

PAPER

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Li–S batteries have attracted great attention for their combined advantages of potentially high energy density and low cost. To tackle the capacity fade from polysulfide dissolution, we have developed a confinement approach by *in situ* encapsulating sulfur with a MOF-derived CoS₂ in a carbon framework (S/Z-CoS₂), which in turn was derived from a sulfur/ZIF-67 composite (S/ZIF-67) *via* heat treatment. The formation of CoS₂ was confirmed by X-ray absorption spectroscopy (XAS) and its microstructure and chemical composition were examined through cryogenic scanning/transmission electron microscopy (Cryo-S/TEM) imaging with energy dispersive spectroscopy (EDX). Quantitative EDX suggests that sulfur resides inside the cages, rather than externally. S/hollow ZIF-67-derived CoS₂ (S/H-CoS₂) was rationally designed to serve as a control material to explore the efficiency of such hollow structures. Cryo-STEM-EDX mapping indicates that the majority of sulfur in S/H-CoS₂ stays outside of the host, despite its high void volumetric fraction of ~85%. The S/Z-CoS₂ composite exhibited highly improved battery performance, when compared to both S/ZIF-67 and S/H-CoS₂, due to both the efficient physical confinement of sulfur inside the host and strong chemical interactions between CoS₂ and sulfur/polysulfides. Electrochemical kinetics investigations revealed that the CoS₂ could serve as an electrocatalyst to accelerate the redox reactions. The composite could provide an areal capacity of 2.2 mA h cm⁻² after 150 cycles at 0.2C and 1.5 mA h cm⁻² at 1C. This novel material provides valuable insights for further development of high-energy, high-rate and long-life Li–S batteries.

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Introduction

Lithium–sulfur (Li–S) batteries have been considered as one of the most promising next-generation electrical energy storage systems due to their ultrahigh theoretical capacity (1675 mA h g⁻¹), low cost and environmental friendliness of sulfur.^{1–4} However, the large-scale application/deployment of Li–S batteries is still impeded by multiple challenges. First, the insulating nature of sulfur and its discharge products, Li₂S₂/Li₂S, gives rise to a limited utilization of the active material,

especially at high C-rates. More importantly, high-order lithium polysulfides (Li₂S_x, 4 ≤ x ≤ 8), present as intermediate products during cycling, have a high solubility in the liquid electrolyte, so that they can shuttle between the two electrodes, reacting at both sides, and inevitably leading to fast capacity fade and decreased coulombic efficiency.^{5–8} Once the soluble and highly polar lithium polysulfides (LiPSs) are formed, they can easily lose electrical contact with the conductive matrix, due to their poor affinity, increasing the charge transfer resistance and slowing the kinetics of the polysulfides redox reactions.⁹ In addition, the large volumetric change (80%) of sulfur during discharge can also affect the integrity of the electrodes.¹⁰ Inspired by the pioneering work of Nazar *et al.*¹¹ using mesoporous carbon CMK-3 to encapsulate sulfur, carbonaceous materials with various morphologies as sulfur hosts, have been reported to improve the electronic conductivity of the sulfur electrode and mitigate the diffusion of LiPSs. These carbonaceous materials, for example, porous carbons,^{12–14} nanotubes,^{15–17} graphene/graphene oxides,^{18–21} and polymers,^{22,23} can enhance the performance of sulfur electrodes by physical constraint/confinement. However, when considering long-term cycling and rate performance, it is difficult for a carbon host, by itself, to meet all the above-mentioned requirements. It is likely

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that since carbon is nonpolar in nature, it cannot provide efficient trapping of highly-polar and ionic polysulfides.²⁴

