

## Electronic Supplementary Information

### **New Insight into the Electrode Mechanism of Lithium Sulfur Batteries via Air-Free Post-Test Analysis**

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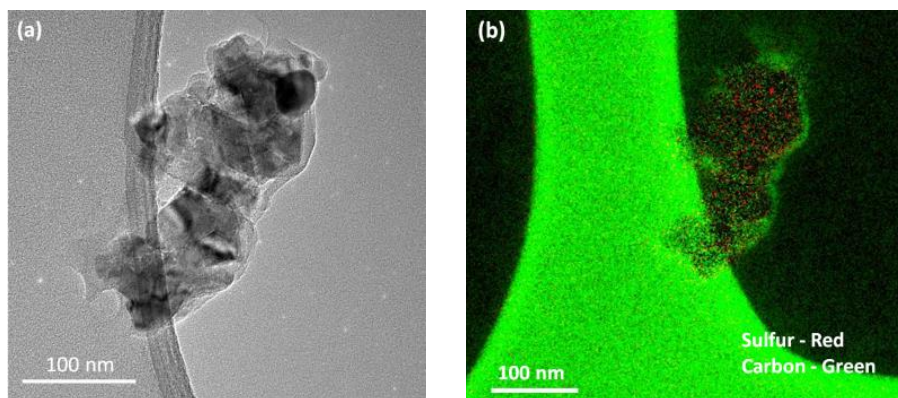
**Preparation of ball-milled Li<sub>2</sub>S and nanoLi<sub>2</sub>S@C:** The preparation of ball-milled Li<sub>2</sub>S was reported previously.<sup>1</sup> Typically, 1 g commercial Li<sub>2</sub>S powders (Alfa Aesar) were mixed with 0.075 g carbon black and 20 g iron balls (different sizes) in a canister within an Ar-filled glove box, where both of moisture and oxygen levels are maintained lower than 0.1 ppm. The mixture was mechanically milled for 6 hours using SPEX Mixer 8000M. Subsequently, the tightly sealed canister was brought back to the glovebox and the materials were collected and termed as ball-milled Li<sub>2</sub>S.

To prepare nanoLi<sub>2</sub>S@C particles, polystyrene (PS) nanoparticles with diameter of 50 nm purchased from Nanocs company were used as hard templates.<sup>2</sup> PS nanoparticles were obtained by the freeze-dry technique for future use. 40 mg PS was dispersed in 5 mL absolute ethanol in a quartz crucible and sonicated for 30 minutes, followed by being transferred to the Ar-filled glove box. 100 mg Li<sub>2</sub>S was then added into the suspension with continued stirring until all ethanol evaporated at 90 °C or at room temperature. The material obtained from the 90°C-evaporation was marked as nanoLi<sub>2</sub>S-1, while the one obtained from the room-temperature-evaporation was assigned as nanoLi<sub>2</sub>S-2. Pyrrole was then added dropwise into the dried powders before they were put into an autoclave under an Ar atmosphere. Subsequently, the sealed autoclaves were treated at 600 °C for 6 hours. After being cooled down, the as-synthesized materials were collected and marked as nanoLi<sub>2</sub>S@C-1 and nanoLi<sub>2</sub>S@C-2, respectively. The particle size of ball-milled Li<sub>2</sub>S

