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Supplementary Information

Unveiling the Synergistic Effect of Polysulfide Additive and MnO_2 Hollow Spheres in Evolving Stable Cyclic Performance in Li-S Batteries

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Experimental section

Chemical and materials

Analytical grade chemicals such as potassium permanganate ($KMnO_4$), butyric acid, polyvinylidene fluoride (PVDF), N-methyl pyrrolidinone (NMP), ketjen black (KB), lithium bis(tri-fluoromethanesulfonyl)imide (LiTFSI), Tetraethylene glycol dimethyl ether (TEGDME) and lithium nitrate ($LiNO_3$) were purchased from sigma Aldrich. All the chemicals were used without further purification.

Synthesis of hollow sphere MnO_2

We have reported synthesis of hollow sphere MnO_2 as electrode material for supercapacitors.[1] In typical synthesis, 3.2 gm of $KMnO_4$ was dissolved in 100 ml of double distilled water containing 10 ml butyric acid (BA). To this 40 ml of 0.5 M of $Na_2S_2O_4$ was added. The solution is kept with constant stirring for 30 min. The brown precipitate obtained was centrifuged, washed copiously with double distilled water several times and then with ethanol. It was dried in a vacuum oven at around 60 °C overnight. Sulfur, KB and MnO_2 hollow spheres were mixed together in a ratio of 70:20:10. The mixture was then transferred into sealed stainless steel vial filled with argon. The mixture was heated at 155 °C for 12 h in a closed vessel.

Preparation of Li_2S_8 additive electrolyte

For a typical polysulfide electrolyte synthesis, sublimed sulfur powder and an appropriate amount of lithium sulfide were added to the blank TEGDME solvent to make 0.15 M Li_2S_8 solution. The mixture solution was heated at 60 °C in an Ar-filled glovebox (water level: < 0.1 ppm) for 18 h to produce a dark brown solution. Afterwards appropriate amount of LITFSI salt and $LiNO_3$ was added to the blank 0.15 M Li_2S_8 solution followed by vigorous stirring to make Li_2S_8 additive electrolyte containing 0.15 M Li_2S_8, 1 M LITFSI and 0.2 M $LiNO_3$ in TEGDME solvent (Referred to as LiPS electrolyte in the manuscript). For use in UV-Vis spectroscopy, 10 mM Li_2S_8 solution was prepared in the same way by diluting conc. Li_2S_8 solution with TEGDME solvent. Reference electrolyte without Li_2S_8 additive was also prepared separately comprising of 1M LITFSI and 0.2 M $LiNO_3$ in TEGDME solvent.

Physico-chemical characterization

The crystal structure and phase purity of the synthesized materials were assessed using powder X-ray diffraction (XRD) pattern which was recorded in RIKAGU, D/Max-2500 with Cu Kα (λ = 1.5418 Å) as source. The morphological characteristics of the samples were analyzed using FE-SEM (S-4800 HITACHI, Japan). TEM studies were carried out using a JEOL, 2010F, Japan with an accelerating voltage of 300 kV. Sulfur contain percentage in the composites was measured using elemental analysis (EA, FLASH 2000 series, Thermo Scientific).

Electrode preparation and electrochemical characterization

The working electrodes were prepared by mixing active material with ketjen black and polyvinylidene fluoride (PVDF) in a weight ratio of 80:10:10 (wt.%), with NMP as a dispersant to make slurry. The slurries are homogenously coated onto carbon paper current collectors. The electrodes are dried at 60 °C for 12 hr under vacuum. This coated carbon paper is cut into disks with a diameter of 12 mm. The sulfur loading in all the composite electrodes was amounted to ~2 mg cm^{-2} .Electrochemical measurements were performed by preparing 2032-type coin cells (MTI Corporation) that were assembled in an argon-filled glovebox. The prepared sample and lithium foil (Alfa Aesar) were used as the working and counter/reference electrodes, respectively. Polypropylene membranes (Celgard, Inc.) were used as separators. 10 µl of the prepared electrolytes was added while making cells. Galvanostatic measurements were performed in the potential range of 1.7-2.8 V vs. Li/Li^+ using a battery cycler (WBS3000, Wonatech). The composites electrodes were subjected to postmortem analysis to investigate the morphological changes of MnO_2.