Recently, polar materials, including metal oxides and metal sulfides, have been investigated as sulfur hosts and employed in composites with sulfur in Li-S cells. Polar hosts, such as metal oxides,^{25–29} metal sulfides,^{30–35} metal nitrides^{36,37} and MXenes^{38–42} have been found to adsorb LiPSs by strong chemical binding, and/or by forming intermediate complexes. However, most of these polar hosts are non-conducting materials and thus cannot transport electrons effectively.^{24,29} In addition, the limited surface area of these hosts cannot provide sufficient contact area for chemical interactions with LiPSs, or physically entrap lithium sulfides within the hosts. In the synthesis of sulfur containing composites, melt-diffusion is a popular and routine method to infuse sulfur into the pores of the hosts. However, recent work by the Liu group⁴³ has shown that melting sulfur into the host materials poses some problems. For example, the sulfur species formed by melt diffusion are often in the form of a continuous film, which leads to the preferential deposition of Li₂S on it. This forms a passivating layer that blocks charge transfer, severely affecting capacity, cycle life and rate performance. Fabricating sulfur composites by *in situ* encapsulating sulfur within a conductive hybrid framework that combines both physical entrapment and chemical interactions, can serve as a promising method to synergistically enhance utilization of the active material and mitigate shuttling issues.

Metal-organic-framework (MOF) materials have been studied as sulfur host materials, due to their facile and cost-effective synthesis, high surface area and tunable porosity. In addition, both the open metal centers and heteroatomic dopant sites can show strong adsorption ability towards lithium polysulfides.^{10,44–49} Zeolitic imidazolate framework-67 (ZIF-67), which is composed of metal ions (Co²⁺) and an organic compound (2-methylimidazole) is a popular type of MOF.⁵⁰ Most previous work utilizing MOF in Li-S cells is based on melt diffusing sulfur into the pores of the MOF materials or initially carbonizing the MOF and subsequently infusing sulfur into the pores *via* melt diffusion.^{44,51–55} Much less work has been conducted by *in situ* encapsulating sulfur by ZIF materials. It should be noted that ZIFs, in themselves, are not conducting due to the existence of organic linkers,¹⁰ so that compositing (insulating) sulfur with a non-conductive ZIF will slow down the charge transfer kinetics of adsorbed polysulfides, leading to a low utilization of active material as well as poor cycling and rate performance.

We have developed a procedure for the *in situ* encapsulation of sulfur nanoparticles by ZIF-67, followed by heat treatment, in vacuum, to carbonize the MOF (rendering it conductive) so as to enhance the conductivity of the composite. More importantly, we found that after the heat treatment, the ZIF-67 was converted, by sulfur, to CoS₂ within the carbon matrix. This CoS₂ in the carbon framework served as a conductive host to help encapsulate sulfur into its interior structure. Moreover, it has been reported that cobalt pyrite, CoS₂, is a sulfiphilic semi-metallic material that could effectively adsorb LiPSs, by chemical interactions, and, furthermore, could also serve as an electrocatalyst to boost Li-S battery performance by enhancing

the redox reactions of polysulfides.⁵⁶ Thus, the resulting composite material, sulfur encapsulated by CoS₂ embedded in a conducting carbon matrix derived from ZIF-67 (S/Z-CoS₂), would synergistically benefit from their combined properties. First, the conductive host, CoS₂ embedded in the carbon matrix, can facilitate electron transfer and ionic transport, increasing the utilization of active material during cycling and enhancing rate performance. Secondly, due to the *in situ* encapsulation, LiPSs diffusion can be largely suppressed by physical entrapment. Thirdly, CoS₂ can serve as both an adsorbent and electrocatalyst for LiPSs. Polar CoS₂ can adsorb polysulfides by chemical interactions and, more importantly, promote the kinetics of the redox reactions. In addition, the materials were obtained by a facile synthesis procedure amenable to large-scale production. With these advantages, the S/Z-CoS₂ composite could deliver, in Li-S cells, a high areal capacity of 2.2 mA h cm⁻² for over 150 cycles at 0.2C and excellent cycle performance at both low and high current densities. An outstanding rate performance was also achieved at 5.0C. S/Z-CoS₂ electrodes with stable and high-areal capacity represent attractive and feasible high energy-density materials for commercial implementation of Li-S batteries.

