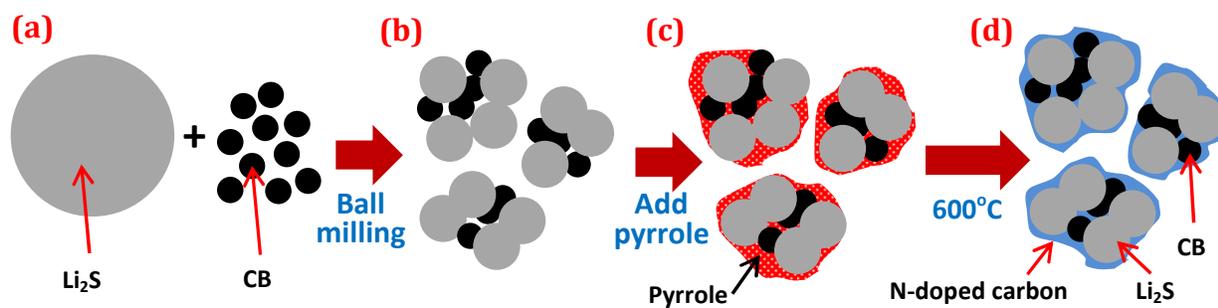




Li₂S Encapsulated by Nitrogen-Doped Carbon for Lithium Sulfur Batteries

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Graphical Abstract



The procedure for the synthesis of $\text{Li}_2\text{S}/\text{C}$ composite particles encapsulated by a nitrogen-doped carbon shell, which exhibit the highest initial discharge specific capacity ever reported in the literature.

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Li₂S Encapsulated by Nitrogen-Doped Carbon for Lithium Sulfur Batteries

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Abstract

Using high-energy ball milling of the Li₂S plus carbon black mixture followed by carbonization of pyrrole, we have established a facile approach to synthesize Li₂S-plus-C composite particles of average size ~400 nm, encapsulated by a nitrogen-doped carbon shell. Such an engineered core-shell structure exhibits an ultrahigh initial discharge specific capacity (1,029 mAh/g), reaching 88% of the theoretical capacity (1,166 mAh/g of Li₂S) and thus offering the highest utilization of Li₂S in the cathode among all of the reported works for the encapsulated Li₂S cathodes. This Li₂S/C composite core with a nitrogen-doped carbon shell can still retain 652 mAh/g after prolonged 100 cycles. These superior properties are attributed to the nitrogen-doped carbon shell that can improve the conductivity to enhance the utilization of Li₂S in the cathode. Fine particle sizes and the presence of carbon black within the Li₂S core may also play a role in high utilization of Li₂S in the cathode.

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Introduction

High power and high energy density rechargeable batteries with long cycle life are in urgent demand for electric vehicles and large-scale energy storage devices.¹⁻⁵ Unfortunately, the state-of-the-art Li-ion batteries (LIBs), which have dominated the market for portable electronics, have fallen short for these emerging applications.⁶ To increase the energy density of rechargeable batteries, one of the active areas of research is to develop anode and cathode materials with high specific capacities.¹⁻¹⁰ In this regard, sulfur-based cathodes are considered as one of the strongest cathode candidates for next generation high capacity LIBs.^{11, 12} Sulfur has a theoretical capacity of 1,673 mA h/g, and when coupled with a Li anode, the theoretical specific energy of the lithium-sulfur (Li-S) cell is ~2,600 Wh/kg,^{13, 14} five times higher than that of the commercial LiCoO₂/graphite batteries. Sulfur also offers other advantages, such as low cost, naturally high abundance and non-toxicity.¹⁵ However, sulfur cathodes suffer from three key deficiencies: (i) large volume change of sulfur (~80%) during cycling, (ii) dissolution of long chain lithium polysulfide products (Li₂S_x, 4 < x ≤ 8)¹⁶ into the electrolyte, and (iii) being an ionic and electronic insulator. Extensive progress of sulfur cathodes, including imbedding particles to porous hosts,¹⁷⁻²⁰ coating sulfur within carbon nanotubes^{21, 22} or graphene,²³ and adding additives to trap polysulfides,²⁴ has been made to improve the cycling performance of the cells, but the intrinsic safety hazard when coupled with lithium metal is still remaining.

Li₂S is a promising cathode material due to the ability to be paired with lithium-free anodes (such as silicon and tin), readily alleviating the safety issues.²⁵ Moreover, Li₂S as the final discharge products would experience the initial process of becoming sulfur during delithiation with a volume shrink, and thus volume expansion to cause structure fracture does not exist. However, Li₂S is also an insulator and has the same tricky problem of polysulfides dissolution as S does. Much effort to address these challenges has been pursued, such as hosting Li₂S in microporous carbon²⁶ and coating Li₂S with a conductive polymer²⁷ or carbon.^{6, 28, 29} Despite these advances, good conductivity and superior electrochemical performance of Li₂S cathodes with high ratio of active materials (>70%) have not been

simultaneously realized yet.

Herein, we design a facile technique to prepare the nitrogen-doped, carbon-encapsulated Li_2S with active materials ratio mass as high as 72%. The nitrogen-doped carbon shell can greatly improve the conductivity while simultaneously enabling the effective confinement of polysulfides within the conductive shell. As a result, the cells with the nitrogen-doped, carbon-encapsulated Li_2S as the cathode exhibit an extremely high initial discharge capacity (as high as 1,029 mA h/g). To the best of our knowledge, this specific capacity is the highest among all of the reported works for the encapsulated Li_2S cathodes.^{6, 27-29} This is also the first time that such good structured Li_2S with a high mass ratio achieving excellent cycling performance and superior capacity retention has been reported.

