MOF-derived Cobalt Sulfide Grown on 3D Graphene Foam as an Efficient Sulfur Host for Long-Life Lithium-Sulfur Batteries

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**HIGHLIGHTS**
- Metal-organic framework-derived Co$_9$S$_8$ arrays are grown onto 3D graphene foam
- Co$_9$S$_8$-3DGF serves as a free-standing, binder-free host for sulfur cathodes
- Co$_9$S$_8$-3DGF/S cathode exhibits high capacity with long cycle life
- Co$_9$S$_8$-3DGF/S cathode displays a remarkably high areal capacity

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MOF-derived Cobalt Sulfide Grown on 3D Graphene Foam as an Efficient Sulfur Host for Long-Life Lithium-Sulfur Batteries

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SUMMARY
Lithium-sulfur (Li-S) batteries are an appealing candidate for advanced energy storage systems because of their high theoretical energy density and low cost. However, rapid capacity decay and short cycle life, mainly resulting from polysulfide dissolution, remains a great challenge for practical applications. Herein, we present a metal-organic framework (MOF)-derived Co9S8 array anchored onto a chemical vapor deposition (CVD)-grown three-dimensional graphene foam (Co9S8-3DGF) as an efficient sulfur host for long-life Li-S batteries with good performance. Without polymeric binders, conductive additives, or metallic current collectors, the free-standing Co9S8-3DGF/S cathode achieves a high areal capacity of 10.9 mA hr cm$^{-2}$ even at a very high sulfur loading (10.4 mg cm$^{-2}$) and sulfur content (86.9 wt%). These results are attributed to the unique hierarchical nanoarchitecture of Co9S8-3DGF/S. This work is expected to open up a promising direction for the practical viability of high-energy Li-S batteries.

INTRODUCTION
With the advances in portable electronics and interest in electric vehicles, the demand for high-performance energy storage devices is exponentially growing (Ji et al., 2016, 2017; Cao et al., 2014; He et al., 2016a, 2016b, 2016c; He et al., 2017a, 2017b). Rechargeable lithium-sulfur (Li-S) batteries are appealing as one of the most attractive candidates for energy storage because of their high theoretical energy density and capacity (Manthiram et al., 2014, 2015; Wu et al., 2016; He et al., 2017a, 2017b; Zhou et al., 2015a, 2015b; Zhong et al., 2018). However, Li-S batteries still face serious drawbacks toward practical applications, including the insulating nature of sulfur and the migration of soluble lithium polysulfides (LiPSs), which give rise to low capacity and rapid capacity decay (Chung and Manthiram, 2018; Kim et al., 2014; He et al., 2016a, 2016b, 2016c; Xia et al., 2017). Extensive strategies have been proposed to address these issues. A combination of sulfur and conductive carbonaceous materials, such as reduced graphene oxide, three-dimensional graphene foam (3DGF), carbon nanotube, or conducting polymers, has been considered as an effective approach to improve the electrical conductivity of the electrode and physically confine the soluble LiPSs (He et al., 2015; Chen et al., 2013; Sun et al., 2014). However, due to the weak physical interaction between nonpolar carbonaceous materials and polar LiPSs, the severe capacity degradation still remains during long-term cycling (Zhou et al., 2017; Li et al., 2015; Liu et al., 2017a, 2017b; Xia et al., 2018).