Experimental section

Preparation of S/ZIF-67

Sulfur nanoparticles were synthesized according to our previous report.²² In a typical synthesis procedure, 0.015 mol of Na₂S₂O₃ dissolved in 50 mL of water were added to 500 mL of a 30 mM sulfuric acid solution containing 1 wt% of polyvinylpyrrolidone (PVP, *M_w* ~ 40 000). After reacting for 2 hours, the resulting sulfur nanoparticles were separated by centrifugation. The obtained particles were homogeneously dispersed in 50 mL of methanol with 2 wt% PVP. 1.95 mmol of Co(NO₃)₂·6H₂O were dissolved in the sulfur/PVP methanol dispersion and the mixture was stirred for 30 min. 5.85 mmol of 2-methylimidazole were added to 50 mL of methanol and after uniformly mixing, the 2-methylimidazole solution was quickly poured into the sulfur mixture. After stirring for 5 min, the mixture was aged for 24 hours at room temperature.

Preparation of S/Z-CoS₂

S/Z-CoS₂ was synthesized by heat treatment under vacuum. The as-prepared S/ZIF-67 composite was sealed in a quartz tube under vacuum, followed by heating at 300 °C for 7 h.

Preparation of hollow ZIF-67

To obtain solid ZIF-67, 1.95 mmol of Co(NO₃)₂·6H₂O and 5.85 mmol of 2-methylimidazole were dissolved in 50 mL of methanol. After fully dissolving, the 2-methylimidazole solution was quickly added into the former solution and after stirring for 5 min, the mixture was aged for 24 hours at room temperature.^{57,58} Tannic acid has been reported to be able to etch the solid MOF to form hollow materials.⁵⁹ Thus, the solid ZIF-67 was further treated with tannic acid through a modified method. Typically, 50 mg of solid ZIF-67 particles were

dispersed in 50 mL of methanol containing 500 mg of tannic acid. After reaction for 1 hour, the particles were collected by centrifugation.

Preparation of S/H-CoS₂

Sublimed sulfur, and as-prepared hollow ZIF-67 were mixed in a mortar and then sealed under vacuum. After heat treatment at 300 °C for 7 hours, S/H-CoS₂ was obtained.

Preparation of Li₂S₆

A Li₂S₆ solution was prepared by dissolving stoichiometric amounts of Li₂S and elemental S into 1,2-dimethoxyethane and 1,3-dioxolane (DME/DOL, 1 : 1 in volume) at 60 °C overnight in an argon glovebox.

Material characterizations

X-ray characterization. Co K-edge X-ray absorption spectroscopy (XAS) measurements were conducted at the F-3 beamline of the Cornell High Energy Synchrotron Source (CHESS) in transmission mode from 150 eV below the metal edge out to $k = 12$ using nitrogen-filled ion chambers. A Co metal foil spectrum was collected concurrently, and served as a standard to calibrate the incident X-ray energy. XANES (X-ray absorption near edge structure) and EXAFS (extended X-ray absorption fine structure) spectra were normalized and analyzed using the DEMETER (Athena and Artemis) software package.⁶⁰ Background removal and spectral normalization were carried out using Athena, and EXAFS fitting was performed with the Artemis package using standard procedures. Fourier transformed EXAFS spectra were obtained by applying a Hanning window from 3 to 10 Å⁻¹ with k^2 -weighting. Spectra of S/ZIF-67 and S/Z-CoS₂ were fitted with standard ZIF-67 and CoS₂ crystal structures, respectively. X-ray diffraction (XRD) patterns were recorded using a Rigaku Ultima VI diffractometer with a Cu K α source. Diffraction patterns were collected at a scan rate of 5° min⁻¹ and with an increment of 0.02°.