Our approach is schematically displayed in Figure 1. Li_2S particles were first ball milled with carbon black (CB) for 6 hours and then pyrrole was added to the ball-milled $\text{Li}_2\text{S}/\text{C}$ mixture with stirring to yield uniform and intimate contact between the particles and pyrrole. After carbonization of the pyrrole in an Ar atmosphere for 8 hours, the as-prepared samples were collected. The Li_2S -plus-C composite core encapsulated with a nitrogen-doped carbon shell (termed as the carbon coated Li_2S hereafter) was achieved by this route. This unique Li_2S core shell structure can improve the conductivity, thereby leading to the extremely high initial discharge capacity and high capacities even after prolonged cycling. The details of our experimental procedures and results are described below.

Experimental

Preparation of ball milled Li_2S : 1 g commercial Li_2S powders (Sigma-Aldrich) were weighed and mixed with 0.075 g CB and 20 g iron balls (different sizes) in a ball milling container within a glove box (MBRAUN), which is maintained with moisture level lower than 0.1 ppm and oxygen level lower than 1 ppm. After sealing the container tightly, the materials were ball-milled for 6 hours in a SPEX machine (SPEX Mixer 8000M).

Subsequently, the tightly sealed container was put back to the glovebox and the materials were collected and termed as “ball milled Li_2S ” for future use.

Synthesis of nitrogen-doped, carbon-encapsulated Li_2S : To prepare the carbon coated Li_2S , 15 droplets of pyrrole (Alfa Aesar) were added to 0.5g of the ball milled $\text{Li}_2\text{S}/\text{C}$ powder in an aluminum oxide crucible. The mixture was stirred for a while to make uniform and intimate contact between the powder and pyrrole. After being sealed within a stainless steel autoclave with a copper gasket inside the glovebox, it was transferred to a furnace for carbonization of pyrrole at 600 °C for 8 hours. After the autoclave was cooled down, it was put back into the glovebox and the materials were collected and marked as “carbon coated Li_2S ”. The quantity of Li_2S in the carbon coated Li_2S was estimated via weight measurement before and after carbonization of pyrrole, and found to be 72 wt% (including the CB in the ball milling step in the calculation).

Characterization: The XRD data were collected in the 2-theta range from 10-100 degree using Bruker X2 with $\text{CuK}\alpha$ radiation. High resolution imaging was conducted with field emission scanning electron microscope (JEOL) in Center for Nanoscale Materials (CNM) at Argonne National Laboratory. EFTEM elemental mapping was obtained with Gatan vacuum transfer holder for protecting Li_2S samples in field emission transmission electron microscopy (JEOL) at CNM. XPS experiments were performed with a Kratos Axis-165 XPS instrument equipped with an Al source (1486.6 eV). Survey and high resolution scans were conducted using pass energy of 80 eV and 20 eV, respectively. Both XPS and EFTEM samples were not exposed to air during loading into the instrument because the sample transfer from the glovebox to the XPS and EFTEM instruments were assisted with an air sensitive transfer holder and Gatan vacuum transfer holder, respectively.

Electrochemical measurements: The carbon coated Li_2S powder was mixed with PVDF and CB (8:1:1 mass ratio) in an Ar-filled glovebox to prepare electrodes with an aluminum foil as the current collector, and the mass loading of active materials for the assembled cells is ~1

mg cm⁻². The electrolyte contained 1 M lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) salt in the dimethoxyethane (DME) and 1,3-dioxolane (DOL) solvents (1:1 v/v) with the LiNO₃ additive (1 wt%). The carbon coated Li₂S cathodes coupled against a lithium metal anode were fabricated in CR2032 coin cells in the glovebox. Cyclic voltammetry (CV) data were achieved using Parstat 4000 (Princeton Applied Research) with a coin cell initially charged from the open circuit voltage to 4.0 V and then the voltage is switched between 1.6 and 3.4 V at a scan rate of 0.025 mV s⁻¹. Electrochemical impedance spectroscopy (EIS) data were also collected with this instrument in the frequency range of 1 MHz to 0.1 Hz upon the discharge state of batteries. The cycling performances were evaluated using Arbin System 2000. All charge-discharge processes were started with a slow charge rate of 0.05 C to 4 V and then cycled between 1.6 and 3.4 V at the desired C-rate.

Results and Discussion

Figure 2 shows the X-ray diffraction (XRD) patterns of Li₂S based samples. Since we sealed Li₂S samples in capillary tubes to protect these particles from air during the XRD data acquisition, the pattern of capillary tubes forms the background. Only Li₂S pattern (JCPDS Card No. 26-1188) was observed in both ball milled Li₂S and carbon coated Li₂S,²⁸ suggesting the amorphous carbon in the samples and no side reactions during the preparation process.

The sizes and morphologies of the carbon coated Li₂S were measured using field emission scanning electron microscopy (FESEM). As shown in Figure 3, it can be seen that the sizes and morphologies of carbon coated Li₂S particles are uniform although some agglomerations are also observed. The sizes of particles range from 300 nm to 1.5 μm with the majority at ~400 nm. This is the first time that such small Li₂S particles have been obtained through the ball milling method. Such small particles can effectively reduce the distance for Li ion migration and electron transfer, thereby improving the kinetics of electrochemical reactions in batteries and allowing most of the Li₂S in the cathode to contribute to the specific

capacity.