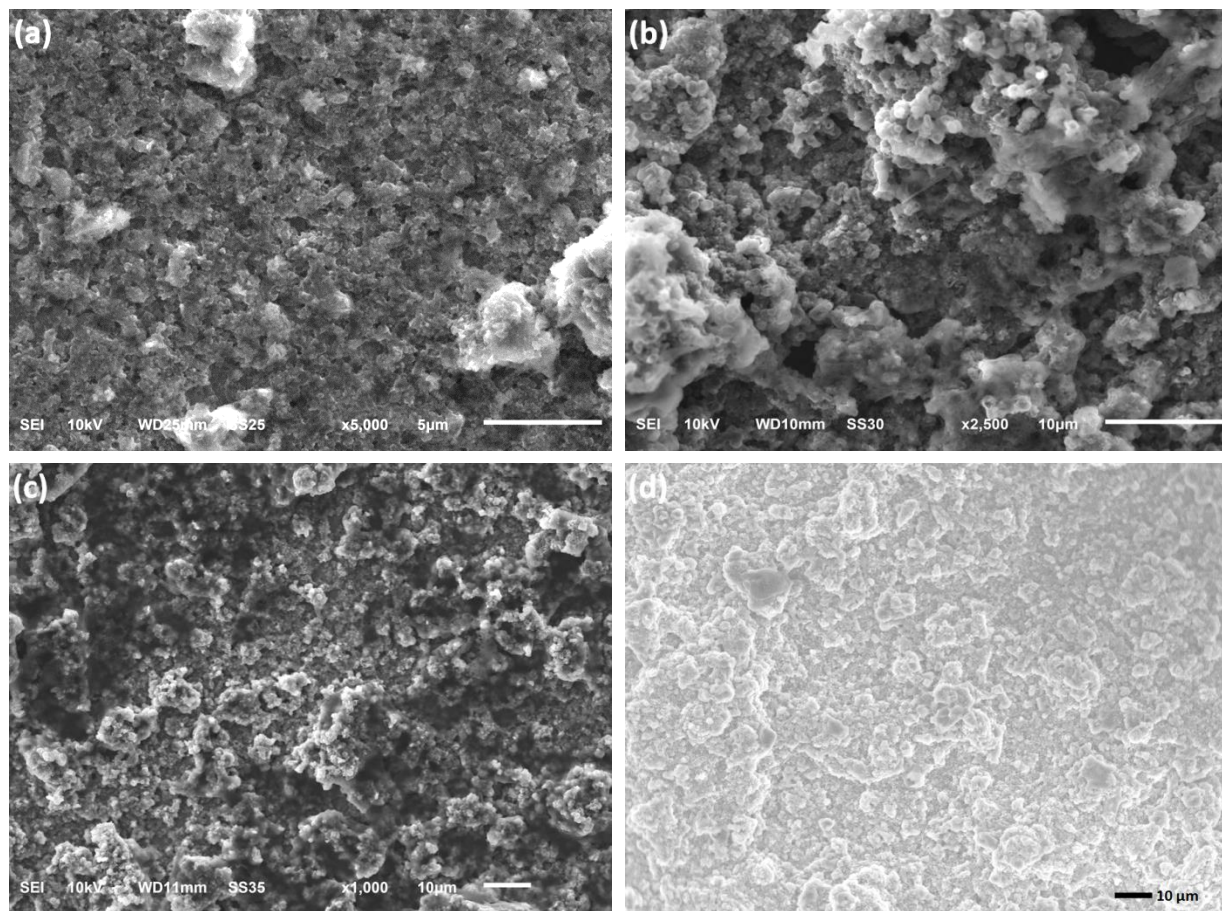
is about 400 nm, while nanoLi<sub>2</sub>S@C has a particle size of ~100 nm, which were declared in our previous reports.

