

Supporting information for:

Lithium Sulfide (Li₂S)/Graphene Oxide Nano-spheres with Conformal Carbon Coating as High-rate, Long- life Cathode for Li/S cells

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1. EXPERIMENTAL PROCEDURE

Material preparation: The $\text{Li}_2\text{S}/\text{GO}$ nano-spheres were prepared as follows: 1 ml (2 mg of GO) commercial single layered graphene oxide (SLGO) dispersion in tetrahydrofuran (flake size: 500 – 800 nm, CHEAP TUBE) was sonicated using an ultrasonicator for an hour. 64 mg of S (Alfa Aesar, Sulfur powder ~ 325 mesh, 99.5 %) was dissolved in 3.5 ml toluene by stirring for 10 min. Both the S-toluene solution and the GO dispersion in THF were mixed and stirred for 1 h to prepare a homogeneous S-toluene/GO-THF mixture. Then the prepared mixture was added into 4.2 mL 1.0 M lithium triethylborohydride in tetrahydrofuran (1M LiEt_3BH in THF, Sigma-Aldrich) and stirred at room temperature. After 2 min, the solution was heated to 90 °C for 8 min until stable $\text{Li}_2\text{S}/\text{GO}$ nano-spheres formed, The Li_2S -GO was washed with THF and hexane using centrifugation. The $\text{Li}_2\text{S}/\text{GO}$ nano-spheres were then heat-treated at 500 °C under Ar atmosphere for 30 min and ground using mortar and pestle. The weight ratio between Li_2S and GO in the $\text{Li}_2\text{S}/\text{GO}$ nano-spheres were simply shown to be as about 98 : 2 by a washing method. The Li_2S -GO powder was weighed and put into a mixture of distilled water and ethanol (1:2 ratio v/v) and the solution was centrifuged at 5000 rpm for 10 min. Then, supernatant was collected and pH of supernatant was checked. This procedure was repeated until pH of supernatant reached to 7. (When Li_2S reacts with H_2O , LiOH forms which increases pH value). Once pH of supernatant reached 7, powder was collected and dried in vacuum oven at 60 °C overnight. The weight ratio between Li_2S and GO could be estimated by comparing the weight of the pristine and washed powders. To obtain the core-shell structured $\text{Li}_2\text{S}/\text{GO}@C$ nano-spheres, the CVD carbon coating procedure was conducted at 700 °C for 30 min with rotation of the quartz tube using a lab-designed rotating furnace. The Ar and acetylene (C_2H_2 , carbon precursor) mixture was supplied with flow rate of 100 SCCM (standard cubic centimeters per minute) and 10 SCCM, respectively. The sample was weighed before and after the CVD coating process to estimate the amount of C obtained by the CVD coating process (13 % C was obtained). Because Li_2S is highly sensitive to moisture, all the synthesis process including furnace tube assembly was conducted in an argon filled glove box with a moisture and oxygen content below 0.1 ppm. For comparison, Li_2S spheres (1 μm) were prepared using the synthesis procedure reported in the previous literature.¹⁶ Briefly, 64 mg Sulfur (Alfa Aesar, Sulfur powder ~ 325 mesh, 99.5 %) was

dissolved in 3 ml toluene and then the S-toluene solution was added into 4.2 mL of 1.0 M LiEt_3BH in THF. After stirring for 2 min at room temperature, the solution was heated to 90 °C for 7 min. The Li_2S powder was collected and washed by a centrifugation method. $\text{Li}_2\text{S}/\text{GO}@C\text{-NR}$ sample was also prepared using typical the CVD coating method under the same coating conditions without rotation of the quartz tube. The obtained carbon amount was same as that of $\text{Li}_2\text{S}/\text{GO}@C$ nano-spheres (13 %).