The core-shell structure of the carbon coated Li_2S was confirmed with energy-filtered transmission electron microscopy (EFTEM) with a Gatan vacuum transfer holder for loading the samples. EFTEM elemental mappings of a carbon-coated Li_2S particle, including carbon, sulfur and nitrogen, are illustrated in Figure 4a, 4b and 4c, respectively. The bright contrast in these images indicates the positions of corresponding element in the particle. This single particle has a size slightly less than 400 nm, consistent with the SEM observation showing that most particles are around 400 nm. Figure 4d is a combination of the elemental mappings where blue, red and green represent carbon, sulfur and lithium, respectively. This EFTEM elemental map unambiguously reveals that sulfur and lithium elements are encapsulated by a carbon shell, demonstrating an excellent core-shell structure. This conclusion is in good accordance with Figure 4a which also displays the presence of a significantly higher carbon concentration at the outer perimeter of the particle than in the interior.

It should be noted that Figure 4a and 4d also reveal the presence of carbon in the interior of the particle. This is not a surprise because the mapping shown in Figure 4 is the projection of a three-dimensional particle, and thus the carbon coating on the surface of the Li_2S particle will result in the appearance of the presence of carbon inside the particle. However, if this is the case, then the carbon distribution within the particle should be uniform and the carbon signal should be significantly weaker than that at the outer perimeter. Clearly, this is not the case because the carbon signal is very strong in some inner regions. We attribute the presence of carbon in some inner regions to the 7 wt% CB (~4.5 vol%) added during ball milling. Therefore, the Li_2S core in this study is, in fact, a Li_2S -plus-C ($\text{Li}_2\text{S}/\text{C}$) composite core. To the best of our knowledge, this is the first time that such $\text{Li}_2\text{S}/\text{C}$ composite cores with an average size ~400 nm are synthesized.

The formation of $\text{Li}_2\text{S}/\text{C}$ composite cores is consistent with the nature of the high-energy ball milling process. It is well established that high-energy ball milling entails repeated fracture

and cold welding of fine particles.^{30,31} Furthermore, when ball milling a two-material mixture with one material having large particle sizes and the other smaller particle sizes, the material with smaller particles are often occluded by the material with larger particles.^{32,33} The CB used in this study is extremely fine, ranging from 20 to 130 nm with majority between 20 and 50 nm (Figure 5). In contrast, the Li_2S powder is coarse ($> 1,000$ nm) before ball milling. Thus, repeated fracture and cold welding of large Li_2S particles during high-energy ball milling could result in occlusion of ultrafine CB, leading to the formation of $\text{Li}_2\text{S}/\text{C}$ composite particles as shown schematically in Figure 1(b). The CB inside the composite particles could form some conductive networks to enhance the utilization of Li_2S in electrochemical reactions.

It is interesting to note that Figure 4c indicates a uniform distribution of nitrogen. This is in a sharp contrast to the carbon mapping which displays strong carbon signals at the outer perimeter along with presence of some carbon inside the particle. This is a bit surprise to us because a previous study³⁴ has shown that the nitrogen atoms from pyrrole are present as a dopant in the carbon coating formed during the carbonization of pyrrole. The nitrogen mapping of Figure 4c, in contrast, may indicate the nitrogen doping of the $\text{Li}_2\text{S}/\text{C}$ composite core. Additional studies are needed in the future to confirm this. For now, it can be concluded that $\text{Li}_2\text{S}/\text{C}$ composite particles are encapsulated by a nitrogen-doped carbon shell, as evidenced by the EFTEM images. Nitrogen doped carbon has a higher electronic conductivity than carbon without nitrogen doping,^{34,35} and thus it can greatly enhance the electronic conductivity of the electrode material, enabling fast charge transfer rates.

Analysis of X-ray photoelectron spectroscopy (XPS) was also performed to investigate the nature of nitrogen in the carbon coated Li_2S . The peaks of high resolution XPS spectra of N1s for the carbon coated sample can be clearly seen in Figure 6, demonstrating the presence of nitrogen in the coating layer. After curve fitting, the peaks at 398.5 eV and 400.5 eV can be attributed to nitrogen in C-N and C=N, respectively.^{36, 37} The C-N, also called pyridinic-N, means that every nitrogen atom is bonded to two carbon atoms and contribute the aromatic π

system with one p-electron. The C=N, named pyrrolic-N as well, refers that nitrogen atoms bond to two carbon atoms and donate two p-electrons to the aromatic π system.³⁸ These results prove that the carbon coating is doped with nitrogen, in good accordance with the analysis of EFTEM.

The electrochemical performance of the carbon coated Li_2S was evaluated with CR2032 coin cells. The EIS data of Li_2S based batteries at the discharge state, shown in Figure 7a, reveals a semicircle in the high frequency range, which is assigned to the charge transfer resistance (R_{ct}).⁸ The carbon coated Li_2S battery has a smaller semicircle compared to that of the ball milled Li_2S battery, indicating the decreased charge transfer resistance due to the improved electronic and ionic conductivities enabled by the nitrogen-doped carbon coating.

