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Lithium Sulfide (Li₂S)/Graphene Oxide Nanospheres with Conformal Carbon Coating as a High-Rate, Long-Life Cathode for Li/S Cells

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S Supporting Information

ABSTRACT: In recent years, lithium/sulfur (Li/S) cells have attracted great attention as a candidate for the next generation of rechargeable batteries due to their high theoretical specific energy of 2600 W·h kg⁻¹, which is much higher than that of Li ion cells (400–600 W·h kg⁻¹). However, problems of the S cathode such as highly soluble intermediate species (polysulfides Li₂S_n, *n* = 4–8) and the insulating nature of S cause poor cycle life and low utilization of S, which prevents the practical use of Li/S cells. Here, a high-rate and long-life Li/S cell is proposed, which has a cathode material with a core-shell nanostructure comprising Li₂S nanospheres with an embedded graphene oxide (GO) sheet as a core material and a conformal carbon layer as a shell. The conformal carbon coating is easily obtained by a unique CVD coating process using a lab-designed rotating furnace without any repetitive steps. The Li₂S/GO@C cathode exhibits a high initial discharge capacity of 650 mA·h g⁻¹ of Li₂S (corresponding to the 942 mA·h g⁻¹ of S) and very low capacity decay rate of only 0.046% per cycle with a high Coulombic efficiency of up to 99.7% for 1500 cycles when cycled at the 2 C discharge rate.

KEYWORDS: lithium batteries, sulfur, energy storage, lithium sulfide, cathodes, graphene oxide

Since elemental sulfur (S) was investigated as the cathode material for high-temperature rechargeable batteries in the 1960s,¹ elemental S has become a strong candidate not only for high-temperature rechargeable cells but also for ambient temperature Li rechargeable Li/S cells, due to the large theoretical specific capacity of S (1675 mA h g⁻¹) given by the reaction between Li and S expressed as S₈ + 16Li⁺ + 16e⁻ ↔ 8Li₂S, very low production cost (~\$150 ton⁻¹), high abundance and low environmental impact.^{2–21} Especially, the theoretical specific energy of the Li/S cells (2600 W·h kg⁻¹) is much higher than that of the Li-ion cells (400–600 W·h kg⁻¹), which is mainly due to the almost 1 order of magnitude higher theoretical specific capacity of S compared to that of conventional transition metal oxide cathodes (130–200 mA·h g⁻¹) for Li ion cells.² The Li/S cell has attracted great attention because of the need of the electrical vehicle (EV) market for high specific energy batteries (~350 W·h kg⁻¹ at C/3 discharge rate),²² which greatly exceeds the practical specific energy of current Li ion cells (100–200 W·h kg⁻¹). However, despite the great advantages of Li/S cells, the early S-based cathodes in organic electrolytes showed a low utilization and a poor cycle life owing to several major problems: (i) The insulating nature of Li₂S and S that are the final products of the S electrode at the fully discharged and charged states, respectively. (ii) A large volume change of the S particles during cycling (~80%) resulting in mechanical degradation of the electrode. (iii) Highly soluble intermediate species (polysulfides, Li₂S_n, *n* = 4–

8) in most organic liquid electrolytes, which causes the loss of active material from the cathode and the polysulfide shuttle effect.²³ When the polysulfides are dissolved into the liquid electrolyte, they can diffuse back and forth between electrodes and can form insoluble Li₂S (or Li₂S₂) on the surface of the Li metal electrode, which leads to lower Coulombic efficiency.²⁴

Therefore, from the S cathode point of view, the key factors to improve the electrochemical performance of Li/S cells are to increase the electronic conductivity of the electrode and to suppress the polysulfide dissolution as well as the mechanical stress caused by the volume change during cycling. Many approaches have been proposed to achieve the goals such as nanofabrication of S (or S-based composites),^{13–19} employing chemically (or mechanically) protective materials on the S particles^{15,16,20} and composites with mesoporous carbon⁴ or graphene oxide (GO)^{8,17,18,21} that can act as S immobilizers. Among them, GO is very attractive for stabilizing the cycling performance of S-based cathodes because the reactive functional groups (such as carbonyl, carboxylic, hydroxyl, and epoxy groups) on the surface of GO can form bonds with S, indicating that S (or polysulfides) can be captured by those functional groups. In a previous study, this chemical bonding between S and GO was successfully demonstrated using Raman, X-ray