Characterization: All preparation of the samples for characterization was conducted in an argon filled glove box with a moisture and oxygen content below 0.1 ppm. Investigation of the crystal structure was conducted using an X-ray diffractometer (XRD, Bruker AXS D8 Discover GADDS microdiffractometer) with an air-free XRD holder to protect Li_2S from moisture. Raman spectra of samples (Labram, Horiba Jobin Yvon USA, Inc.) were collected in the confocal backscattering configuration with a excitation wavelength of 488 nm. To keep the sample in an inert atmosphere, a linkam cell with constant argon flow was applied. The morphology of the powdered samples was observed using a field emission scanning electron microscope (FESEM, JEOL JSM-7500F) with elemental mapping using energy-dispersive X-ray spectroscopy (EDS, Oxford). High resolution transmission electron microscopy images were collected using a JEOL TEM instrument (HRTEM, JEOL 2100-F) with elemental mapping using energy filtered TEM (EFTEM). For the polysulfide dissolution test, 1 mg of Li_2S , $\text{Li}_2\text{S}/\text{GO}@C\text{-NR}$, $\text{Li}_2\text{S}/\text{GO}@C$ spheres were added into the test solution comprising 7 mg of S dissolved in 1.5 mL THF/toluene mixture solution (1:1, v/v).

Electrochemical Tests: To fabricate the electrodes, 60 % of Li_2S , 35 % of carbon materials (including GO, carbon obtained by CVD and carbon black (Super P) as conducting agent) and 5 % of Polyvinylpyrrolidone (PVP; $M_w \sim 1,300\text{K}$) as binder were mixed, and then the slurry was drop-casted onto carbon fiber paper (Hesen Electrical Ltd, HCP010N; 0.1 mm thickness, 75% porosity) used as current collector, and dried. The mass loading of Li_2S in the electrodes was $0.7\text{-}0.9 \text{ mg cm}^{-2}$. 1 M Lithium Bis(Trifluoromethanesulfonyl)Imide (LiTFSI) in N-methyl-N-butylpyrrolidinium bis(trifluoromethane sulfonyl)imide ($\text{PYR}_{14}\text{TFSI}$)/dioxolane (DOL)/Dimethoxyethane (DME) (2:1:1, v/v) containing 1 wt% LiNO_3 was prepared for the electrolyte. CR2325-type coin cells were

fabricated with a lithium metal foil (99.98%, Cyprus Foote Mineral) as counter/reference electrode and a porous polypropylene separator (2400, Celgard) in a glove box filled with Ar gas. Galvanostatic cycling tests of the coin cells was conducted using a battery cycler (Arbin BT2000) at different rates between 1.5 and 2.8V after the first charge to 4.0 V at 0.05 C in order to activate the Li_2S .