Cryogenic electron microscopy characterization. Sulfur-containing samples were dispersed in ethanol and transferred to Cu TEM transmission electron microscope (TEM) grids with a lacey carbon film (Electron Microscopy Sciences, EMS). The TEM grids were loaded into a Gatan model 914 single-tilt Cryo-holder under nitrogen gas, at near liquid N₂ temperature. The holder kept the sample at a stable temperature of about -183 °C to suppress sulfur sublimation. Cryogenic bright-field (BF) TEM and high-angle annular dark-field (HAADF) STEM images were acquired using a field-emission-gun (FEG) FEI Tecnai F-20 microscope. XEDS elemental mapping was performed using an Oxford X-Max detector. EDX maps were acquired for 10–15 min to achieve more than 100 counts per pixel for sulfur and more than 50 counts per pixel for cobalt before noticeable sample drift was observed. STEM-EDX mapping was set at a beam voltage of 200 keV and a pixel size of 128 × 128. Beam damage of STEM-EDX maps has been routinely examined before and after EDX mapping. For Cryo-SEM imaging, sulfur-containing samples were loaded onto a single-crystal Si wafer on a Cryo-SEM stage at -165 °C with a surrounding cold finger

set at -183 °C to prevent ice contamination. Samples were imaged using a FEI Strata 400 STEM FIB electron microscope with a beam voltage of 30 keV and beam current of 1 nA.

Electrochemical tests

The cells were assembled with the prepared sulfur composite electrodes (composite : Super P : PVDF = 80 : 15 : 5 by weight), lithium foil, electrolyte and separator (Celgard 2300) in an argon filled glovebox with low H₂O and O₂ levels (<0.3 ppm). The electrolyte was 1.0 M lithium bis(trifluoromethane) sulfonamide (LiTFSI) dissolved in a mixed solvent of 1,3-dioxolane (DOL) and 1,2-dimethoxyethane (DME) (1 : 1, v/v) with 0.2 M LiNO₃ as an additive. The galvanostatic charge/discharge and cyclic voltammetry (CV) tests were performed on an Arbin battery cycler (Arbin, BT 2000, USA) between 1.7 to 3.0 V (vs. Li⁺/Li). The specific capacity and C rates (1C = 1675 mA g⁻¹) were calculated based on the sulfur mass in the electrode.

Results and discussion

Materials synthesis and characterization

The S, composited with CoS₂ in the carbon matrix derived from ZIF-67 (S/Z-CoS₂), was synthesized as illustrated in Fig. 1. Sulfur nanoparticles (NPs) were prepared *via* the method we previously reported.²² The sulfur NPs were *in situ* encapsulated by ZIF-67 in the presence of polyvinylpyrrolidone (PVP). To increase the conductivity of the composite, the obtained S/ZIF-67 composite was annealed under vacuum to carbonize the ZIF-67. Fig. S1† shows that the purple S/ZIF-67 changed to black after heat treatment. X-ray diffraction (XRD) patterns (Fig. 2a) indicate that the S/ZIF-67 composite is a mixture of ZIF-67 and sulfur. After the heat treatment, cubic-phase CoS₂ (JCPDS no. 41-1471) was formed. Distinct diffraction peaks at 27.8, 32.5, 36.2, 39.5, 46.5 and 55.2° can be indexed to the (111), (200), (210), (211), (220) and (311) crystal planes of CoS₂, respectively. The broad peaks of CoS₂ indicate a small crystal (domain) size and, based on the Scherrer equation, the average size of the crystallites was calculated to be 20–25 nm.

In order to further confirm the formation of CoS₂ in the S/ZIF-67 derived composite after heat treatment, we performed powder X-ray absorption spectroscopy (XAS) measurements at the Cornell High Energy Synchrotron (CHESS). The extended X-ray absorption fine structure (EXAFS) spectra exhibited a significant change between S/ZIF-67 and S/Z-CoS₂ (Fig. 2b). The first shell peak, representing the chemical bond between Co and its closest neighbors, at around 1.5 Å in the S/ZIF-67 sample shifted to about 1.9 Å in S/Z-CoS₂ (both without phase correction), suggesting a transformation from a Co-N bond in ZIF-67 to a Co-S bond in CoS₂. The Co-N and Co-S bond lengths were calculated to be 1.988 Å and 2.253 Å, respectively, through EXAFS fitting using ZIF-67 and CoS₂ standards, respectively (Fig. S2†). Powder X-ray absorption near edge structure (XANES) spectra at the Co-K edge further confirmed that the majority of Co in ZIF-67 was successfully converted to CoS₂, as evidenced by the shift in the Co K-edge energy, as well as the similar spectral features between S/Z-CoS₂ and the CoS₂