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Figure 1. Synthesis and characterization of Li₂S/GO@C nanospheres. (a) Schematic illustration of the synthesis process, (b) XRD patterns, and (c) Raman spectra at each synthesis step.

photoelectron (XPS) and X-ray absorption (XAS) spectroscopies, and the S/GO cathode exhibited quite stable cycling performance with high utilization of about 1000 mA·h g⁻¹ at 0.1 C for more than 50 cycles.²¹

A new concept of the S cathode has been investigated recently for Li/S cells, which employs a fully lithiated S phase, lithium sulfide (Li₂S, theoretical specific capacity: 1166 mA·h g⁻¹) as the initial cathode material instead of S.^{16,17,20,25–30} When Li₂S is employed as the cathode material, the mechanical damage of the cathode due to the volume expansion of S particles (up to 80%) caused by the lithiation process during discharge can be reduced because Li₂S particles already occupy the maximum volume relative to S. Empty space generated during the charging process can accommodate the volume expansion of the S particles when the cathode is discharged. In addition, the prelithiated state of the Li₂S cathode can be coupled with Li-free anodes such as silicon (Si)²⁸ and tin (Sn).²⁹ This can prevent internal shorts of the cell caused by the dendritic growth of Li on the Li metal anode during cycling. Moreover, the melting temperature of Li₂S (1372 °C)³¹ is much higher than that of S (119 °C) so high temperature material modification methods such as the chemical vapor deposition (CVD) method and high-temperature heat treat-

ment can be conducted without any loss of material. However, similar to the S cathode, the Li₂S cathode suffers from very poor electronic conductivity, polysulfide dissolution and the shuttle effect, which cause low S utilization, low Coulombic efficiency, and rapid degradation during cycling. Therefore, it is also crucial to prevent polysulfide dissolution into the liquid electrolyte and provide good electrical pathways for the Li₂S cathode material, in order to achieve high-rate and long-cycle performance of Li/S cells. Some recent research has been conducted to solve these problems; for example, Li₂S cathodes coated with various materials such as carbon,¹⁶ two-dimensional layered transition metal disulfides,²⁰ and conductive polymers.²⁵

Herein, the use of Li₂S/GO nanospheres with a conformal carbon coating on the surface (Li₂S/GO@C) is reported in a high-rate and long-life Li/S cell. The strategies of using Li₂S/GO@C to improve the cell performance are as follows: (i) The conformal carbon coating not only prohibits polysulfide dissolution into the electrolyte by preventing direct contact between Li₂S and the liquid electrolyte, but also acts as an electrical pathway resulting in the reduction of the electrode resistance. (ii) The spherical shape of the submicron size particles can provide a short solid-state Li diffusion pathway

Figure 2. SEM images of (a) as-synthesized $\text{Li}_2\text{S}/\text{GO}$, (b) heat-treated $\text{Li}_2\text{S}/\text{GO}$, and (c) $\text{Li}_2\text{S}/\text{GO}@C$ nanospheres. (d) Elemental mapping of $\text{Li}_2\text{S}/\text{GO}@C$ nanosphere by energy filtered transmission electron microscope (EFTEM, inset: zero loss image of $\text{Li}_2\text{S}/\text{GO}@C$ nanosphere). (e) TEM image of hollow carbon nanosphere including GO in its structure obtained by removal of Li_2S from the $\text{Li}_2\text{S}/\text{GO}@C$ nanosphere.