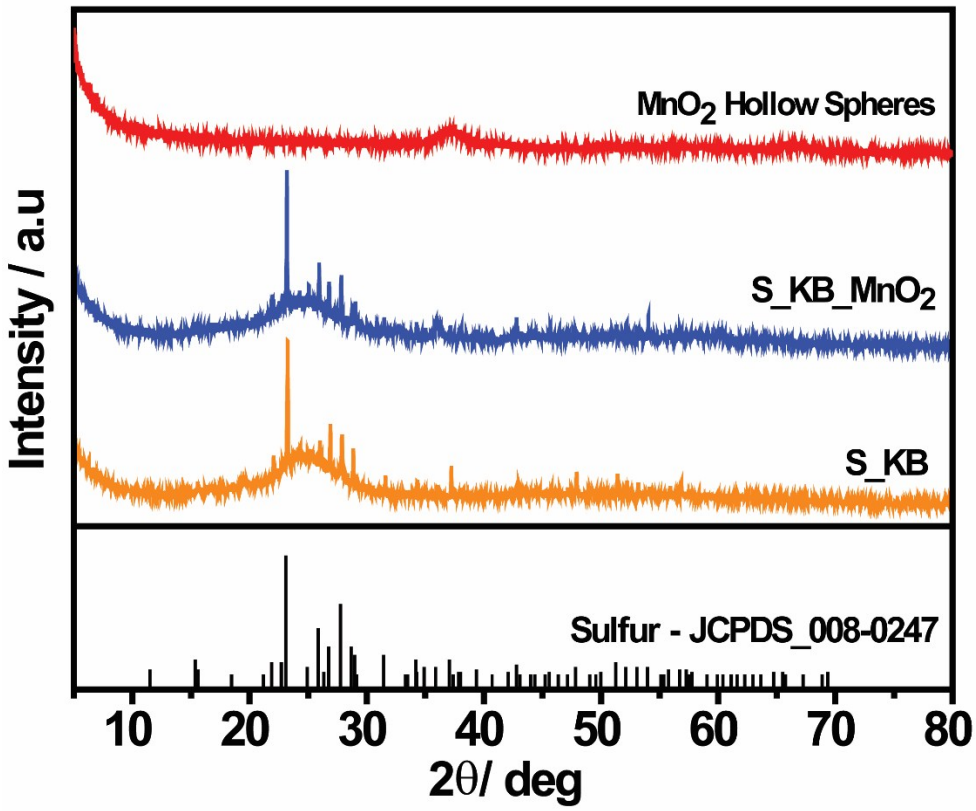

Fig. S1 XRD patterns for MnO_2 hollow spheres, S/KB and S/KB/MnO_2 composite. The orthorhombic sulfur JCPDS pattern (008-0247) is also provided.