Recently, it has been illustrated that polar materials can significantly improve the chemical adsorption capability for LiPSs, and strenuous efforts have been pursued to develop polar sulfur hosts with strong chemical interaction toward polysulfides species. For example, metal-organic frameworks (MOF) with strong Lewis acid-base interactions for LiPSs are efficient in entrapping polar LiPSs (Zheng et al., 2014; He et al., 2016a, 2016b, 2016c) and improving cycling stability when used in the cathodes of Li-S batteries. Polar oxides, such as TiO$_2$, MnO$_2$, SiO$_2$, and V$_2$O$_5$, have also been explored as host materials for Li-S batteries owing to their strong affinity to LiPSs (Zhou et al., 2015a, 2015b; Kong et al., 2017; Liu et al., 2017a, 2017b). However, these oxides usually have relatively poor electrical conductivity, which tends to slow down the electrode kinetics and thus compromises the utilization of sulfur and the rate capability (Pu et al., 2017). Therefore, metal sulfides (Co$_9$S$_8$, Co$_5$S$_9$, and Co$_3$S$_4$) and metal nitride (TiN) with high conductivity and strong chemical interaction for LiPSs have been proposed as hosts for sulfur in Li-S batteries (Pang et al., 2016; Yuan et al., 2016; Chen et al., 2017; Li et al., 2017). However, rational nanoarchitecture designs to improve the utilization of sulfur particularly at higher sulfur loading and content is still challenging, and most of such sulfur composite cathodes still require polymer binders, conductive additives, and metallic...
current collectors, which not only reduce the power density of the cell but also degrade the long-term cycling.

Herein, we choose a chemical vapor deposition (CVD)-grown 3DGF with high conductivity and excellent flexibility as a binder-free, free-standing skeleton and the conductive hollow polar cobalt sulfide (Co$_9$S$_8$) arrays directly grown on 3DGF skeleton as an efficient sulfur host for Li-S batteries. Benefiting from the well-designed hierarchical Co$_9$S$_8$-3DGF nanoarchitecture, the hollow Co$_9$S$_8$ nanowall arrays anchored onto 3DGF offer abundant nanoporous space to accommodate a large amount of sulfur, allow sufficient electrolyte penetration, and facilitate the transport of ions/electrons. The binder-free, free-standing Co$_9$S$_8$-3DGF/S cathode without polymer binders, conductive additives, and metallic current collectors delivers a remarkably high areal capacity of 10.9 mA hr cm$^{-2}$ even with a very high sulfur loading (10.4 mg cm$^{-2}$) and sulfur content (86.9 wt%) and exhibits significant improvement in the specific capacity, rate capability, and long-term cycling stability.

RESULTS

The synthetic strategy of the Co$_9$S$_8$-3DGF/S is schematically shown in Figure 1A; for detailed synthesis procedure, see the Transparent Methods. First, a facile solution method was used to grow cobalt-based MOF solid nanowall arrays onto a piece of 3DGF. Then, through a subsequent solvothermal reaction with thiocacetamide (TAA) in ethanol, the Co-MOF solid nanowall arrays were transformed to hollow Co$_9$S$_8$ arrays. The color of Co-MOF/3DGF changed from purple to black after the transformation to Co$_9$S$_8$-3DGF (Figure S1). After this sulfurization treatment, the obtained Co$_9$S$_8$-3DGF was mixed with an appropriate amount of sulfur, and the sulfur was impregnated into the Co$_9$S$_8$-3DGF by a modified melt-diffusion strategy. Benefiting from the efficient surface bonding between the Co$_9$S$_8$ nanowall arrays and the sulfur species, the dissolution and migration of LiPSs were effectively alleviated during the charge/discharge process (Figure 1B).