FIGURES

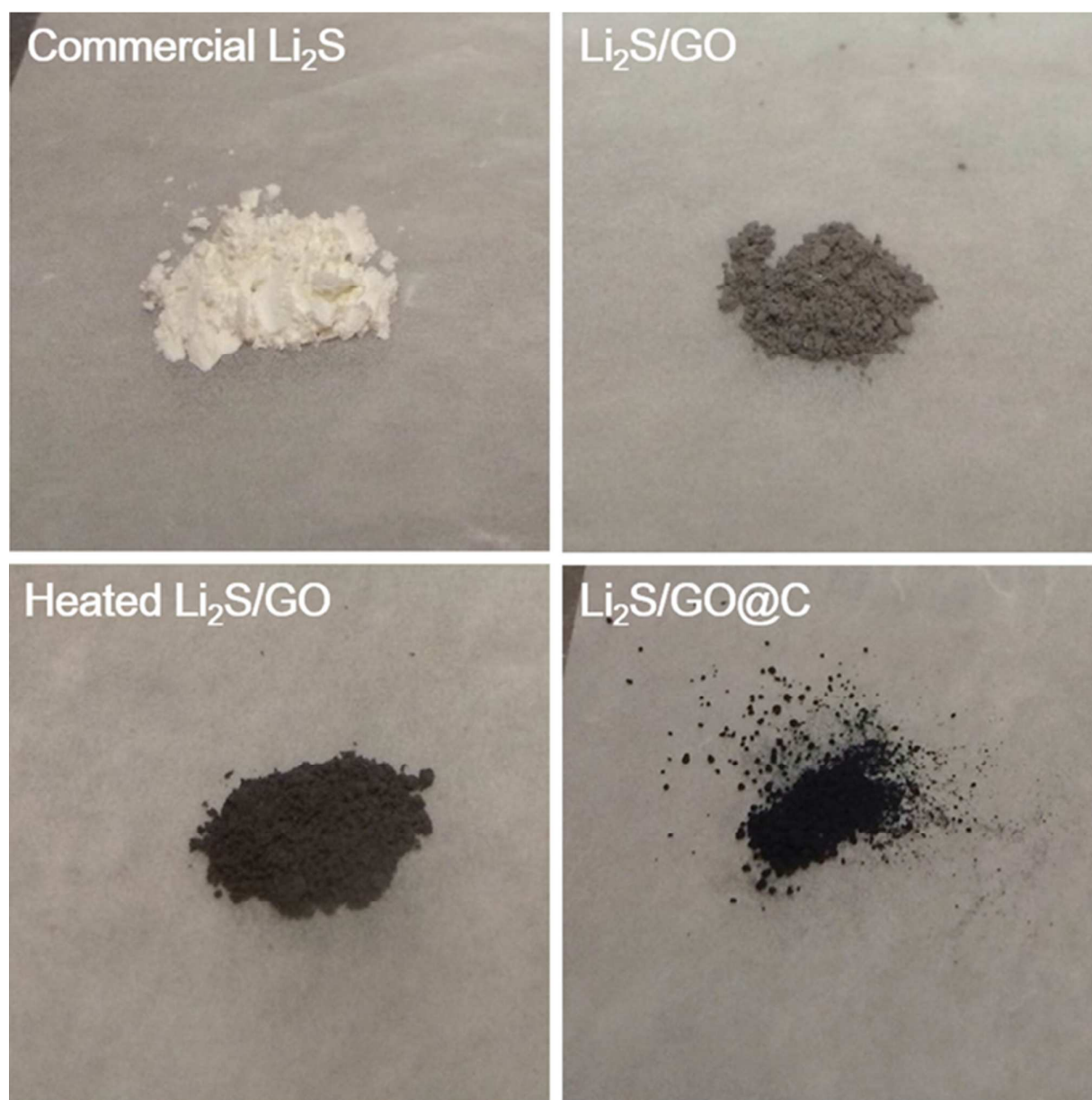


Figure S1. Powder colors of the commercial Li₂S, as-synthesized Li₂S/GO, heat-treated Li₂S/GO and Li₂S/GO@C nano-spheres.

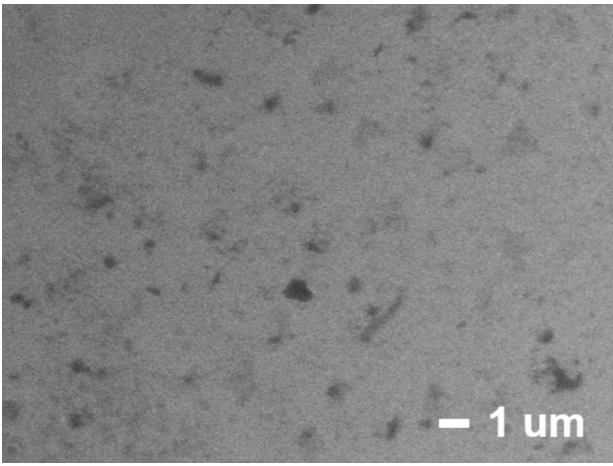


Figure S2. SEM image of commercial SLGO.

