Electronic Supplementary Information

High-capacity Li_2S–graphene oxide composite cathodes with stable cycling performance

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Experimental Methods

Materials synthesis. Mildly-oxidized graphene oxide (GO) was synthesized using the modified Hummer's method[1] (Fig. S1) and re-dispersed into anhydrous ethyl acetate. Commercial Li_2S particles was then added (Li_2S: GO = 75: 25 by weight), followed by ultrasonication for 10 min and stirring in an argon-filled glove box. The as-synthesized Li_2S–GO composite was collected by centrifugation and allowed to dry in the glove box.

Characterization. To prevent moisture contamination of Li_2S, special precautions were taken during characterization. Scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDX) were performed using a FEI XL30 Sirion SEM. X-ray photoelectron spectroscopy (XPS) was carried out using a PHI 5000 VersaProbe. For SEM, EDX and XPS, the samples were first tightly sealed in foil/poly bags before being transferred into the chamber via an argon-filled glove bag. Raman spectra were obtained using a WITEC Raman spectrometer (531 nm excitation laser) after the samples were tightly sealed in a glass holder.

Electrochemical measurements. Due to the sensitivity of Li_2S to moisture, all the electrode preparation and cell assembly procedures were carried out in an argon-filled glove box with moisture and oxygen levels below 0.5 ppm. The Li_2S–GO composites were ground with conductive carbon black (Super P) and polyvinylidene fluoride (PVDF) binder in a weight ratio of 70: 25: 5 using a mortar and pestle, followed by dispersion in *N*-methyl-2-pyrrolidinone (NMP) to form a slurry. After overnight stirring, the slurry was then coated onto aluminum foil (carbon-coated; Exopack) using doctor blade and dried at 60^{o}C to form the working electrode. For comparison, pristine Li_2S cathodes were also prepared in the same way by mixing Li_2S with Super P and PVDF binder in a weight ratio 70: 25: 5. 2032-type coin cells were assembled using lithium foil as the counter electrode. The electrolyte used was a freshly-prepared solution of lithium bis(trifluoromethanesulfonyl)imide (LiTFSI, 1 M) in 1:1 v/v 1,2-dimethoxyethane (DME) and 1,3-dioxolane (DOL) containing $LiNO_3$ additive (1 wt%). Galvanostatic cycling was carried out using a 96-channel (Arbin Instruments) or a 8-channel (MTI Corporation) battery tester. The cathodes were first activated at C/20 (1C = 1,166 mA g^{-1}) by charging to a high cutoff voltage of 3.8 V vs. Li^+/Li to overcome the initial potential barrier (Fig. S3),[2] followed by discharge to 1.8 V. Galvanostatic cycling was then carried out from 1.8 - 2.6 V vs. Li^+/Li. The typical mass loading of Li_2S was ~1 mg cm^{-2} and specific capacity values were calculated based on the mass of Li_2S.

Electrolyte testing. For analysis of sulfur content in the electrolyte, a sulfur-free lithium salt of $LiClO_4$ (1 M) in 1:1 v/v DME/DOL solution with $LiNO_3$ (1 wt%) was used as the electrolyte (25 μL in each cell). All other cell assembly procedures are the same as that described above. The cells were disassembled at various points during a discharge/charge cycle, after which the contents (cathode, anode and electrolyte-soaked separator) were washed with DOL solution. This polysulfide-containing solution was then oxidized with concentrated HNO_3 and diluted with deionized water for analysis of sulfur content using inductively coupled plasma-optical emission spectroscopy (ICP-OES; Thermo Scientific ICAP 6300 Duo View Spectrometer).[3]

References:

1. H. Wang, Y. Yang, Y. Liang, J. T. Robinson, Y. Li, A. Jackson, Y. Cui and H. Dai, *Nano Lett.*, 2011, **11**, 2644-2647.

2. Y. Yang, G. Zheng, S. Misra, J. Nelson, M. F. Toney and Y. Cui, *J. Am. Chem. Soc.*, 2012, **134,** 15387-15394.

3. Z. W. Seh, Q. Zhang, W. Li, G. Zheng, H. Yao and Y. Cui, *Chem. Sci.*, 2013, **4**, 3673-3677.

4. Y. Xu, K. Sheng, C. Li and G. Shi, *J. Mater. Chem.*, 2011, **21**, 7376-7380.

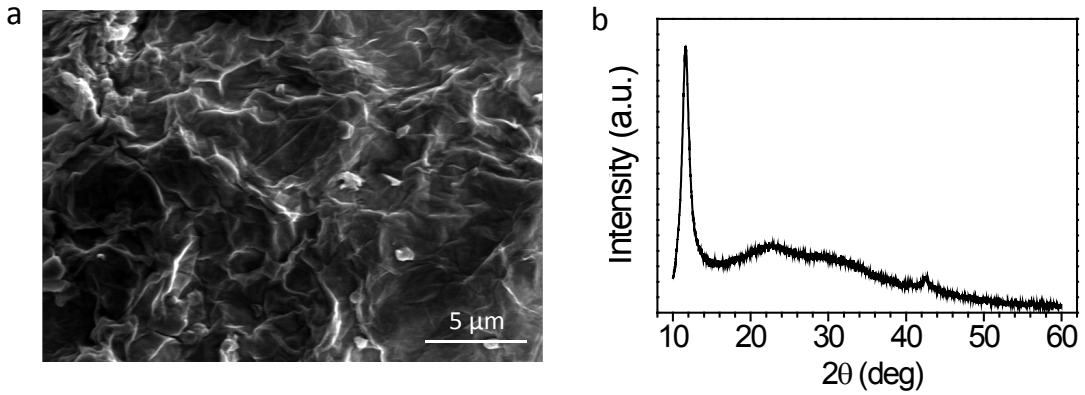

Fig. S1 (a) SEM image and **(b)** X-ray diffraction (XRD) pattern of as-synthesized mildly-oxidized GO, showing the characteristic peaks of GO.[4] XRD was performed using a PANalytical X'Pert Diffractometer using Cu Kα radiation.