Through a facile solution method, the solid Co-MOF nanowall arrays are uniformly grown onto the 3DGF. The scanning electron microscopic (SEM) images in Figures 2A–2C show that the skeleton of 3DGF is homogenously coated by a solid Co-MOF with nanowall morphology. The X-ray diffraction (XRD) patterns of the Co-MOF in Figure S2 are in agreement with previous reports (Guan et al., 2017). Figure 2D illustrates that the typical array morphology and a uniform coating on 3DGF are maintained after sulfurization treatment with TAA. As shown in Figures 2E, 2F, and S3, a hollow structure is formed in Co$_9$S$_8$-3DGF, which can be attributed to the Kirkendall effect (Liu et al., 2016). Specific surface area results further confirm the high specific area of Co$_9$S$_8$-3DGF (Figure S4). The absence of the Co-MOF peaks in the XRD pattern of Co$_9$S$_8$-3DGF (Figure S5A) confirms the successful transformation from Co-MOF to Co$_9$S$_8$. After the sulfur impregnation into Co$_9$S$_8$-3DGF, the architecture of Co$_9$S$_8$-3DGF/S still remains as nanowall arrays, as shown in Figure 2G. It is worth noticing that those nanowall arrays are solid, indicating that the sulfur has been
effectively confined into the hollow Co$_9$S$_8$ nanowall arrays (Figures 2H and 2I). Such a unique architecture with an excellent interfacial contact between sulfur-Co$_9$S$_8$ and 3DGF can help realize the fast diffusion of LiPSs on the Co$_9$S$_8$ surface to the highly conductive graphene surface. As a result, strong entrapment (by Co$_9$S$_8$) and fast electron transfer (by 3DGF) for LiPS conversion can be simultaneously realized, avoiding the accumulation of LiPSs and improving their utilization. The XRD pattern of Co$_9$S$_8$-3DGF/S (Figure S5A) also suggests the successful introduction of sulfur. The SEM images and the corresponding elemental mappings in Figures S6A–S6F evidently indicate a uniform distribution of Co$_9$S$_8$ and S in Co$_9$S$_8$-3DGF/S. The TGA curves (Figure S5B) show that the content of sulfur in Co$_9$S$_8$-3DGF/S is 79.2 wt.% (6.2 mg cm$^{-2}$). For comparison, 3DGF/S was also prepared. Owing to the hydrophobic nature of the 3DGF, the hosted sulfur on 3DGF tends to severely aggregate into bulk particles (Figure S7).

**DISCUSSION**

To demonstrate that such a rational architecture of Co$_9$S$_8$-3DGF is beneficial for the electrochemical properties of Li-S batteries, the Co$_9$S$_8$-3DGF/S was cut and directly used as a binder-free, free-standing cathode. As shown in Figure 3A, the cyclic voltammetry (CV) profiles in the first four cycles of the cell with Co$_9$S$_8$-3DGF/S are obtained with a sulfur loading of 6.2 mg cm$^{-2}$ at a scan rate of 0.1 mV s$^{-1}$ in the voltage range of 1.8–2.8 V. Compared with our previous reports, Co$_9$S$_8$-3DGF/S shows a similar electrochemical reaction (Gie and Manthiram, 2016; Su and Manthiram, 2012; Xu and Manthiram, 2017; Xu et al., 2016). The two main reduction peaks at 2.34 and 1.97 V in the initial cathodic sweep reflect the transformation of S to long-chain LiPSs and ultimately to Li$_2$S. The oxidation peak located at 2.41 V corresponds to the conversion of Li$_2$S to LiPSs and finally to sulfur. The overlapped CV profiles after the initial cycles evidence the highly reversible electrochemical process. As shown in Figure S8, the rate-dependent CV curves of Co$_9$S$_8$-3DGF/S were obtained and the corresponding Li-ion diffusion coefficient ($D_{Li^+}$) was calculated. The $D_{Li^+}$ values of C1, C2, and A peaks are, respectively, $1.72 \times 10^{-8}$, $4.85 \times 10^{-8}$, and $2.91 \times 10^{-8}$ cm$^2$ s$^{-1}$. These $D_{Li^+}$ values are close to the values in our previous report (Chung et al., 2016). Importantly, the polarization of the Co$_9$S$_8$-3DGF/S cathode with a high sulfur loading (6.2 mg cm$^{-2}$) and high sulfur content (79.6 wt.%) remains low during the electrochemical process. Considering the above structural analyses on Co$_9$S$_8$-3DGF/S, such low polarization is due to the unique architecture of Co$_9$S$_8$-3DGF/S offering...
excellent trapping-diffusion conversion process. Such results were further confirmed by the impedance values of Co$_9$S$_8$-3DGF/S relative to those of 3DGF/S (Figure S9). The charge/discharge curves of the cell with Co$_9$S$_8$-3DGF/S at C/10 rate (1C = 1,675 mA g$^{-1}$) well coincide with its CV behavior. (Figure 3B) Remarkably, the potential plateaus remain the same even after 200 cycles, implying an excellent immobilization of Co$_9$S$_8$-3DGF/S for sulfur species.