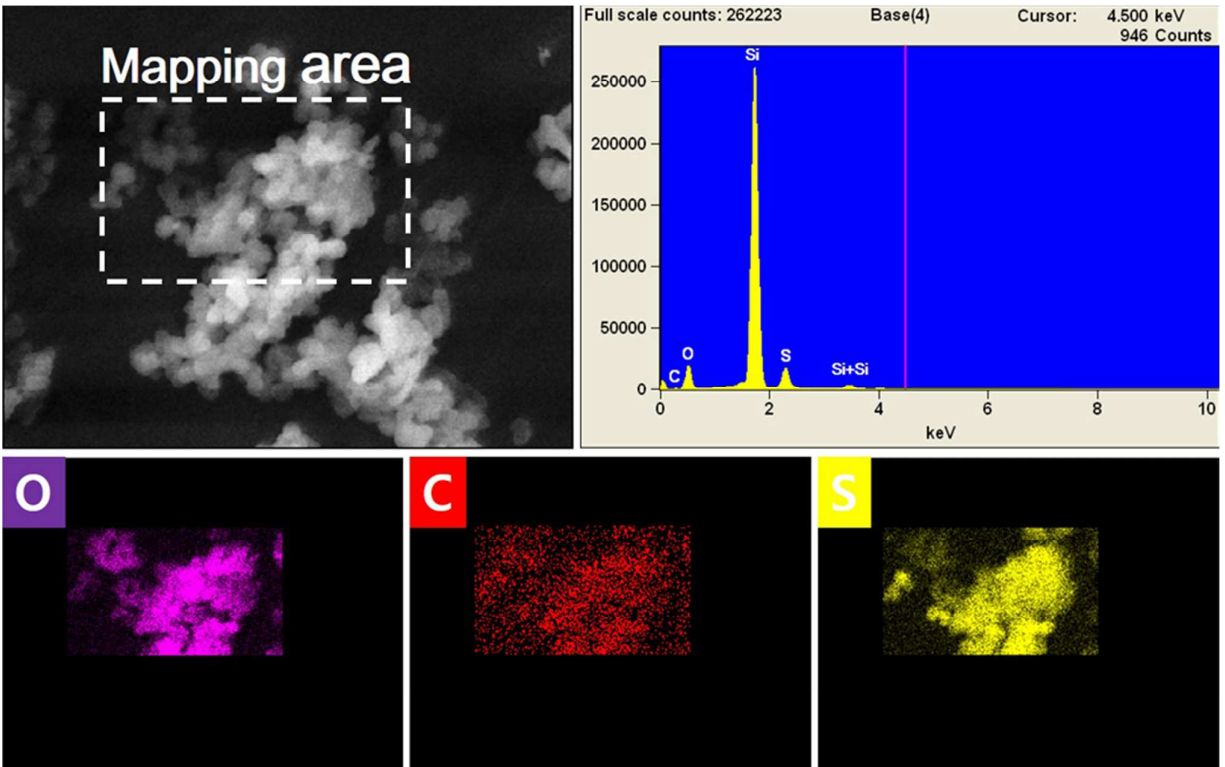


Figure S3. SEM image of heat-treated $\text{Li}_2\text{S}/\text{GO}$ nano-spheres with EDS mapping.

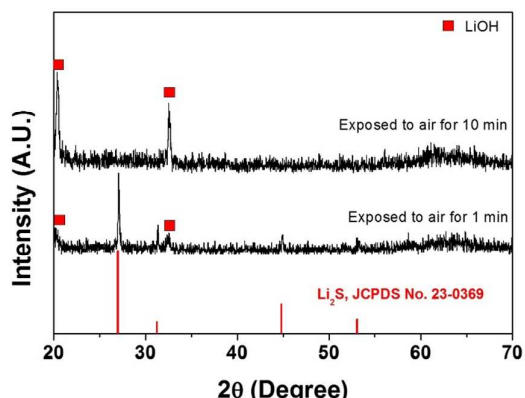


Figure S4. XRD patterns of Li₂S/GO nano-powder exposed to air.

To confirm the byproduct derived from chemical reaction between Li₂S and H₂O, XRD patterns were obtained after the Li₂S/GO powder was exposed to air for 1 and 10 min. As shown in this figure, a LiOH phase formed immediately and only the LiOH phase existed after 10 min, which indicates that the chemical reaction between Li₂S and H₂O in air occurred very quickly. The chemical reaction can be expressed as $\text{Li}_2\text{S} + 2\text{H}_2\text{O} = 2\text{LiOH} + \text{H}_2\text{S (g)}$.