In order to further analyze the effect of the nitrogen-doped carbon shell on the electrochemical performance of the electrode materials, CV tests were performed. The CV curves of uncoated and coated Li_2S batteries were compared in Figure 7b and 7c. Based on the report by Yang et al.,³⁹ we used 4 V as the cutoff voltage in the first scan to activate Li_2S , while the remaining cycles were scanned between 1.6 and 3.4 V. Overall, the CV profiles of two cells look similar, but with some subtle differences. Both cells show three peaks in the first anodic scan. However, in the subsequent anodic scans the three anodic peaks shift to lower potentials and merge into a broad anodic peak the peak position of which is located at 2.45 V for both the carbon coated and uncoated cells. Furthermore, the carbon coated cell also displays a shoulder peak at 2.35 V, whereas this shoulder peak is not obvious in the uncoated cell. For the cathodic scans both cells exhibit two major cathodic peaks at around 2.3 and 2.0 V after the initial scan. These two cathodic peaks are related to the change from elemental sulfur to higher-order lithium polysulfides (Li_2S_x , $x > 4$) and the reduction of higher-order polysulfides to lower-order polysulfides (Li_2S_x , $x \leq 4$), respectively. The anodic peak at 2.45 V corresponds to the conversion from lower-order polysulfides to higher-order polysulfides and then to elemental sulfur. However, the fact that the uncoated cell does not have an obvious shoulder peak at 2.35 V suggests that the conversion from lower-order

polysulfides to higher-order polysulfides is less active in the uncoated cell than that in the coated cell. Another important difference between the two cells is that all the peak currents in the coated cell are higher than those in the uncoated cell, indicating the increased ion and electron transport enabled by the nitrogen-doped carbon coating.

The galvanostatic charge-discharge tests of coin cells with the coated Li_2S -based cathode were performed to further measure the performance of the as-prepared materials. The representative voltage profiles at different C rates are shown in Figure 8a. All of them are the second cycle curves after the C rate is changed from one to another (as shown in Figure 8c), and exhibit one major plateau for charging processes and two major plateaus for discharging processes, consistent with one major oxidation peak and two major reduction peaks observed during the anodic and cathodic scans of the CV test, respectively.

It is noted that the discharge capacities are extremely high. Specifically, as shown in Figure 8b, an initial discharge capacity as high as 1,029 mA h/g was obtained at the 0.2 C rate ($1\text{C} = 1166 \text{ mA/g}$). This specific capacity is 88% of the theoretical (1,166 mA h/g), indicating high utilization of Li_2S in the cathode. This high specific capacity demonstrates an excellent lithium uptake during lithiation in the cathode. In fact, 1,029 mA h/g is higher than *all* of the specific capacities of the encapsulated Li_2S reported by other researchers.^{6, 27-29} We attribute the ultrahigh high specific capacity to the superior core-shell structure which greatly enhance the utilization of Li_2S in the cathode, and further hypothesize that the $\text{Li}_2\text{S}/\text{C}$ composite core may play a role in attaining such a high initial specific capacity by providing some conductive networks within the Li_2S core to allow for most of the Li_2S to participate in electrochemical reactions.

The capacity retention of the coated Li_2S cathode is also very good. With prolonged cycles, the coin cell exhibits good capacity retention with around 650 mA h/g after 100 cycles at the 0.2 C rate. It should be pointed out that the capacity values achieved in this work are all based on the Li_2S active mass in the cathode. The quantity of the Li_2S in the carbon coated

Li_2S is estimated via weight measurement before and after carbonization of pyrrole, and found to be 72 wt%. The high Li_2S loading in the carbon coated Li_2S allows such carbon coated Li_2S cathodes to be coupled with lithium free anodes, circumventing the safety issues associated with the use of metallic Li anodes. Finally, as shown in Figure 8b, the Coulombic efficiency was not high initially, but gradually approached 98% after 100 cycles.

To further evaluate the electrode kinetics and stability of the core-shell structure, the coin cell was subject to cycling at different C-rates (Figure 8c). As indicated in the rate capability plot, when the rate was increased from 0.2 C to 0.5 C, the capacity decreased from 851 to 805 mA h/g. The capacity decreased again from 734 to 665 mA h/g when the rate increased from 0.5 C to 1 C. It is important to note that the battery still delivered a high capacity of 526 mA h/g even at the 2 C rate. After 40 cycles with different rates, the C rate was switched back to 0.2 C and the capacity was recovered to 758 mA h/g that is slightly higher than the capacity displayed by the cell if the cell is subject to 40 cycles at the 0.2 C rate continuously. These results illustrate the possibilities of fast kinetic reactions and the highly robust ability of our materials.

It should be mentioned that there is difference in the first charge voltage profile between the uncoated and carbon coated cells although the first activation charge is a transient process. As shown in Supplementary Information (Figure S1), both types of cells exhibit an initial potential hump at the early stage of the activation charging curve. This potential hump has been attributed to the energy barrier for nucleation of polysulfides.³⁹ Furthermore, the height of the potential hump is found to be associated with the thermodynamic barrier for nucleation as well as the kinetic factors, particularly the charge transfer overpotential associated with the formation of polysulfides.³⁹ In general, the carbon-coated cells have a lower potential barrier for nucleation than most of the uncoated cells, indicating the benefit of the nitrogen-doped carbon coating in reducing the charge transfer overpotential and facilitating the nucleation process. Furthermore, the carbon coated cells exhibit a long flat plateau after the initial potential hump. This long flat plateau is related to conversion of Li_2S to lower-order

polysulfides, then to higher-order polysulfides, and finally to elemental sulfur.³⁹ In contrast, the uncoated cells not only have higher potential barriers in most cases, but also exhibit a variety of different behaviors after the initial potential hump (Figure S1). We ascribe these different behaviors of the uncoated cells to the statistically random processes of ball milling of Li_2S with ~4.5 vol% CB and subsequent mixing of CB with the ball milled Li_2S during cathode fabrication. More discussions on the variation in the first charge behavior of the uncoated cells can be found in Supplementary Information.