and better structural stability of the carbon shell during cycling. (iii) Void space will be created within the carbon shell during charge, and it will provide enough space to accommodate the volume expansion of up to 80% during discharge. As a result, better structural stability of the carbon shell can be secured because the carbon shell will not need to expand during cycling. (iv) Even if some percentage of the carbon shells is broken due to physical imperfections, the GO in the particles can act as a second inhibitor for polysulfide dissolution due to its S immobilizing nature. It is worthwhile to point out that the conformal carbon protection layer was easily formed by a CVD coating process using a lab-designed rotating tube furnace. The $\text{Li}_2\text{S}/\text{GO}@C$ nanosphere cathode demonstrated promising electrochemical performance, for example, a prolonged cycle life (1500 cycles) at the 2.0 C discharge rate (1.0 C = 1.163 A g^{-1} of Li_2S) with a high initial capacity of 650 $\text{mA}\cdot\text{h g}^{-1}$ of Li_2S (corresponding to 942 $\text{mA}\cdot\text{h g}^{-1}$ of S) and 699 $\text{mA}\cdot\text{h g}^{-1}$ of Li_2S (1012 $\text{mA}\cdot\text{h g}^{-1}$ of S) at 0.05 C after 400 cycles at 2.0 C discharge; excellent capacity retention of more than 84% with a high Coulombic efficiency of up to 99.7% after 150 cycles at various discharge C-rates (2.0, 3.0, 4.0, and 6.0 C discharge rates).

The $\text{Li}_2\text{S}/\text{GO}@C$ nanospheres were synthesized as shown in Figure 1a. Briefly, S powder was dissolved in toluene, followed by the addition of commercial single-layered graphene oxide (SLGO) dispersed in tetrahydrofuran (THF) to prepare a uniform S/SLGO composite solution. This S/SLGO composite solution was added to a solution of lithium triethylborohydride

(LiEt_3BH) in THF and heated with stirring to remove the THF until stable $\text{Li}_2\text{S}/\text{GO}$ spheres formed. The reaction chemistry of Li_2S formation is as follows:³²

The Li_2S formed in chemical reaction 1 was heterogeneously deposited on the surface of GO and finally $\text{Li}_2\text{S}/\text{GO}$ nanospheres were obtained. The CVD coating process was conducted using a lab-designed rotating tube furnace to simply form a conformal carbon protection layer on the surface of the $\text{Li}_2\text{S}/\text{GO}$ nanospheres. During the CVD process, the horizontal furnace tube was rotated to continuously mix the $\text{Li}_2\text{S}/\text{GO}$ powder, and the fresh surface of the $\text{Li}_2\text{S}/\text{GO}$ powder can be covered by C resulting in the formation of a conformal carbon coating on the surface of $\text{Li}_2\text{S}/\text{GO}$ nanospheres. The weight ratio of $\text{Li}_2\text{S}:\text{GO}:\text{C}$ was approximately 85:2:13. The detailed synthesis and characterization procedure is available in the Supporting Information. As shown in Figure 1b, all XRD peaks of each sample only correspond to Li_2S (Cubic, JCPDS No. 23-0369), which indicates that the Li_2S was successfully formed after chemical reaction 1 and no side reaction occurred during the following heat-treatment and CVD carbon coating step. XRD peaks related to GO were not observed due to the poor ordering of the sheets along the stacking direction. However, the existence of GO is clearly demonstrated by Raman spectra of as-synthesized $\text{Li}_2\text{S}/\text{GO}$ spheres (Figure 1c), which shows two Raman shifts near 1377 and 1588 cm^{-1} corresponding to the D band and G bands of carbon, respectively, with some

Figure 3. Electrochemical test results of synthesized Li_2S , $\text{Li}_2\text{S}/\text{GO}$, $\text{Li}_2\text{S}/\text{GO}@C\text{-NR}$, and $\text{Li}_2\text{S}/\text{GO}@C$ electrode. (a) Voltage profiles of the electrodes at the 0.2 C rate. (b) Comparisons of cycling performances of the electrodes at 0.2 C. (c) Test time vs discharge capacity plots of the electrodes for 50 cycles at 0.2 C.