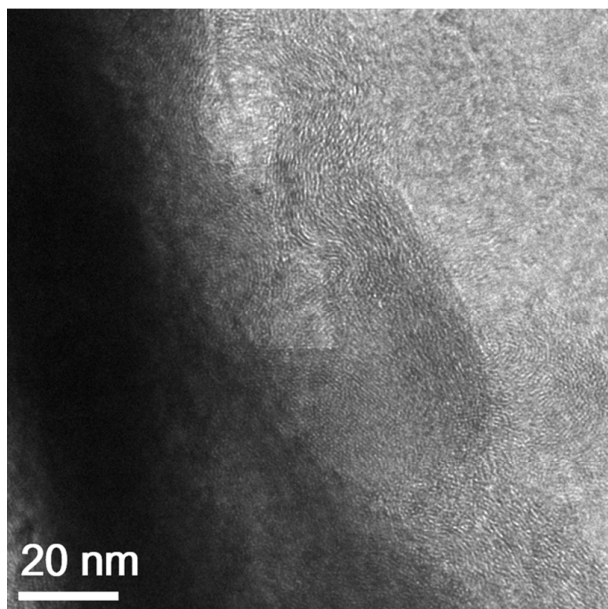


Figure S5. HRTEM image of GO@C after eliminating Li₂S from the Li₂S/GO@C nano-particles.

An onion-like structure related to the graphitic carbon structure was observed in the HRTEM image of a GO sheet placed in the hollow carbon sphere. Li₂S was removed from the Li₂S/GO@C nano-particles to observe the GO sheet embedded in Li₂S.

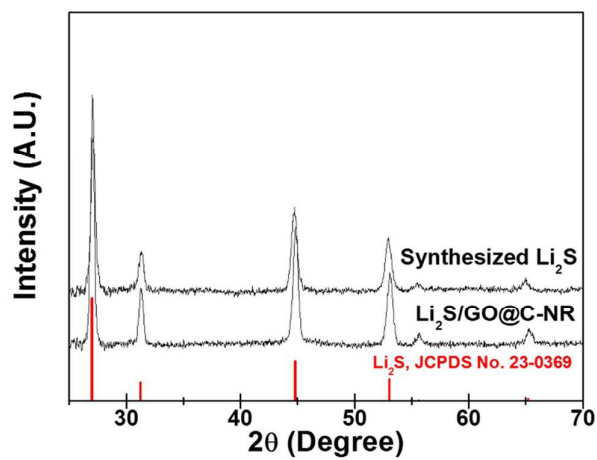


Figure S6. XRD patterns of synthesized Li₂S and Li₂S/GO@C-NR nano-spheres.

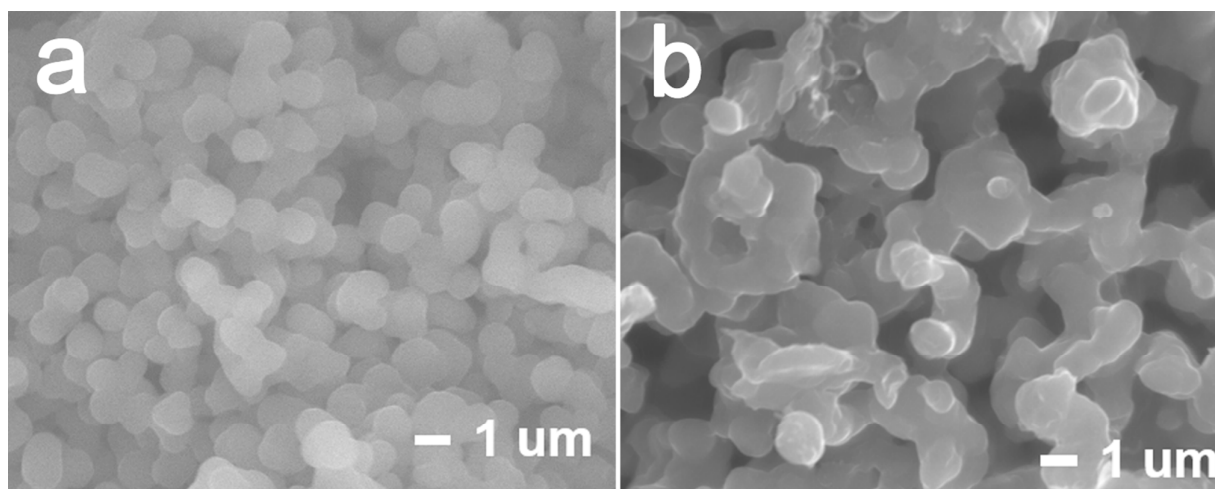


Figure S7. SEM images of synthesized Li₂S and Li₂S/GO@C-NR nano-spheres.