To directly determine the enhanced capacity due to the nitrogen-doped carbon shell, comparisons in the electrochemical performance between the ball milled and coated electrodes were also investigated at 0.5 C. As shown in Figure 9, the cell with the carbon coated Li_2S electrode yielded an initial capacity of more than 850 mA h/g and retained 518 mA h/g even after 100 cycles at 0.5 C, while the battery with ball milled Li_2S cathodes delivered very low capacities. Compared to the uncoated Li_2S cathode, the carbon coated Li_2S electrode achieves much enhanced capacity, indicating that the carbon coating has increased the utilization of Li_2S in the cathode. However, Figure 9 also shows that the two cells have a very similar capacity fading rate, indicating that the carbon coating synthesized in this study is not very effective in reducing the dissolution and out-diffusion of high-order polysulfides. Therefore, the quality of the carbon coating needs to be improved in the future to enhance the capacity retention. Finally, it should be pointed out that the phenomenon of the similar capacity fading rate may not mean that the carbon coating has no effect on dissolution of polysulfides *at all*. The discussion on the possible effect of the carbon coating is provided in Supplementary Information.

Conclusions

In summary, we have established a facile method to prepare the $\text{Li}_2\text{S}/\text{C}$ composite particles encapsulated by nitrogen-doped carbon shells. Such an engineered $\text{Li}_2\text{S}-\text{C}$ structure proves to be excellent in achieving the extremely high initial discharge specific capacity, which is

higher than any previously reported values. Cells with this carbon-encapsulated Li_2S also exhibit good capacity retention. The excellent properties observed are attributed to the nitrogen-doped carbon shell which enhances both electronic and ionic conductivities, thereby greatly enhancing the utilization of Li_2S in the cathode. The $\text{Li}_2\text{S}/\text{C}$ composite core may also play a role in attaining the high discharge capacity. With a high mass ratio (72%) of active materials, the carbon coated Li_2S can be coupled with lithium free anodes, circumventing the safety issues associated with metallic lithium. Furthermore, the results and characterizations provided here enable better understanding of Li_2S cathodes and offer a way to design better electrodes in the future.

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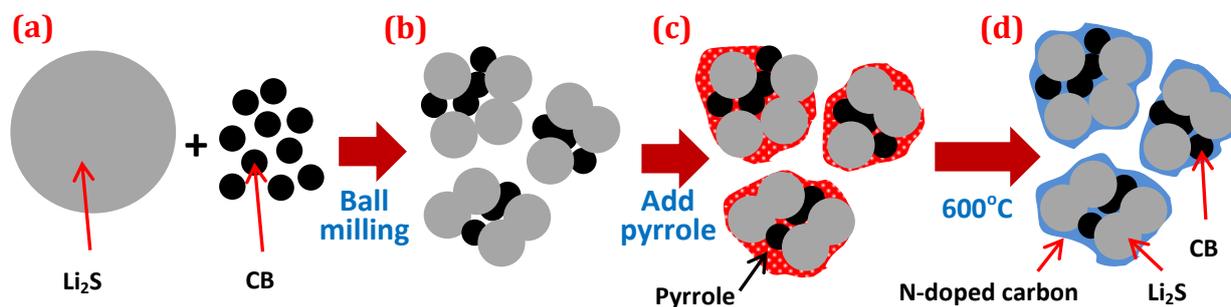


Figure 1. Schematic of the approach for synthesizing the $\text{Li}_2\text{S}/\text{C}$ composite particles encapsulated by a nitrogen-doped carbon shell: (a) mixing Li_2S with carbon black (CB), (b) the $\text{Li}_2\text{S}/\text{C}$ composite particles produced from high-energy ball milling, (c) mixing the composite particles with pyrrole, and (d) the $\text{Li}_2\text{S}/\text{C}$ composite particles encapsulated by a nitrogen-doped carbon shell.

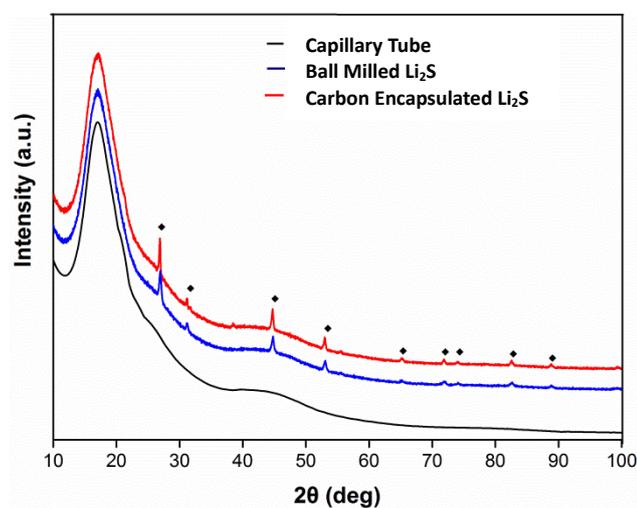


Figure 2. X-ray diffraction patterns of capillary tube, ball milled Li_2S and carbon encapsulated Li_2S . The black diamonds indicate the peaks of Li_2S (JCPDS Card No. 26-1188).