The cyclic performances at C/10 rate in the voltage range of 1.8–2.8 V for the Co$_9$S$_8$-3DGF/S and 3DGF/S cathodes were measured with the same sulfur loading of 6.2 mg cm$^{-2}$. Co$_9$S$_8$-3DGF/S exhibits pronounced cycling stability with a high capacity retention of 84.9% after 200 cycles, as shown in Figure 3C. Importantly, even after 200 cycles, Co$_9$S$_8$-3DGF/S still can maintain its nanowall array morphology (Figure S10). By sharp contrast, the 3DGF/S cathode shows a rapid capacity degradation after 200 cycles with a poor capacity retention of 42.8%. The fast capacity decay of 3DGF/S is attributed to the weak affinity of 3DGF to sulfur species and poor physical entrapment. To better understand the synergistic effect of each component and to optimize the electrochemical performances, the electrochemical performance of Co$_9$S$_8$-3DGF/S with a Co$_9$S$_8$ loading of 2.3 mg cm$^{-2}$ was obtained. As shown in Figure S11, although a higher content of Co$_9$S$_8$ can improve the adsorption toward LiPSs, it will decrease the conductivity of the electrode. As a result, the utilization of active materials decreases and the specific capacity of the cathode is low. The visual observations of Co$_9$S$_8$-3DGF/S and 3DGF/S confirm that

Figure 3. Electrochemical Performance of the Co$_9$S$_8$-3DGF/S Cathode
(A) CV curves of the Co$_9$S$_8$-3DGF/S cathode at 0.1 mV s$^{-1}$ at 1.8–2.8 V.
(B) Charge/discharge profiles of the Co$_9$S$_8$-3DGF/S cathode.
(C) Cycling stability of the Co$_9$S$_8$-3DGF/S and 3DGF/S cathodes at C/10 rate for 200 cycles.
(D) Rate performances at various cycling rates of the Co$_9$S$_8$-3DGF/S and 3DGF/S electrodes.
(E) Cycling performances of the Co$_9$S$_8$-3DGF/S electrodes for long-term cycling at 1C rate.
polysulfide dissolution is effectively mitigated in Co$_9$S$_8$-3DGF/S during the charge/discharge process (Figure S12).

The rate capabilities of the cells with Co$_9$S$_8$-3DGF/S at various rates from C/20 to 2C are shown in Figures 3D and S13. At a C/20 rate, the cell with Co$_9$S$_8$-3DGF/S delivers a high specific capacity of 1,306 mA hr g$^{-1}$. Even at a high rate of 2C, the capacity of the cell with Co$_9$S$_8$-3DGF/S still remains stable at 670 mA hr g$^{-1}$, which is significantly better than that of the cell with 3DGF/S (74.9 mA hr g$^{-1}$) under the same conditions. Furthermore, when the C-rate is switched back to C/20, the capacity of the cell with Co$_9$S$_8$-3DGF/S recovers to the original value, indicating the excellent mechanical stability within the cathode. It is known that the long-term charge/discharge process is still a challenge for high-sulfur-loading cathodes. To further illustrate the structural advantages of Co$_9$S$_8$-3DGF/S, the prolonged cycling performance was evaluated at 1C rate for 500 cycles. As shown in Figure 3E, the Co$_9$S$_8$-3DGF/S cathode exhibits an extraordinary cyclic stability with a high capacity retention of 77.2%. Even at a high rate of 1C after 500 cycles, the Co$_9$S$_8$-3DGF/S cathode still delivers 736 mA hr g$^{-1}$.