**Electrochemical Measurements:** The ball-milled Li<sub>2</sub>S powder was mixed with polyvinylidene fluoride (PVDF) and carbon black (in the 8:1:1 mass ratio) to prepare electrodes. The as-prepared nanoLi<sub>2</sub>S@C-1 and nanoLi<sub>2</sub>S@C-2 were mixed with PVDF and carbon black (in the 70:15:15 mass ratio) in an Ar-filled glovebox to prepare electrodes with an aluminum foil as the current collector. The mass loading of the active materials for assembled cells was ~1 mg/cm<sup>2</sup>. Lithium metal was used as the counter anode. The electrolyte contained 1M lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) salt in the dimethoxyethane (DME) and 1,3-dioxolane (DOL) solvents (1:1 v/v) with the LiNO<sub>3</sub> additive (1 wt%). The separator was Celgard 2325 and 2032 coin cells were assembled in the glovebox. The cycling performances were evaluated using Arbin System BT2000. All electrochemical cycling processes were initially charged to 4.0 volt and then cycled between 1.6 and 3.0 V. The ball-milled Li<sub>2</sub>S cell was cycled for 31 cycles at 0.5 C. The nanoLi<sub>2</sub>S@C-1 cell was conducted for 200 cycles at 0.2 C. Cycling of nanoLi<sub>2</sub>S@C-2 at 0.2 C and nanoLi<sub>2</sub>S@C-2 at 0.5 C were performed for 200 cycles and 300 cycles, respectively.

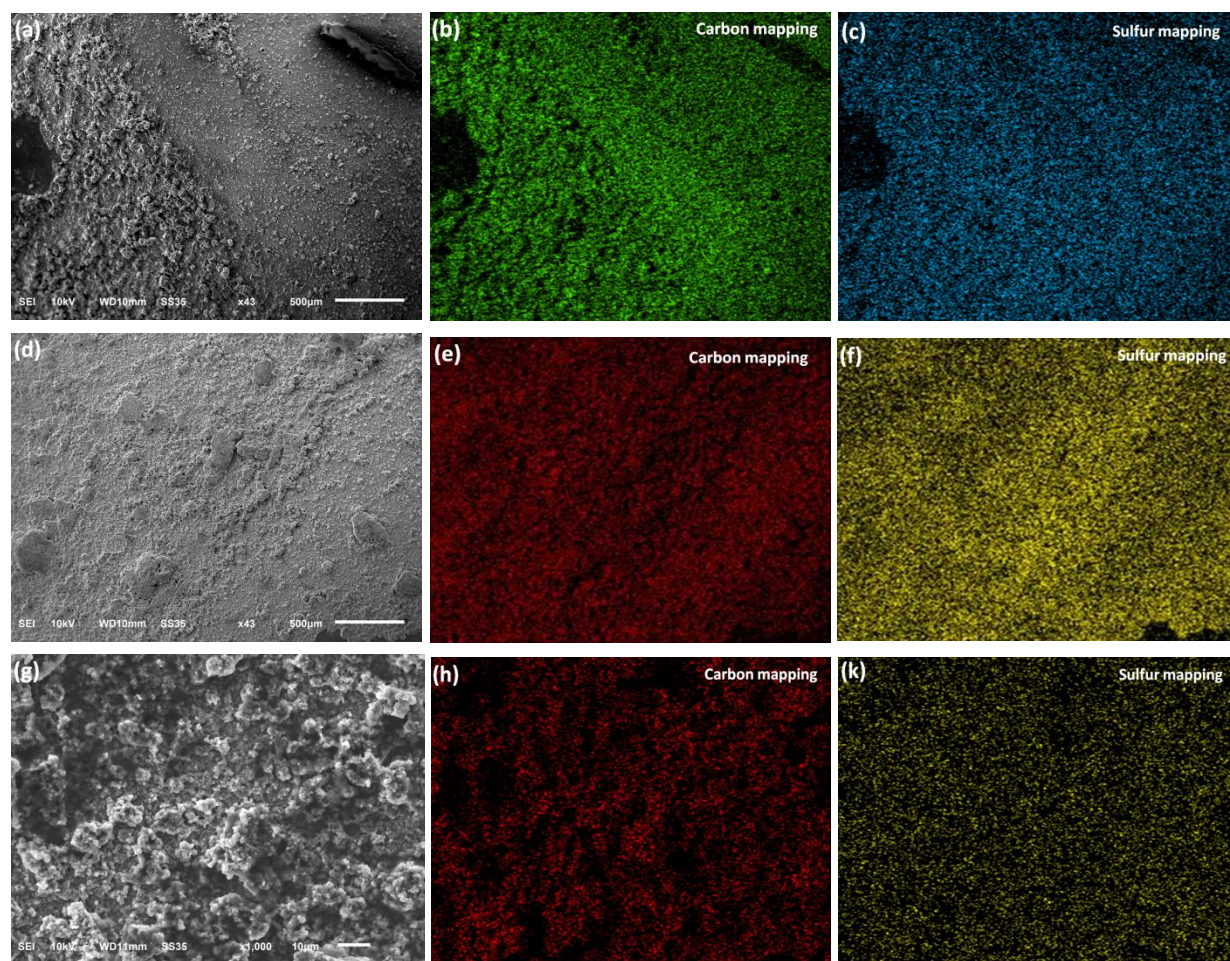
**Air-free Post-test Analysis in Ar-filled Gloveboxes:** Four coin cells, i.e., ball-milled Li<sub>2</sub>S after 31 cycles at 0.5 C, nanoLi<sub>2</sub>S@C-1 after 200 cycles at 0.2 C, nanoLi<sub>2</sub>S@C-2 after 200 cycles at 0.2 C and nanoLi<sub>2</sub>S@C-2 after 300 cycles at 0.5 C, were opened in an Ar-filled glovebox at Argonne National Laboratory (ANL). The disassembled electrodes were then soaked for 5 minutes and washed with dimethyl ether (DME), followed by a treatment in vacuum for 1 hour. This process was repeated twice to completely remove electrolyte residues. The samples were transferred from an Ar-filled glovebox to another one containing a scanning electron microscope (SEM). Thus, all of sample handling and analysis processes were conducted in the Ar-atmosphere, which completely circumvents the influences from oxygen and moisture on the post-testing samples. To make direct comparison, uncycled ball-milled Li<sub>2</sub>S electrode was also examined using the SEM at ANL.