organic residue ($\text{S}-\text{O}$ bonds).^{11,16} Raman peaks corresponding to the organic residues are successfully removed by the heat-treatment process at 500 °C under argon (Ar) atmosphere (labeled as $\text{Li}_2\text{S}/\text{GO}\text{-}500$ °C). Based on the changes of the Raman spectra and the color change of the powder (light gray $\rightarrow$ dark gray, shown in Supporting Information Figure S1), the organic residue should be completely carbonized during the heat-treatment process. After carbon coating, the Raman peak of Li_2S at ~ 370 cm^{-1} almost disappeared and the color of the powder became nearly black (Supporting Information Figure S1), which implied that the carbon deposited by the CVD process successfully covered the surface of Li_2S and blocked the Raman signal of Li_2S .

When synthesizing the $\text{Li}_2\text{S}/\text{GO}$ nanospheres, the flake size of GO embedded in the Li_2S spheres, the amount of toluene¹⁶ and the weight ratio between GO and S can strongly influence the size and shape of the product. Therefore, a relatively small amount of SLGO (2 mg) with a flake size of 500–800 nm (SEM image of commercial SLGO, Supporting Information Figure S2) was chosen to obtain the spherical $\text{Li}_2\text{S}/\text{GO}$ nanoparticles. $\text{Li}_2\text{S}/\text{GO}$ of spherical shape with particle size of approximately 800 nm was successfully obtained as confirmed by the scanning electron microscopy (SEM) images shown in Figure 2a. The particles remained spherical after the heat-treatment and the CVD coating processes conducted at 500 and 700 °C, respectively, because of the high melting point (1372 °C) of Li_2S , but they were obviously interconnected after the CVD coating process, indicating the formation of a continuous carbon shell. Energy dispersive X-ray spectroscopy (EDS) results for the heat-treated $\text{Li}_2\text{S}/\text{GO}$ nanospheres shown in Supporting Information Figure S3 demonstrated the

existence of S (corresponding to Li_2S based on the XRD pattern of $\text{Li}_2\text{S}/\text{GO}$) and C (GO or carbon obtained by carbonization of organic residues) on the particles. Oxygen spectra were also detected but this was mainly due to the high sensitivity of Li_2S to moisture and the formation of small amounts of LiOH during transfer of the $\text{Li}_2\text{S}/\text{GO}$ nanospheres into the SEM chamber. XRD patterns of $\text{Li}_2\text{S}/\text{GO}$ nanospheres exposed to air confirmed the formation of LiOH (Supporting Information Figure S4).

To clearly demonstrate the carbon shell on the surface of the $\text{Li}_2\text{S}/\text{GO}@C$ nanospheres, elemental mapping was conducted using energy filtered TEM (EFTEM) with a selected energy window corresponding to the Li K-edge and C K-edge. The three-window method (pre-edge, 1, 2, and postedge images) was used to subtract the background.³³ As shown in Figure 2d, the dark shell area in the zero loss image of $\text{Li}_2\text{S}/\text{GO}@C$ nanospheres (inset of Figure 2d) coincided with the C region (light blue) surrounding the Li region (yellow) of the Li_2S , which demonstrates the core-shell structure of the $\text{Li}_2\text{S}/\text{GO}@C$ nanospheres with an approximately 25 nm thick carbon shell. Moreover, a very thin GO sheet was observed inside of the hollow carbon shell after removing the Li_2S from the $\text{Li}_2\text{S}/\text{GO}@C$ nanospheres (Figure 2e), and the typical graphitic structure of GO was verified by high resolution TEM (Supporting Information Figure S5, selected area in Figure 2e). This proved that the thin-layered GO was successfully embedded in the Li_2S particles during the synthesis process as designed to improve the electrochemical performance of the Li_2S -based cathode.