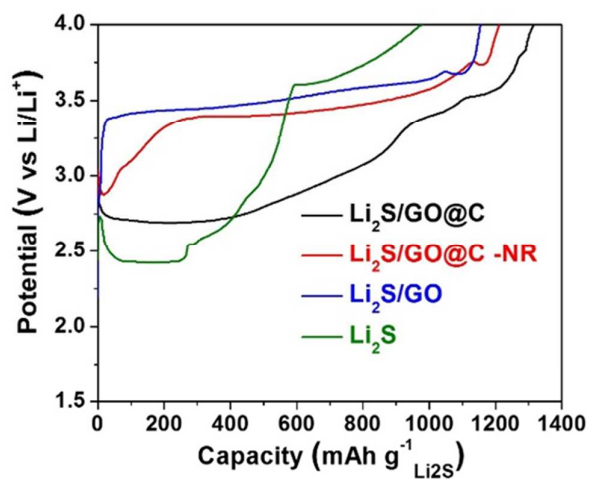


Figure S8. Voltage profiles of synthesized Li₂S, Li₂S/GO, Li₂S/GO@C-NR and Li₂S/GO@C electrode at the first charge.

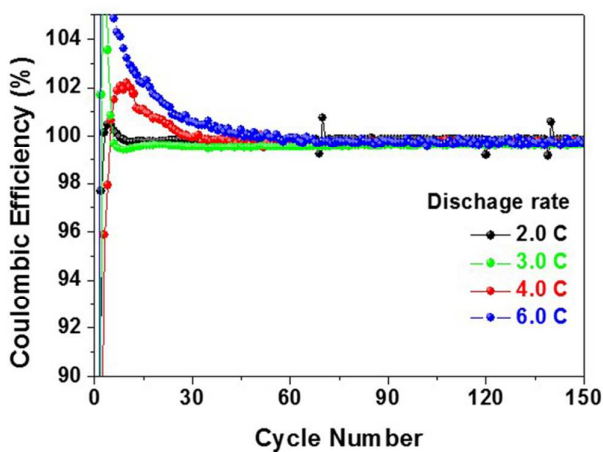


Figure S9. Coulombic efficiency of a $\text{Li}_2\text{S}/\text{GO}@\text{C}$ electrode cycled at various C-rates.

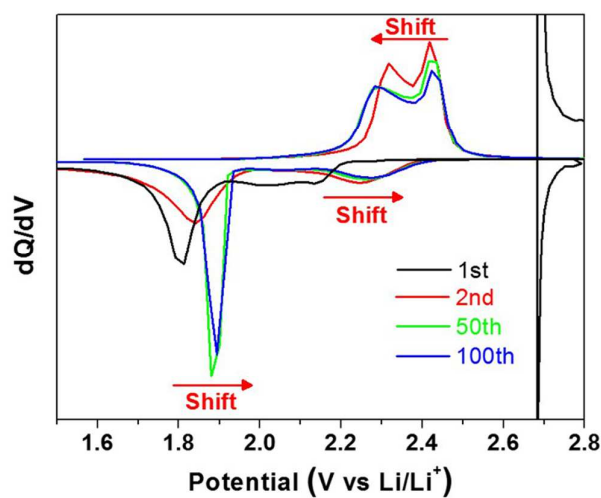


Figure S10. Differential capacity plot (DCP) of $\text{Li}_2\text{S}/\text{GO}@\text{C}$ electrode corresponding to the voltage profiles shown in Figure 5c.

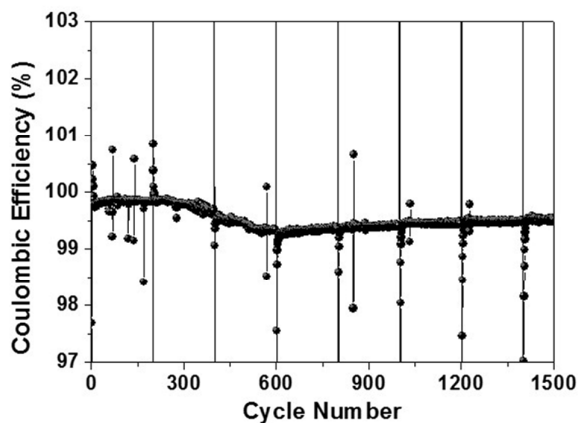


Figure S11. Coulombic efficiency of a $\text{Li}_2\text{S}/\text{GO}@\text{C}$ electrode charged at 1.0 C and discharged at 2.0 C for 1500 cycles. At every 200th cycle, the electrode was cycled once at 0.05 C.