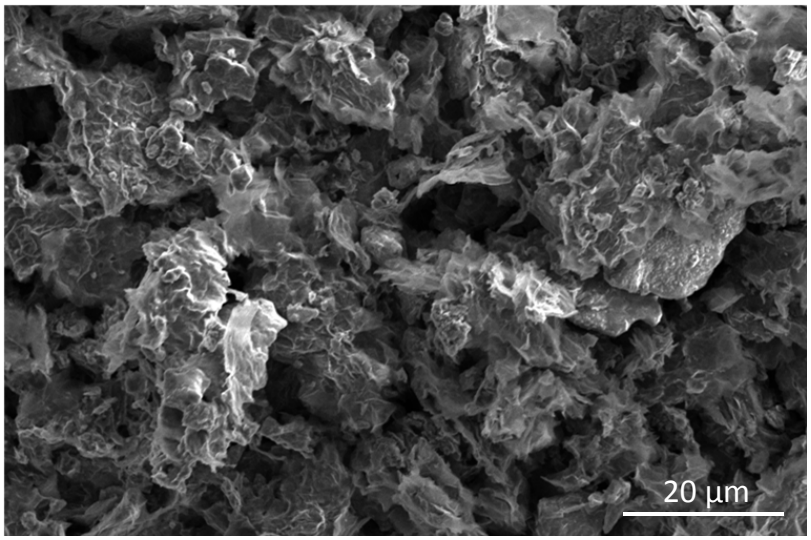

Fig. S2 Low-magnification SEM image of the as-synthesized Li_2S–GO composites.

	Li	S	C	O
at% (measured)	-	47.5	38.2	14.3
wt% (calculated)	23.0	53.0	16.0	8.0
Composition	76.0 wt% Li_2S		24.0 wt% GO	

Table S1. Elemental composition of the Li_2S–GO composites determined using large-area EDX analysis, showing the measured at% of the various elements (except Li which cannot be measured by EDX). The wt% of Li was calculated from the at% of S based on the empirical formula Li_2S. From the results, we can determine the overall Li_2S content in the Li_2S–GO composites to be ~76 wt%. This is consistent with the relative amounts of Li_2S and GO added during the synthesis process (75: 25 by weight).

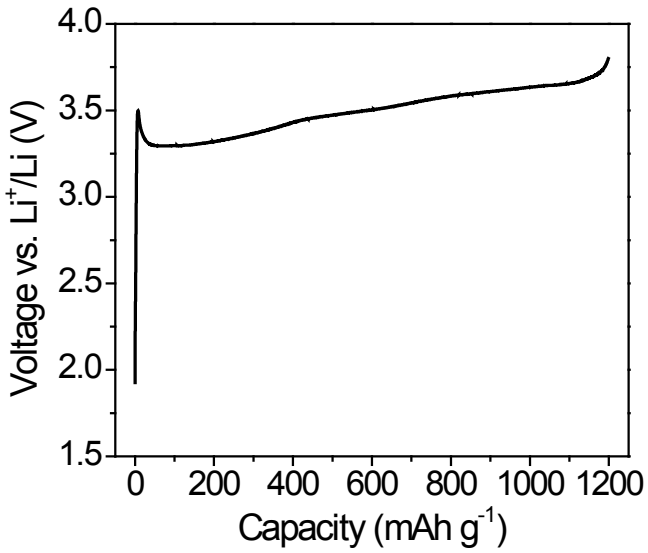

Fig. S3 Typical activation charge profile of the Li_2S–GO composite cathodes. A high cutoff voltage of 3.8 V vs. Li^+/Li was used to overcome the initial potential barrier associated with micron-sized Li_2S particles as described in previous work.[2]

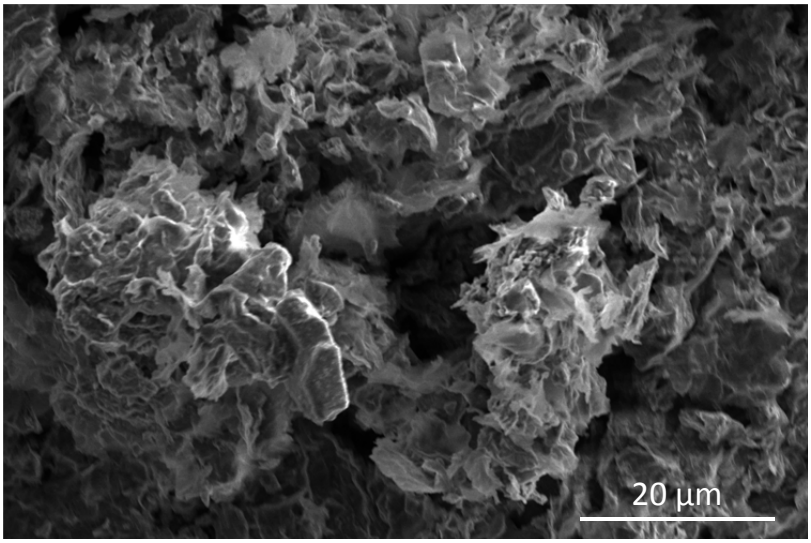

Fig. S4 Morphology of the Li_2S–GO composite cathodes after 150 cycles at 0.2C. The cell was disassembled in the discharged state after the voltage was maintained at 1.8 V vs. Li^+/Li for over 20 h.