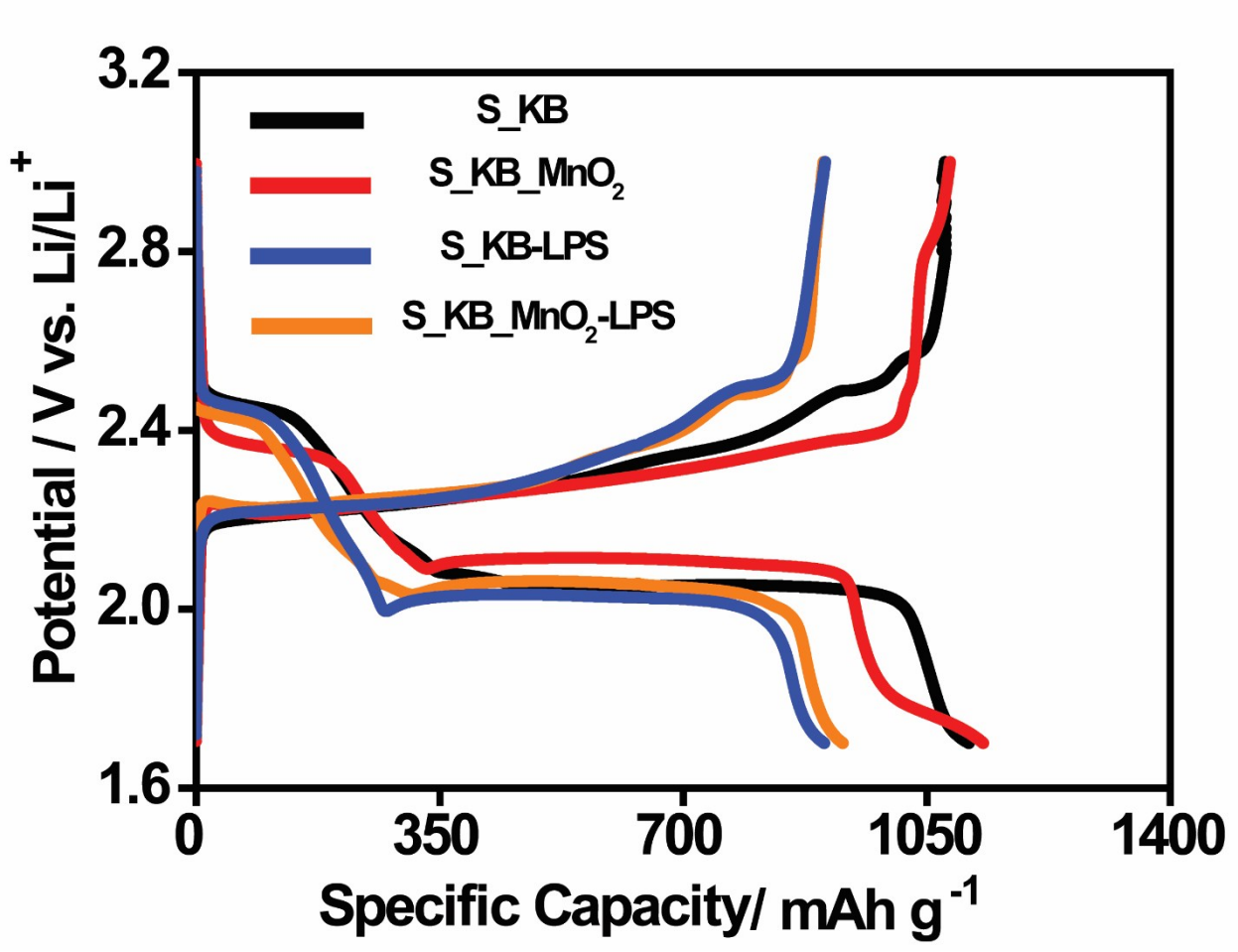

Fig S2. Voltage capacity curve representing 1st cycle S/KB, S/KB/LiPS, S/KB/MnO_2 and S/KB/MnO_2/LiPS.