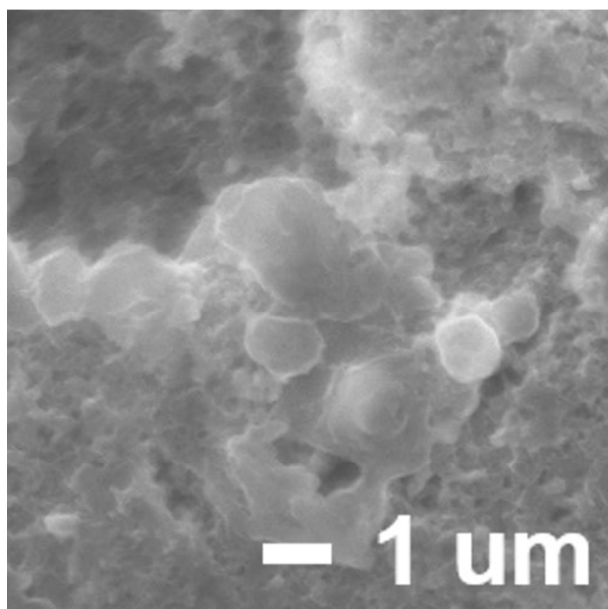


Figure S12. SEM image of $\text{Li}_2\text{S}/\text{GO}@\text{C}$ electrode discharged after 1500 cycles.

For ex situ SEM observation, the cell was fully discharged after 1500 cycles and disassembled immediately to collect the cycled cathode. The cathode was washed with a DOL/DME mixture (1:1 v/v) and dried at 60 °C overnight in the glove-box filled with Ar gas.

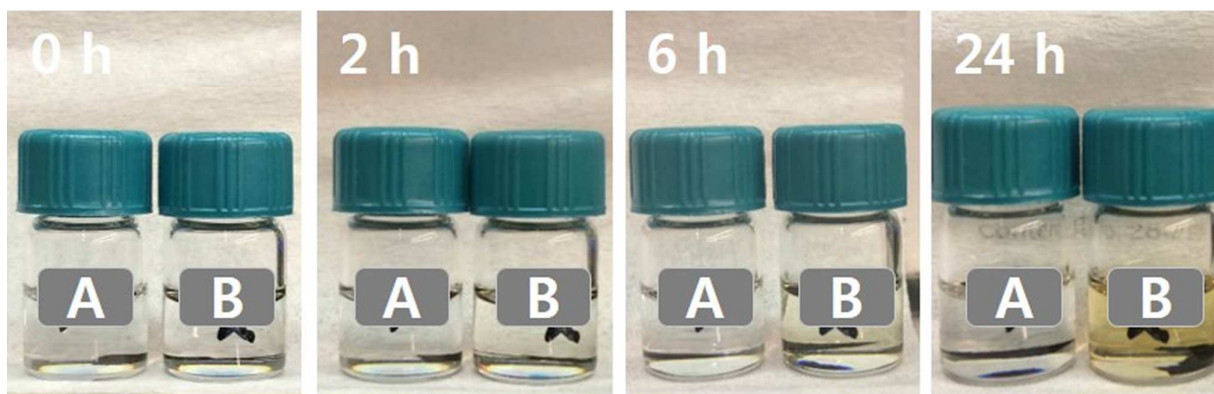


Figure S13. Polysulfide dissolution test of (A) pristine electrode and (B) $\text{Li}_2\text{S}/\text{GO}@\text{C}$ electrode discharged after 1000 cycles.

For the polysulfide dissolution test of a cycled $\text{Li}_2\text{S}/\text{GO}@\text{C}$ electrode, the cell was fully discharged after 1000 cycles and disassembled immediately to collect the cycled cathode. The cathode was washed with a DOL/DME mixture (1:1 v/v) and dried at 60 °C overnight in the glove-box filled with Ar gas. Then, a pristine electrode and the cycled electrode were put into the test solution composed of 7 mg S dissolved in 1.5 ml of THF/toluene mixture (1:1 v/v).