In order to verify the effect of these material modifications on the electrochemical performance, Li_2S (1 μm), $\text{Li}_2\text{S}/\text{GO}$, and

$\text{Li}_2\text{S}/\text{GO}@C$ obtained by a typical CVD coating process ($\text{Li}_2\text{S}/\text{GO}@C\text{-NR}$) and $\text{Li}_2\text{S}/\text{GO}@C$ electrodes were fabricated. XRD patterns and SEM images of the prepared Li_2S spheres (1 μm) and $\text{Li}_2\text{S}/\text{GO}@C\text{-NR}$ are shown in Supporting Information Figures S6 and S7, respectively, and they show the crystal structures and morphologies of the synthesized Li_2S and the $\text{Li}_2\text{S}/\text{GO}@C\text{-NR}$ particles. To fabricate the electrodes, 60% of Li_2S , 35% of carbon materials (including GO, carbon obtained by CVD, and carbon black as conducting agent) and 5% of polyvinylpyrrolidone (PVP) as binder were mixed in NMP, and then the slurries were drop-casted onto carbon fiber paper current collector. The electrolyte was composed of a mixture of $\text{PYR}_{14}\text{TFSI}/\text{DOL}/\text{DME}$ (2:1:1 v/v/v) containing 1 M LiTFSI and 1 wt % LiNO_3 . The LiNO_3 was added to the electrolyte in order to improve the coulombic efficiency by passivating the Li metal surface against the polysulfide shuttle.³⁴ The fabricated electrodes and electrolyte were employed in 2325-type coin cells with Li foil as the negative electrode. All fabrication procedures were conducted under Ar atmosphere. The fabricated cells were cycled in a voltage range between 1.5 and 2.8 V at the 0.2 C rate after the first charge to 4.0 V at 0.05 C in order to activate the Li_2S ,²⁷ and the results are shown in Figure 3.

As shown in the voltage profiles (Figure 3a), the $\text{Li}_2\text{S}/\text{GO}@C$ electrode exhibited the lowest charge and discharge overpotentials among all electrodes, even lower than that of the $\text{Li}_2\text{S}/\text{GO}@C\text{-NR}$ electrode, which indicates that the carbon coating obtained by the CVD process using the rotating furnace can provide a good electrical pathway in order to overcome the insulating nature of Li_2S and S. In the comparison of the cycling performance of the electrodes (Figure 3b), the Li_2S and the $\text{Li}_2\text{S}/\text{GO}$ electrodes showed similar initial specific capacity of about 740 $\text{mA}\cdot\text{h g}^{-1}$ of Li_2S . However, the Li_2S electrode exhibited a significant capacity decrease on the second discharge (528 $\text{mA}\cdot\text{h g}^{-1}$ of Li_2S), whereas the $\text{Li}_2\text{S}/\text{GO}$ electrodes showed a relatively gradual capacity loss (665 $\text{mA}\cdot\text{h g}^{-1}$ of Li_2S). This is mainly due to the S-immobilizing nature of GO that can help to stabilize the cycling performance by suppressing polysulfide dissolution into the electrolyte.²¹ In contrast, both carbon coated electrodes, $\text{Li}_2\text{S}/\text{GO}@C$ and $\text{Li}_2\text{S}/\text{GO}@C\text{-NR}$ showed specific discharge capacities of up to 964 and 896 $\text{mA}\cdot\text{h g}^{-1}$ of Li_2S (corresponding to 1397 and 1298 $\text{mA}\cdot\text{h g}^{-1}$ of S) at the first discharge, respectively, which is much higher than those of uncoated electrodes. The high S utilization of these two electrodes can be attributed to the presence of the carbon shell that not only acts as protection to suppress the polysulfide dissolution into the electrolyte by preventing direct contact between the Li_2S and the electrolyte but also provides a better electrical pathway to compensate for the insulating nature of Li_2S and S. In addition, the $\text{Li}_2\text{S}/\text{GO}@C$ electrode showed much better cyclability compared to $\text{Li}_2\text{S}/\text{GO}@C\text{-NR}$ electrode for 50 cycles with a high Coulombic efficiency of up to 99.7%. This means the carbon coating layer obtained using the rotating furnace was much more effective than that of the $\text{Li}_2\text{S}/\text{GO}@C\text{-NR}$ electrode to suppress the polysulfide dissolution into the liquid electrolyte during cycling. Capacity degradation caused by polysulfide dissolution into the liquid electrolyte can be more clearly seen in the discharge capacity vs accumulated test time plot (Figure 3c), because the quantity of dissolved polysulfide into the liquid electrolyte from the cathode is time dependent. The more rapidly the polysulfide dissolves, the steeper the slope of the plot. As shown in Figure 3c, $\text{Li}_2\text{S}/\text{GO}@C$ electrode exhibited the highest capacity