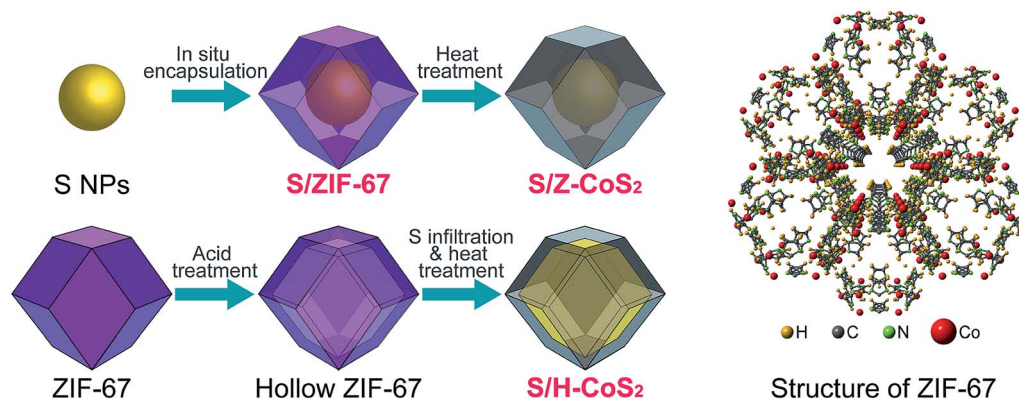


Fig. 1 Schematic illustration of the synthesis procedures of S/ZIF-67, S/Z-CoS₂ and S/H-CoS₂.

standard (Fig. S3†). Moreover, the signature pre-edge peak feature for S/ZIF-67 disappeared after heat treatment, indicating a decomposition of the MOF structure. In addition, the microstructure of the S/Z-CoS₂ composite particles was examined by bright-field (BF) TEM under cryogenic conditions. As shown in Fig. 2c, S/Z-CoS₂ exhibits a projected hexagonal symmetry with a rough surface morphology. The atomic-scale BF-TEM image in Fig. 2d reveals a lattice *d*-spacing of 2.3 Å, which matches the (211) lattice plane of CoS₂. Raman spectra of the composites before and after the heat treatment were presented in Fig. S4a.†

Two new dominant peaks were found at 1350 cm⁻¹ and 1585 cm⁻¹ corresponding to the characteristic D and G bands of the carbon matrix, respectively, demonstrating that ZIF-67 was carbonized during the heat treatment. About 78 wt% of elemental sulfur was incorporated in the S/ZIF-67, while it was 59 wt% in the S/Z-CoS₂ as determined from thermogravimetric analysis (TGA) in Fig. S4b.†

Traditionally, researchers have employed scanning/transmission electron microscopy (SEM/TEM) to study the microscale and nanoscale distribution of sulfur in host

