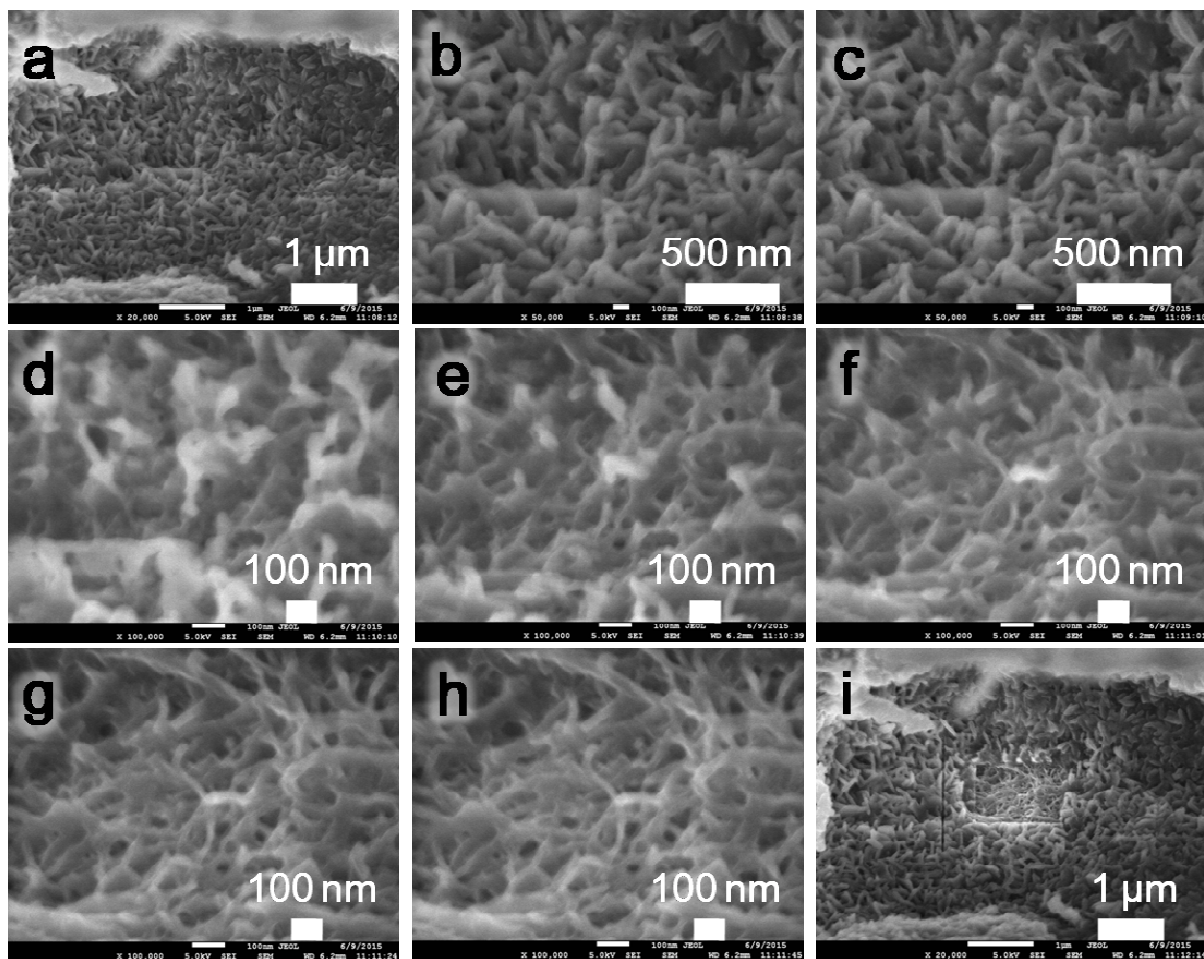


Figure S4. (a)-(i) SEM images taken continuously on the same spot in the middle of area in (a).