The areal capacity of the Co$_9$S$_8$-3DGF/S cathode was also assessed. As shown in Figure 4, the Co$_9$S$_8$-3DGF/S cathode with a sulfur loading of 6.2 mg cm$^{-2}$ delivers at C/10 rate a high areal capacity of 7.6 mA hr cm$^{-2}$, which is much higher than that of commercial lithium-ion batteries (typically 4 mA hr cm$^{-2}$) (Hu et al., 2016). Furthermore, an even higher areal capacity of 10.9 mA hr cm$^{-2}$ could be realized at a rate of C/10 by increasing the sulfur loading to 10.4 mg cm$^{-2}$ (86.9 wt.%). It is obvious that the areal capacity of our Co$_9$S$_8$-3DGF/S cathode is much higher compared with those of recently reported high-areal-capacity Li-S cathodes with higher sulfur loading (Table S1). This value is nearly three times more than that of commercial Li-ion batteries, indicating the promise of Co$_9$S$_8$-3DGF/S cathodes. In addition, even with such a high sulfur loading of 10.4 mg cm$^{-2}$, the Co$_9$S$_8$-3DGF/S cathode still exhibits good cycling stability for 200 cycles. Such impressive features imply that the Co$_9$S$_8$-3DGF/S is an attractive cathode for the practical Li-S batteries.

The SEM images of the lithium foils and the photographs of the separators recovered from the cells with the Co$_9$S$_8$-3DGF/S and 3DGF/S cathodes after 200 cycles were further analyzed to elucidate the excellent confinement of the sulfur species within Co$_9$S$_8$-3DGF/S (Figures S14 and S15). Severe corrosion observed on the surface of lithium foil with the 3DGF/S cathode indicates that the 3DGF can only provide weak
protection for lithium foil from LiPSs. The obvious color changes of the separator in the cell with 3DGF/S further imply the existence of severe shuttle effects. In addition, the photographs of the absorption experiments of 3DGF and Co9S8-3DGF visually demonstrate that Co9S8 can provide strong interaction for LiPSs (Figure 5). Correspondingly, a dramatic decrease can also be detected in the ultraviolet (UV)-visible absorption spectra. The peak intensity of the $S_2^2-/Co$ species is much lower for Co9S8-3DGF than for 3DGF, implying that Co9S8-3DGF has better affinity and strong adsorption. Moreover, to further quantitatively evaluate the chemical adsorption of Co9S8 for LiPSs, X-ray photoelectron spectroscopy (XPS) analysis was carried out. After contacting with Li2S6 for 1 hr, the peaks of Co 2p shifts toward higher binding energies and the satellite peaks become obvious, implying electron transfer from Li2S6 molecules to Co, as shown in Figure S16 (Pu et al., 2017). Such an analysis directly indicates a strong chemical interaction between Co9S8 and Li2S6 and evidently provides insights on the electrochemical improvement offered by Co9S8-3DGF/S.

In summary, the rational design and fabrication of MOF-derived cobalt sulfide arrays anchored onto 3DGF (Co9S8-3DGF) has been presented as an efficient sulfur host for long-life, highly efficient Li-S batteries. The Co9S8-3DGF/S can be directly used as a binder-free, free-standing cathode. Moreover, the Co9S8-3DGF/S exhibits pronounced electrochemical performance owing to its unique 3D hierarchical nanoarchitecture, which can synergistically realize a strong chemical entrapment of LiPSs (by Co9S8) and fast transport of electrons (by 3DGF), avoid the accumulation of LiPSs, and improve the utilization of sulfur. As a result, Co9S8-3DGF/S with a very high sulfur loading of 10.4 mg cm$^{-2}$ delivers excellent electrochemical performance. This work provides new insights into the rational design of binder-free, free-standing cathodes for highly efficient Li-S batteries.