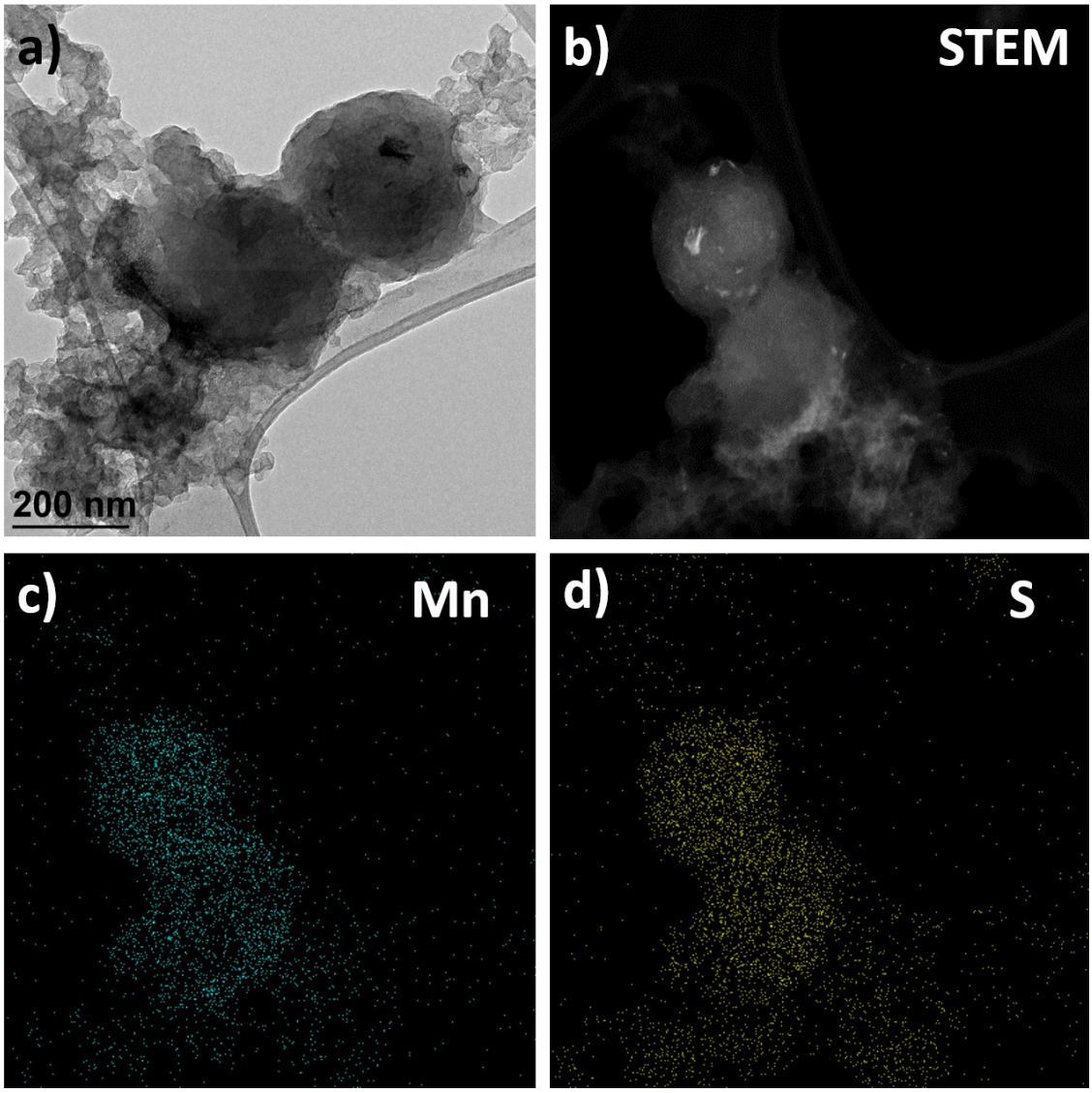

Fig S3. Postmortem TEM analysis of (a) S/KB/MnO_2/LiPS after 100 cycles at 0.2 C, (b), (c) & (d) STEM image and the corresponding elemental mapping of the shown region.

Table 1. Elemental analysis results of S/KB and S/KB/MnO_2 composite showing C, H, S and Mn content.

Materials	C	S	H	*MnO_2
S/KB	29.26	71.03	0.06	0.00
S/KB/MnO_2	20.12	71.56	0.14	8.18

*Amount of MnO_2 calculated is based on the CHS elemental analysis results.

Formula to calculate MnO_2 = 100 % – C (wt.%) - S (wt.%) – H (wt. %)

References

1 Y. Munaiah, B. G. Sundara Raj, T. Prem Kumar and P. Ragupathy, *J. Mater. Chem. A*, 2013, **1**, 4300–4306.