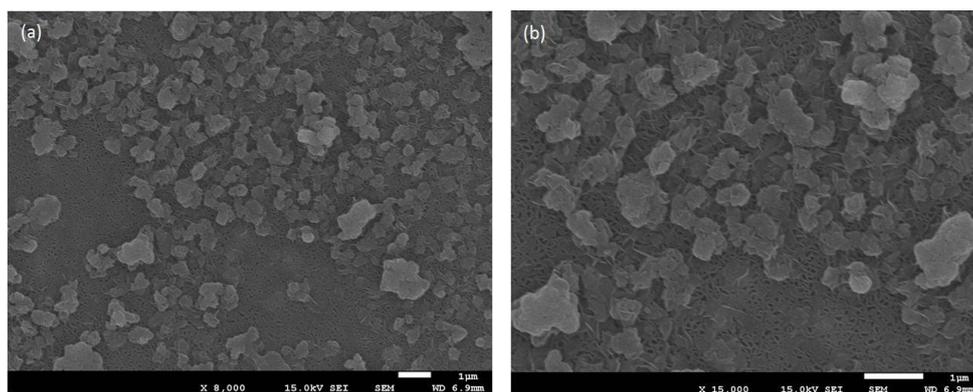


Figure 3. FESEM images of the carbon coated Li_2S : (a) Magnification $\times 8,000$, and (b) Magnification $\times 15,000$. The scale bar in both (a) and (b) corresponds to $1 \mu\text{m}$.

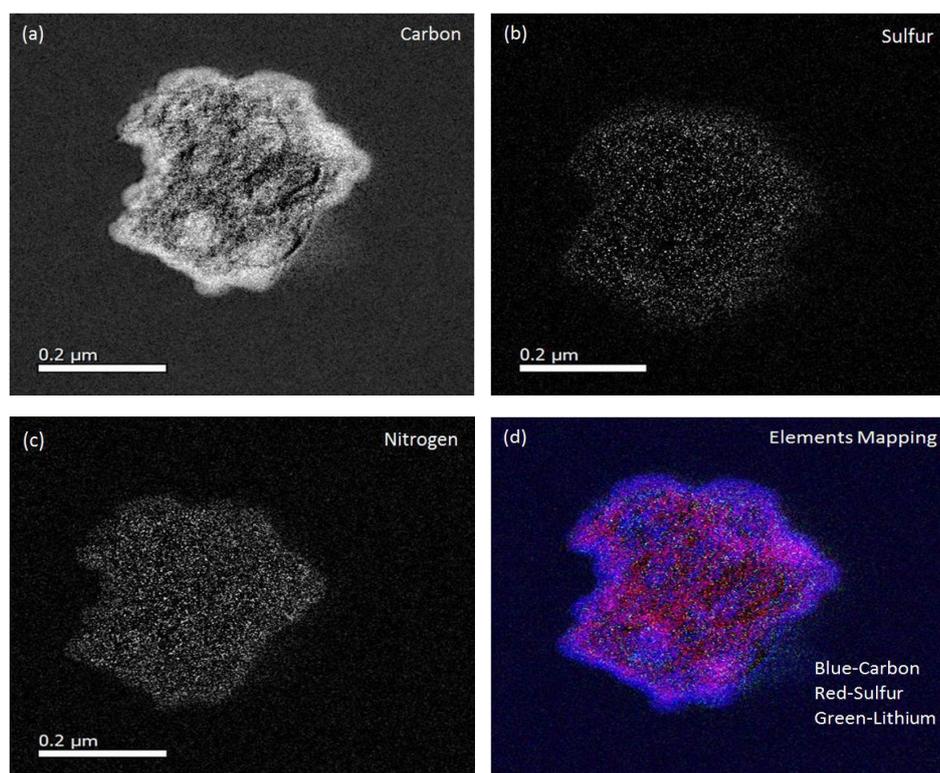


Figure 4. EFTEM elemental mapping of the carbon coated Li_2S : (a) carbon, (b) sulfur, (c) nitrogen, and (d) multi-element mapping (keys: blue-carbon, red-sulfur, and green-lithium).

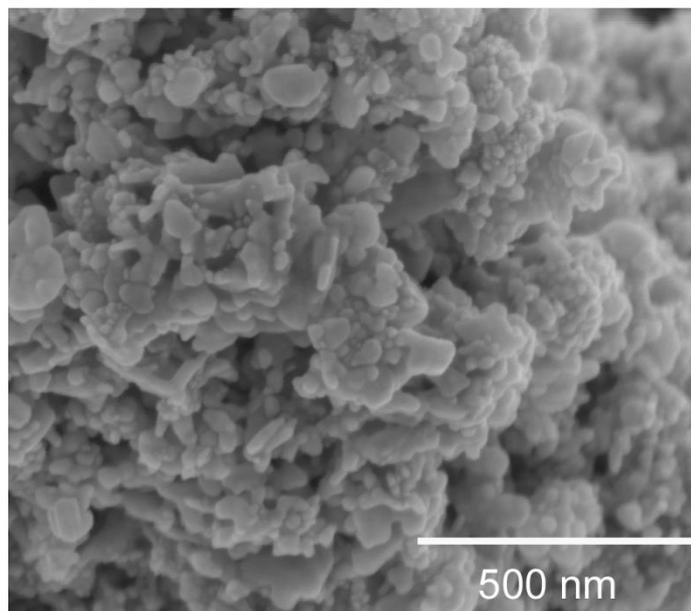


Figure 5. SEM image of the carbon black used with most particles in the range of 20 to 50 nm.