**METHODS**

All methods can be found in the accompanying Transparent Methods supplemental file.

**SUPPLEMENTAL INFORMATION**

Supplemental Information includes Transparent Methods, 16 figures, and 1 table and can be found with this article online at https://doi.org/10.1016/j.isci.2018.05.005.

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AUTHOR CONTRIBUTIONS

J.H. designed and carried out the experimental work, J.H., Y.C., and A.M. contributed to the preparation of the manuscript.

DECLARATION OF INTERESTS

The authors declare no competing interests.

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Transparent Methods

Synthesis of 3D graphene foam

Three-dimensional graphene foam was grown with chemical vapor deposition (CVD). Nickel foam (0.5 mm thick, Alantum Advanced Technology Materials, China) was used as a substrate and placed into a quartz tube. It was then heated up to 1000 °C at a heating rate of 50 °C min⁻¹ and maintained for 10 min with a gas flow of H₂/Ar (H₂/Ar = 50:100 sccm) to clean the surface of nickel foam. After 20 min of graphene growth under H₂/Ar/CH₄ flow (H₂/Ar/CH₄= 50:100:50 sccm), the sample was rapidly cooled to room temperature at a cooling rate of 100 °C min⁻¹. Finally, the nickel template was etched off with HCl/FeCl₃ (HCl/FeCl₃=1:1 M) solution at 80 °C to result in free-standing 3DGF.

Synthesis of MOF-3DGF and MOF

1.3 g of 2-methylimidazole and 0.582 g of Co(NO₃)₂·6H₂O were dissolved separately in 40 mL of deionized (DI water). Then the two solutions were quickly mixed and a piece of 3DGF was immersed into the mixture for 3 h. The 3DGF was then taken out, cleaned with deionized water, and vacuum dried overnight. The MOF was prepared by the same procedure with the absence of 3DGF.

Preparation of CooS₈-3DGF

A piece of the MOF arrays on 3DGF was immersed into ethanol solution (60 mL) containing thioacetamide (TAA) (0.6 g). After the reaction at 120 °C for 6 h, the sample was taken out, washed with ethanol and DI water, and dried at 60 °C. The mass loading
of Co$_9$S$_8$ on 3DGF was measured to be $\sim 1.1$ mg cm$^{-2}$. Co$_9$S$_8$ was obtained through the same procedure except for using the MOF powder.

**Synthesis of Co$_9$S$_8$-3DGF/S, 3DGF/S, and Co$_9$S$_8$/S**

Co$_9$S$_8$-3DGF/S was obtained by a modified melt-diffusion method. Co$_9$S$_8$-3DGF was mixed with an appropriate amount sulfur, and the mixture was heated at 155 °C for 12 h in a sealed vial under Ar atmosphere. Then, the as-obtained product was heated at 200 °C for 30 min in flowing Ar atmosphere in a tube furnace to remove the residual sulfur outside the Co$_9$S$_8$-3DGF. Co$_9$S$_8$/S was obtained through the same procedure except for using Co$_9$S$_8$ as a sulfur host. 3DGF/S was prepared by heating a mixture of sulfur and 3DGF at 155 °C for 12 h in a sealed vial.

**Preparation of Co$_9$S$_8$-3DGF/Li$_2$S$_6$ for absorptivity measurements**

A 0.05 M Li$_2$S$_6$ solution was prepared by dissolving elemental S and Li$_2$S in a molar ratio of 5 : 1 in 1,3-dioxolane and 1,2-dimethoxyethane (v/v = 1:1) at 50 °C with vigorous stirring for 24 h. Then, a piece of Co$_9$S$_8$-3DGF was immersed in 20 mL of Li$_2$S$_6$ solution to obtain the Co$_9$S$_8$-3DGF/Li$_2$S$_6$ solution. After settling the solution for 1h, the precipitated product was dried. Finally, the Co$_9$S$_8$-3DGF/Li$_2$S$_6$ sample was obtained for XPS analysis. All the procedures were performed in an argon-filled glovebox.