**Fig. S1:** (a) TEM image of NanoLi<sub>2</sub>S@C-2 and (b) its energy-filtered TEM elemental mapping. A carbon shell (green color) is clearly visible [2].



**Fig. S2:** SEM images of cycled and uncycled Li<sub>2</sub>S cathodes: (a) SEM image of nanoLi<sub>2</sub>S@C-1 cathode after 200 cycles at 0.2 C; (b) SEM image of nanoLi<sub>2</sub>S@C-2 cathode after for 200 cycles at 0.2 C; (c) SEM image of nanoLi<sub>2</sub>S@C cathode-2 after 300 cycles at 0.5 C; and (d) SEM image of ball-milled Li<sub>2</sub>S without cycling.



**Fig. S3:** SEM images and EDS elemental mapping of cycled  $\text{Li}_2\text{S}$  cathodes: (a) SEM image of  $\text{nanoLi}_2\text{S}@C-1$  cathode after 200 cycles at 0.2 C; (b-c) EDS carbon and sulfur mappings of  $\text{nanoLi}_2\text{S}@C-1$  cathode with 200 cycles at 0.2 C; (d) SEM image of  $\text{nanoLi}_2\text{S}@C-2$  cathode after for 200 cycles at 0.2 C; (e-f) EDS carbon and sulfur mappings of  $\text{nanoLi}_2\text{S}@C-2$  cathode after 200 cycles at 0.2 C; (g) SEM image of  $\text{nanoLi}_2\text{S}@C-2$  cathode after 300 cycles at 0.5 C; and (h-k) EDS carbon and sulfur mappings of  $\text{nanoLi}_2\text{S}@C-2$  cathode after 300 cycles at 0.5 C.

### References:

1. L. Chen, Y. Liu, M. Ashuri, C. Liu and L. L. Shaw, *J. Mater. Chem. A*, 2014, **2**, 18026-18032.
2. L. Chen, Y. Liu, N. Dietz-Rago and L. L. Shaw, *Nanoscale*, 2015, **7**, 18071-18080.