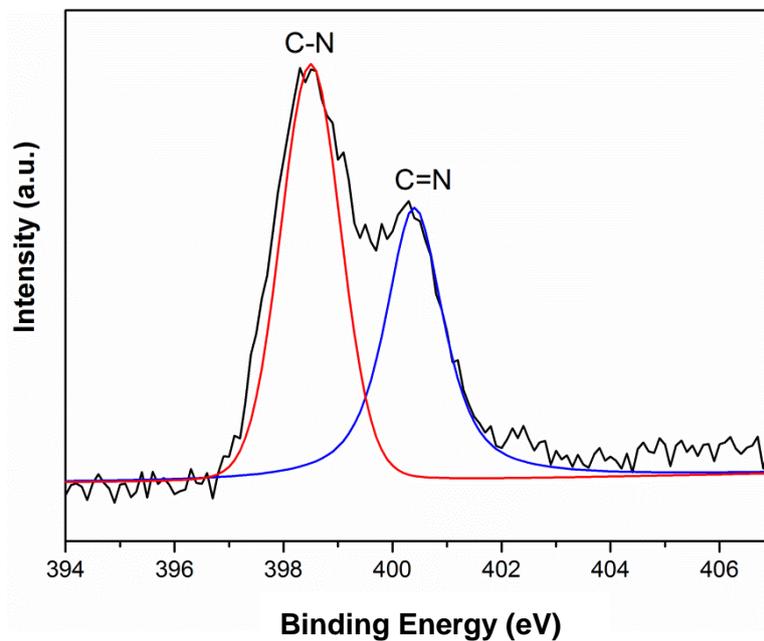


Figure 6. XPS spectra of N1s of the carbon coated Li₂S.

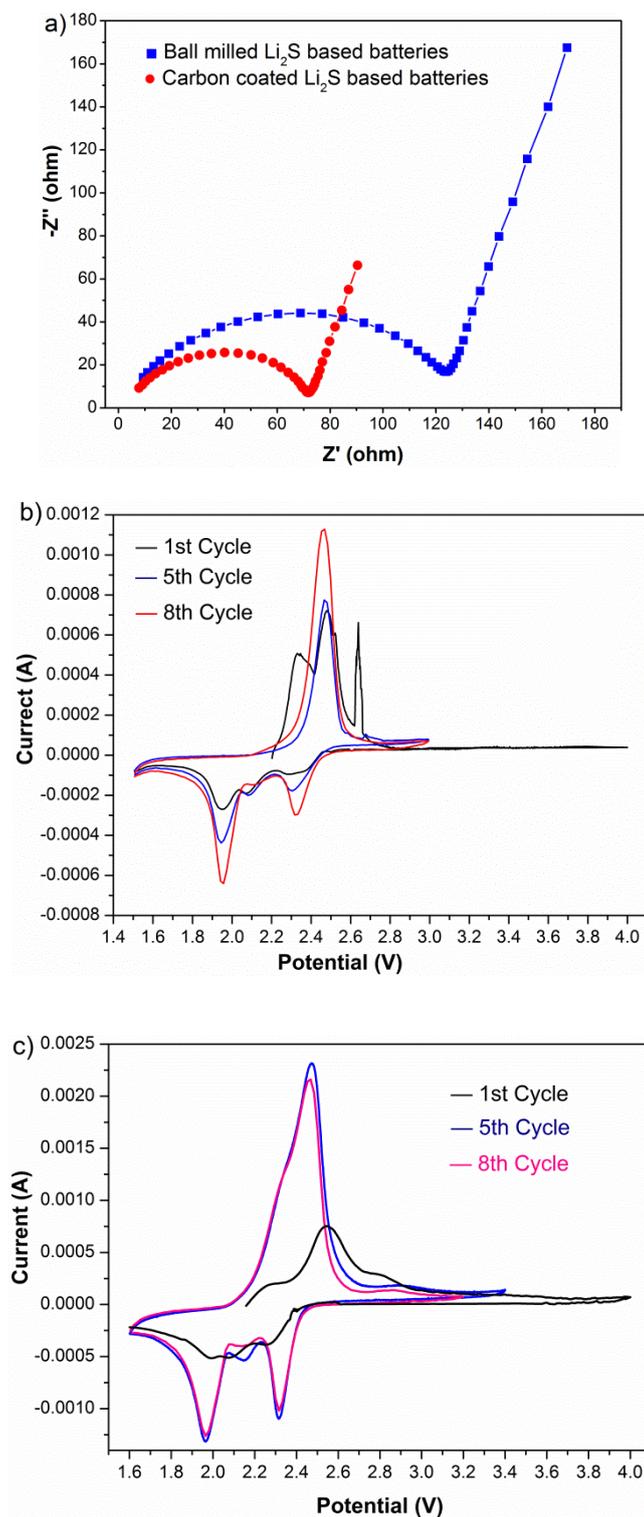


Figure 7. (a) EIS plots of Li_2S based batteries; (b) CV of the ball milled Li_2S -based cell at a potential sweep rate of 0.025 mV s^{-1} with an initial cutoff charge voltage of 4 V; and (c) CV of the carbon coated Li_2S -based cell at a potential sweep rate of 0.025 mV s^{-1} between 1.6 and 3.4 V, including an initial potential sweeping to 4 V.