retention among all electrodes, whereas bare Li_2S electrode showed very steep slope for the first 30 h. After 200 h, the specific discharge capacity of the $\text{Li}_2\text{S}/\text{GO}@C$ electrode was about 760 $\text{mA}\cdot\text{h g}^{-1}$ of Li_2S , but all the other electrodes only showed 425, 465, and 520 $\text{mA}\cdot\text{h g}^{-1}$ of Li_2S , respectively. It is also notable that the $\text{Li}_2\text{S}/\text{GO}$ electrode exhibited a relatively better capacity retention than the bare Li_2S electrode, which verifies the effect of GO as S immobilizer.

To verify the carbon protection effect of the $\text{Li}_2\text{S}/\text{GO}@C$ nanospheres and the $\text{Li}_2\text{S}/\text{GO}@C\text{-NR}$ nanospheres, polysulfide dissolution tests were conducted using a solution composed of THF (Li_2S is slightly soluble in THF) and toluene (S is soluble in toluene) with dissolved S. If the Li_2S particles are not protected and in direct contact with the test solution, polysulfide will form and the color of the test solution will change. When the bare Li_2S was put into the test solution (Sample A), the color of the test solution immediately changed to light orange, which indicates that the bare Li_2S quickly reacted with the dissolved S and formed polysulfide. After 4 h, no solid particles of Li_2S remained in Sample A, but the test solutions of carbon-coated samples did not show any color change. After 6 days, the test solution of $\text{Li}_2\text{S}/\text{GO}@C\text{-NR}$ (Sample B) exhibited an orange color, whereas the test solution of the $\text{Li}_2\text{S}/\text{GO}@C$ (batch C) was still clear and colorless. After a month, Sample C showed a slight color change, whereas both Samples A and B exhibited a dark orange color. This verifies that the conformal carbon shell of the $\text{Li}_2\text{S}/\text{GO}@C$ successfully prevents the dissolution of Li_2S into the test solution. The results of the polysulfide dissolution test strongly support the electrochemical test results shown in Figure 3 and indicate that the excellent cyclability of the $\text{Li}_2\text{S}/\text{GO}@C$ electrode was achieved by the protective carbon layer formed using the rotating furnace. As indicated in Figure 4b, in the typical CVD coating process, the carbon precursor gas in the quartz tube mostly flowed over the top of the bed of $\text{Li}_2\text{S}/\text{GO}$ nanospheres, and the carbon formed from the precursor gas was mainly

Figure 4. (a) Polysulfide dissolution test results of Li_2S (sample A), $\text{Li}_2\text{S}/\text{GO}@C\text{-NR}$ (sample B), and $\text{Li}_2\text{S}/\text{GO}@C$ (sample C). (b) Schematic illustration of carbon deposition process using the conventional CVD method and CVD using the rotating furnace.

Figure 5. Electrochemical performance of the $\text{Li}_2\text{S}/\text{GO}@C$ electrode. (a) Voltage profiles and (b) cycling performance of the electrodes cycled at various rates. (c) Voltage profiles of the electrode discharged at 2.0 C and charged at 1.0 C. (d) Voltage profiles of the electrode at 0.05 C after hundreds of cycles. (e) Long-term cycling performance of the electrode for 1500 cycles.

deposited on the top layer of the $\text{Li}_2\text{S}/\text{GO}$ nanospheres. Therefore, multiple C deposition steps were needed to obtain a uniform carbon coating.¹⁶ In contrast, the $\text{Li}_2\text{S}/\text{GO}$ nanospheres were continuously mixed in the rotating furnace through a “lifting and falling” process during the CVD coating. During this process, carbon could be deposited on the $\text{Li}_2\text{S}/\text{GO}$ nanospheres uniformly. This one-step, conformal carbon coating facilitated the material preparation process and should greatly reduce the production cost.