**Characterizations**

The crystalline structures of the obtained samples were characterized by X-ray diffraction (XRD Rigaku D/MAX-rA diffractometer) with Cu K$\alpha$ radiation. The morphology investigation was performed with a scanning electron microscope (FEI
Quanta 650 SEM operated at 20 kV) and an energy dispersive X-ray (EDX) spectrometer to detect the elemental signals. Specific surface area measurements were obtained with an automated gas sorption analyzer (AutoSorb iQ2, Quantachrome Instruments). TGA data were collected with a thermogravimetric analyzer (Mettler-Toledo) to determine the content of each component in the composites. XPS analysis was performed with a Kratos Analytical spectrometer at room temperature with monochromatic Al Kα (1,486.6 eV) radiation. The UV-visible absorption spectra of polysulfide adsorption tests were collected with a Cary 5000 spectrophotometer with baseline correction (Varian).

**Electrochemical measurements**

Co$_9$S$_8$-3DGF/S and 3DGF/S were cut into rectangular plates with an area of 0.5 cm$^2$ and directly used as free-standing electrodes. Coin-type (CR2032) cells were assembled in an Ar-filled glove box with lithium metal as the anode. The Co$_9$S$_8$/S electrodes contained 80 wt.% active material, 10 wt.% Super-P, and 10 wt.% polyvinylidene fluoride (PVDF). Celgard 2500 was used as the separator. The electrolyte was composed of 1.85 M LiCF$_3$SO$_3$ in 1,3-dioxolane and 1,2-dimethoxyethane (v/v = 1:1) with 0.1 M LiNO$_3$ as an additive. The amount of electrolyte is 10 μL mg$^{-1}$ in each cell. An Arbin battery cycler was used to conduct cycling performance between 1.8 and 2.8 V at room temperature. Cyclic voltammetry (CV) measurements were carried out with a VoltaLab PGZ 402 Potentiostat with a scan rate of 0.1 mV s$^{-1}$ in the potential range of 1.8 and 2.8 V. Electrochemical impedance spectroscopy (EIS) data were collected with a CHI 660D electrochemical workstation in the frequency range of 100 kHz to
0.01 Hz. In this work, the specific capacity values were calculated on the basis of sulfur mass.
Supplemental Figures

Figure S1. Preparation of CoS$_8$-3DGF/S, related to Figure 2.
Photographs of 3DGF, Co-MOF-3DGF, Co$_9$S$_8$-3DGF, and Co$_9$S$_8$-3DGF/S.

Figure S2. Characterization of Co-MOF-3DGF, related to Figure 2.
XRD patterns of 3DGF (blue) and Co-MOF-3DGF (black).

Figure S3. Characterization of Co$_9$S$_8$-3DGF, related to Figure 2.
SEM image of Co$_9$S$_8$-3DGF, revealing the hollow structure.
Figure S4. Characterization of Co$_9$S$_8$-3DGF, related to Figure 2. N$_2$ sorption isotherm plots of 3DGF (black) and Co$_9$S$_8$-3DGF (red).

Figure S5. Characterization of Co$_9$S$_8$-3DGF/S, related to Figure 2. (A) XRD patterns of Co$_9$S$_8$-3DGF (blue) and Co$_9$S$_8$-3DGF/S (black). (B) TGA curves of Co$_9$S$_8$-3DGF/S.
Figure S6. Characterization of Co$_9$S$_8$-3DGF/S, related to Figure 2.
(A) SEM image of Co$_9$S$_8$-3DGF/S and (B-F) the corresponding elemental mappings of C, Co, N, S, and overlapped element image.

Figure S7. Characterization of 3DGF/S, related to Figure 2.
(A) photograph of 3DGF/S and (B) SEM image of 3DGF/S.
Figure S8. Reaction kinetic study of Co$_9$S$_8$-3DGF/S, related to Figure 3. Rate-dependent CV curves of Co$_9$S$_8$-3DGF/S.