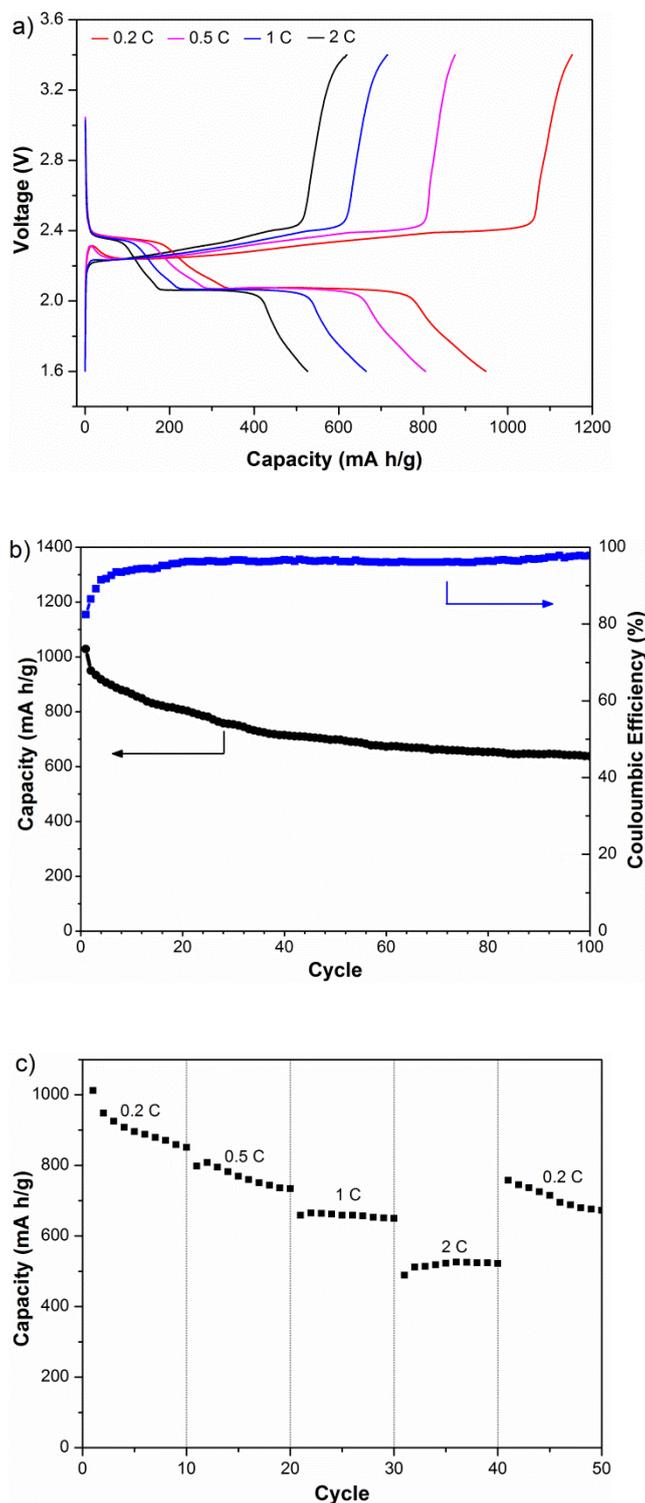


Figure 8. Electrochemical properties of the carbon coated Li_2S cells: (a) voltage profiles of the 2nd cycle at different C rates. 10 charge/discharge cycles were conducted at each C rate sequentially; (b) cycling performance and Coulombic efficiency at 0.2 C; and (c) specific capacity at different C rates and cycle numbers. The capacity values achieved in this work are based on the Li_2S active mass.

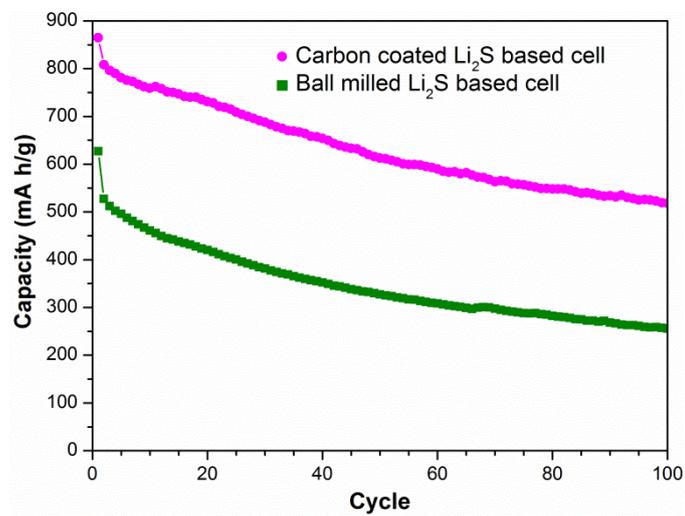


Figure 9. Cycling performances of the carbon coated Li₂S cell vs the ball milled Li₂S cell at the 0.5 C rate.