The high-rate and long-term cycling performance of the $\text{Li}_2\text{S}/\text{GO}@C$ electrode were also investigated and the results are shown in Figure 5. For the high-rate cycling test, the $\text{Li}_2\text{S}/\text{GO}@C$ electrode was galvanostatically cycled at various charge (1.0, 1.5, 2.0, and 3.0 C) and discharge C-rates (2.0, 3.0, 4.0, and 6.0 C) for 150 cycles ($1.0\text{ C} = 1.136\text{ A g}^{-1}$ of Li_2S). As shown in Figure 5a, discharge and charge plateaus, which

correspond to the formation and decomposition of Li_2S , remained in the voltage range of 1.7–1.9 V and 2.3–2.5 V, respectively, although discharge and charge overpotentials obviously increased as the applied current (C-rate) increased. This indicates that the $\text{Li}_2\text{S}/\text{GO}@C$ electrode could undergo reversible redox reaction even when the electrode was galvanostatically cycled at discharge C-rates as high as 6.0 C. The $\text{Li}_2\text{S}/\text{GO}@C$ electrode exhibited a discharge capacity of 584, 477, 394, and 185 $\text{mA}\cdot\text{h g}^{-1}$ of Li_2S (845, 691, 571, and 269 $\text{mA}\cdot\text{h g}^{-1}$ of S) after 150 cycles with a capacity retention of more than 84% and a very high Coulombic efficiency of up to 99.7% (Supporting Information Figure S9) when the electrode was discharged at 2.0, 3.0, 4.0, and 6.0 C, respectively. The long-term cycling performance of the $\text{Li}_2\text{S}/\text{GO}@C$ electrode was also demonstrated at 2.0 C discharge rate and 1.0 C charge rate for 1500 cycles and periodically cycled at 0.05 C (every 200

cycles) in order to check the S utilization at a low C-rate (Figure 5c–e). In Figure 5c, no significant first plateau corresponding to the formation of highly soluble high-order polysulfide (Li_2S_n , $n \geq 4$) was observed during the first discharge process, and it appeared beginning with the second discharge at around 2.3 V.²⁴ This probably indicates that the carbon protective layer was very effective for preventing a direct contact between S and electrolyte for the first cycle,^{35,36} but it was partially degraded during cycling. The differential capacity plot (DCP) (Supporting Information Figure S10) corresponding to the voltage profile in Figure 5c showed this change more clearly. Figure 5d shows the voltage profiles of the $\text{Li}_2\text{S}/\text{GO}@C$ electrode cycled at 0.05 C at the 200th, 400th, 600th, and 1000th cycles. A high discharge specific capacity of 812 $\text{mA}\cdot\text{h g}^{-1}$ of Li_2S (1176 $\text{mA}\cdot\text{h g}^{-1}$ of S) and 441 $\text{mA}\cdot\text{h g}^{-1}$ (640 $\text{mA}\cdot\text{h g}^{-1}$ of S) were observed after 200 cycles and 1000 cycles, respectively. The reason that the charge capacity was lower than the discharge capacity in Figure 5d is the limited Li_2S formation caused by cycling at a high discharge C-rate (2.0 C) before the charge process at 0.05 C. During 1500 cycles, the $\text{Li}_2\text{S}/\text{GO}@C$ electrode exhibited a very low capacity decay rate of 0.046% per cycle (Figure 5e) with a Coulombic efficiency of higher than 99.5% (Supporting Information Figure S11), which is competitive with previous results that reported on the long-term cycling performance of Li/S cells.^{8,10,15}