Figure S9. Impedance study of Co$_9$S$_8$-3DGF/S, related to Figure 3. EIS plots of the cycled cells with Co$_9$S$_8$-3DGF/S (red) and 3DGF/S (black) cathodes.

Figure S10. Structural stability study of Co$_9$S$_8$-3DGF/S, related to Figure 3. SEM image of Co$_9$S$_8$-3DGF/S after 200 cycles.
Figure S11. Synergistic effect of each component, related to Figure 3.
Cycling performance of Co$_9$S$_8$-3DGF/S with various Co$_9$S$_8$ loading and Co$_9$S$_8$/S.

Figure S12. Adsorption of Co$_9$S$_8$-3DGF/S towards lithium polysulfides, related to Figure 5.
Digital photos of the glass vials of the (A) Co$_9$S$_8$-3DGF/S and (B) 3DGF/S cells with increasing discharge time. Both cells were discharged at C/20 rate and maintained under identical conditions.
Figure S13. Electrochemical performance of Co$_9$S$_8$-3DGF/S, related to Figure 3. Galvanostatic charge-discharge curves at various current densities of Co$_9$S$_8$-3DGF/S.

Figure S14. Morphologies of lithium foil after cycling, related to Figure 5. SEM images of the cycled lithium foil from the cells with (A) Co$_9$S$_8$-3DGF/S and (B) 3DGF/S cathodes.

Figure S15. Color changes of separators after cycling, related to Figure 5. Digital photos of the separators from the cycled cells with Co$_9$S$_8$-3DGF/S and 3DGF/S cathodes.
Figure S16. Quantitatively evaluation of the strong chemical interaction between Co$_9$S$_8$-3DGF and lithium polysulfides, related to Figure 5
High-resolution XPS spectra: Co 2p spectra of (A) Co$_9$S$_8$-3DGF and (B) Co$_9$S$_8$-3DGF/Li$_2$S$_6$.

Table S1. Comparison of the areal capacity of Co$_9$S$_8$-3DGF/S cathode with those of the previously reported high areal capacity Li-S batteries, Related to Figure 3 and Figure 4.

| Material                  | S Content (%) | S loading (mg cm$^{-2}$) | Cycling rate (C) | Areal Capacity (mA h g$^{-1}$) | Ref.                     |
|---------------------------|---------------|--------------------------|------------------|--------------------------------|--------------------------|
| Co$_9$S$_8$-3DGF/S        | 86.9          | 10.4                     | C/10             | 10.9                           | This Work                |
| Sulfur-PDMS/GF            | 70            | 10.1                     | 0.21C            | 9.3                            | (Zhou et al., 2015)      |
| few-layered graphene foam/S | 52            | 2                        | 0.5C             | 1.24                           | (Xi et al., 2014)        |
| PCF/VN/S                  | 60.1          | 8.1                      | 0.1C             | 10.6                           | (Zhong et al., 2018)     |
| NG/CNT/S                  | 53            | 8.1                      | 0.25C            | 7.9                            | (Yu et al., 2017)        |
| S-a-MCNF                  | 80            | 4.6                      | 0.2C             | 5.2                            | (Lee et al., 2017)       |
| S/GN–CNT                  | 70            | 4.7                      | 0.1C             | 2.3                            | (Zhang et al., 2017)     |
| PRC/Ni/S                  | 76.1          | 4                        | 0.05C            | 3.58                           | (Zhong et al., 2018)     |
| NPCSMs                    | 65            | 2.5                      | 0.06C            | 2.12                           | (Xia et al., 2017)       |
### Ni(OH)$_2$@PYC/S

| Capacity | Rate | C-rate | (Xia et al., 2018) |
|----------|------|--------|--------------------|
| 49.7     | 1.5  | 0.2C   | 1.76               |

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