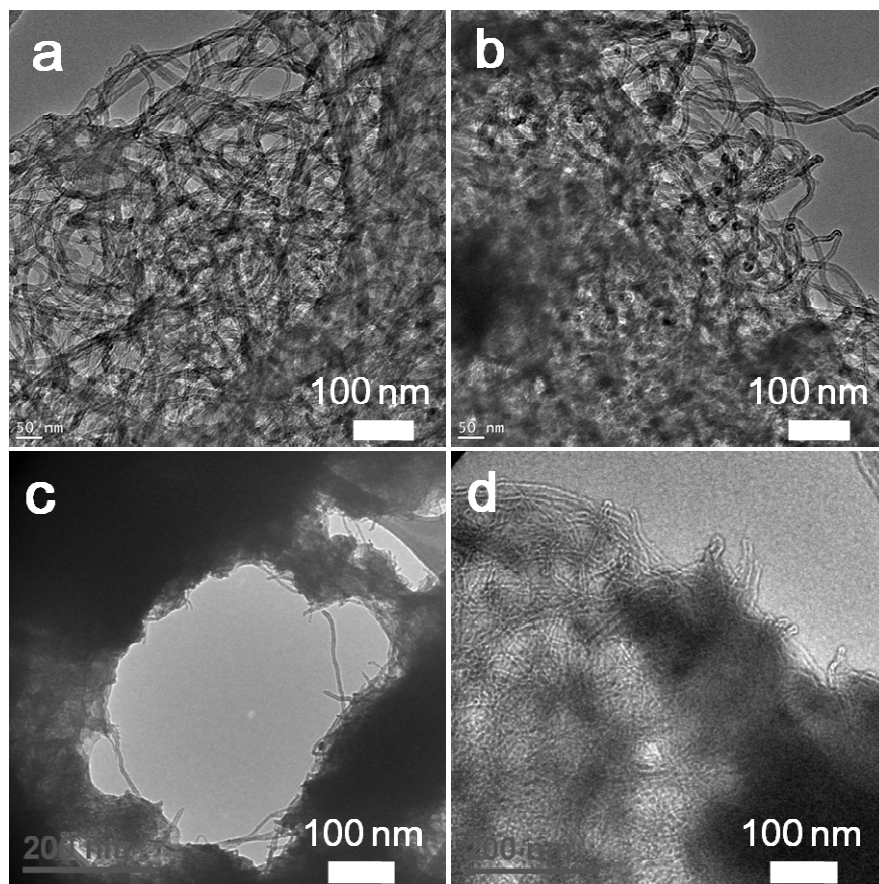


Figure S5. TEM images of the regular CNT-S electrode (a, b) and nest-structure CNT-nest-S electrode (c, d).



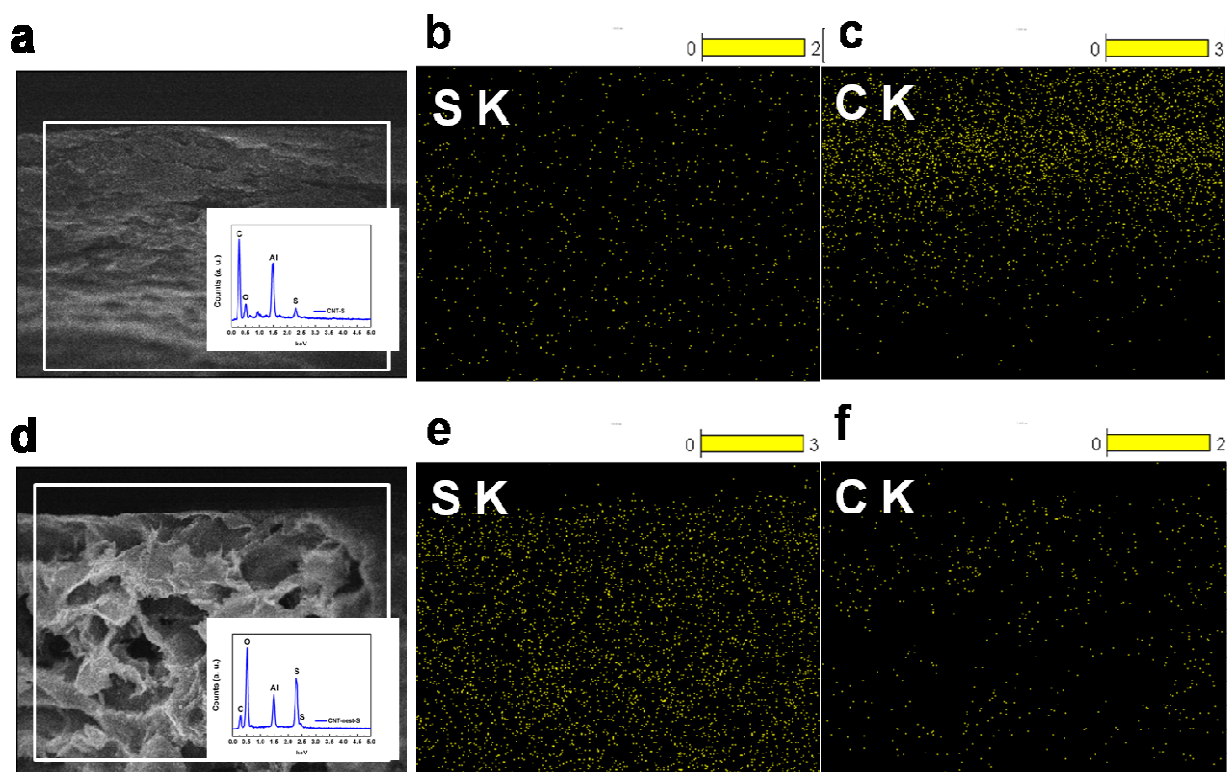


Figure S6. EDX mapping of CNT-S fresh electrode (a) and nest-structure CNT-nest-S electrode (d) of the selected area. The EDX data is shown in the inset of (a) and (d). S and C mapping for CNT-S is shown in (b) and (c). S and C mapping for CNT-nest-S is shown in (d) and (f).

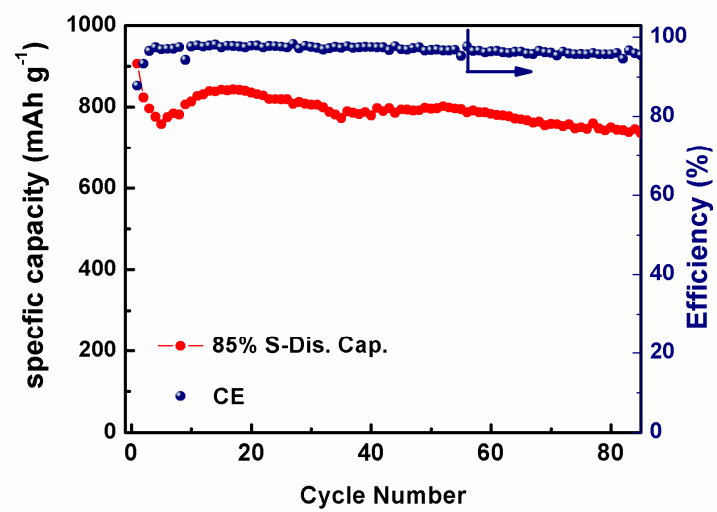


Figure S7. Cycling performance of the CNT-nest-85%S electrode with  $2.65\text{mg}\cdot\text{cm}^{-2}$  sulfur and 85% sulfur ratio in the electrode.