As discussed and demonstrated above, it is clear that the performances of the $\text{Li}_2\text{S}/\text{GO}@C$ electrode with high rate and long-term cycling could be achieved by the use of a conformal carbon coating layer obtained through the CVD process using a rotating furnace, which not only mitigates polysulfide dissolution into the electrolyte during cycling but also improves the electrical conductivity of the electrode. In addition, the carbon shell is mechanically stable because nanosized spherical Li_2S is used as the starting cathode material instead of S. Therefore, the rapid degradation of the carbon protective layer could be avoided, and the electrochemical performance of the $\text{Li}_2\text{S}/\text{GO}@C$ electrode could be greatly improved. SEM observations and polysulfide dissolution tests of cycled electrodes were conducted to demonstrate the structural stability of the carbon shell, and the results are shown in Supporting Information Figure S11 and S12. As shown in Supporting Information Figure S12, spherical $\text{Li}_2\text{S}/\text{GO}@C$ particles were still observed in the electrode cycled for 1500 cycles, which indicates that the $\text{Li}_2\text{S}/\text{GO}@C$ nanospheres successfully maintained their structure after the volume change of Li_2S particles during the lithiation/delithiation process. As shown in Supporting Information Figure S13, (the polysulfide dissolution test), the pristine electrode (before cycling) did not show any color change (sample A), and the cycled electrode after 1000 cycles showed a very slight color change after 6 h, indicating little loss of Li_2S owing to polysulfide dissolution into the test solution (sample B). The carbon protection layer was still effective after 1000 cycles based on the polysulfide dissolution test result of bare Li_2S shown in Figure 4a, which showed a strong color change immediately. These results are consistent with the long cycle life of 1500 cycles shown in Figure 5e.

In summary, $\text{Li}_2\text{S}/\text{GO}@C$ nanospheres were developed as a high-rate and long-life cathode material for Li/S cells by embedding GO sheets in the Li_2S nanospheres and depositing a conformal carbon coating on the surface of $\text{Li}_2\text{S}/\text{GO}$ nanospheres by means of a simple CVD process using a rotating furnace. Because the Li_2S particles occupied their

maximum volume relative to S at the initial stage, the carbon shell on the $\text{Li}_2\text{S}/\text{GO}$ nanospheres could maintain good structural stability during cycling. The carbon shell not only physically surrounds the $\text{Li}_2\text{S}/\text{GO}$ nanospheres to prevent the direct contact between Li_2S and electrolyte but also provides electrical conductivity during cycling. Furthermore, GO sheets embedded in the $\text{Li}_2\text{S}/\text{GO}@C$ act as a second barrier to prevent polysulfide dissolution due to its S immobilizing nature. This $\text{Li}_2\text{S}/\text{GO}@C$ electrode exhibited a very high initial discharge capacity of 964 $\text{mA}\cdot\text{h g}^{-1}$ of Li_2S (corresponding to 1397 $\text{mA}\cdot\text{h g}^{-1}$ of S) with high Coulombic efficiency of up to 99.7% at 0.2 C. High rate cycling capability was demonstrated at various C-rates, for example, discharge capacities of 584, 477, 394, and 185 $\text{mA}\cdot\text{h g}^{-1}$ of Li_2S (845, 691, 571, and 269 $\text{mA}\cdot\text{h g}^{-1}$ of S) after 150 cycles with excellent coulombic efficiency of up to 99.7% when the electrode was discharged at 2.0, 3.0, 4.0, and 6.0 C, respectively. In long-term cycling tests, the $\text{Li}_2\text{S}/\text{GO}@C$ electrode exhibited a specific capacity of 699 $\text{mA}\cdot\text{h g}^{-1}$ of Li_2S (1012 $\text{mA}\cdot\text{h g}^{-1}$ of S) at 0.05 C after 400 cycles at 2.0 C discharge and a very low capacity decay rate of only 0.046% per cycle for 1500 cycles. With these demonstrations of high sulfur utilizations, high rate capability, and long cycle life, combined with a simple fabrication process, the $\text{Li}_2\text{S}/\text{GO}@C$ cathode can be regarded as a strong candidate for use in advanced Li/S cells.

■ ASSOCIATED CONTENT

● Supporting Information

Experimental details and additional figures. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.nanolett.5b00820.

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Notes

The authors declare no competing financial interest.

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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).