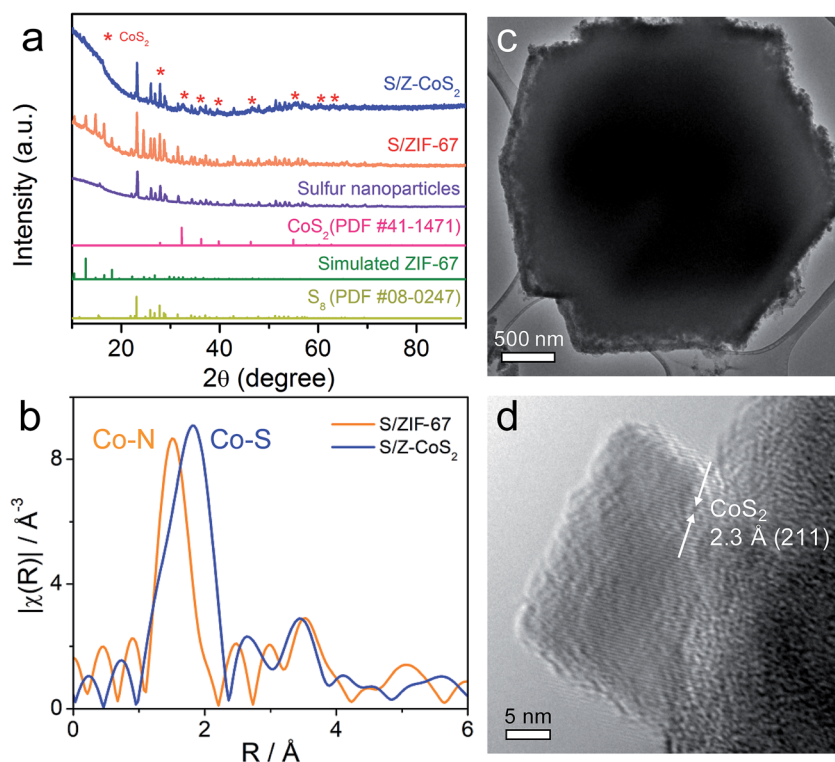


Fig. 2 (a) Powder XRD patterns of sulfur/ZIF-67 composite (S/ZIF-67), sulfur/ZIF-67-derived CoS₂ in a carbon framework (S/Z-CoS₂) and as-synthesized sulfur nanoparticles and standard XRD patterns of CoS₂, ZIF-67 and elemental S₈. (b) EXAFS spectra of S/ZIF-67 and S/Z-CoS₂ with *k*²-weighting and no phase correction. EXAFS fitting results and XANES spectra can be found in Fig. S2 and S3.† (c) Cryogenic bright-field (BF) TEM images of S/Z-CoS₂ showing the projected hexagonal symmetry and the rough surface at *T* = −183 °C. (d) Atomic-scale BF-TEM image of a CoS₂ nanoparticle.

materials. However, under the high-vacuum conditions (10^{-5} Pa) of conventional electron microscopes, elemental sulfur readily sublimates, and some of the sublimed sulfur can redistribute to other parts of the sample, precluding the intrinsic distribution of sulfur from being reliably characterized.^{61–65} Our previous work has shown that cryogenic scanning/transmission electron microscopy (Cryo-S/TEM) can effectively suppress sulfur sublimation by keeping the sample at near liquid N₂ temperature, enabling a reliable characterization of the distribution of sulfur in sulfur-host material composites.^{66–68}

The Cryo-SEM image of the S/ZIF-67 composite displays a 2–3 μm particle with the typical geometry of a rhombic dodecahedron with twelve rhombic faces (Fig. 3a and S5a†). The 2D projected geometry of a rhombic dodecahedron can be either a hexagon or rhombus. Cryo-STEM image of S/ZIF-67 composite at $T = -183^\circ\text{C}$ shows a particle with a hexagonal symmetry and well-defined sharp edges (Fig. 3b). The corresponding EDX elemental maps in Fig. 3c–e demonstrate the homogenous distribution of Co and S elements in the composite particle at the nanometer scale, which is supported by further examination of the elemental distribution of Co and S in four other different regions (Fig. S6†). The signals in S and Co maps reached more than 100 and 50 counts per pixel, respectively, before noticeable sample drift and beam damage was observed (Fig. S7†). Considering that the signal-to-noise (S/N) ratio is proportional to $\sqrt{N}$, S and Co elemental maps have a high S/N ratio of more than 10 and 7, respectively. This confirms the successful encapsulation of sulfur in the ZIF-67 cage. In contrast to the well-defined sharp edges in Fig. 3a and b, S/Z-CoS₂, obtained by heat treatment, exhibits a rougher surface morphology as shown in the Cryo-SEM image in Fig. 3f and S5b,† as was previously confirmed by BF-TEM images (Fig. 2d) to have CoS₂ nanoparticles on the surface. The Cryo-STEM image of a S/Z-CoS₂ particle reveals a size of 2–3 μm with hexagonal symmetry, similar to S/ZIF-67 (Fig. 3g). The corresponding EDX elemental maps of Co, S and Co vs. S again demonstrate the homogenous

elemental distribution of Co and S in the S/Z-CoS₂ composite, which is further evidenced by the EDX maps of other different S/Z-CoS₂ composite particles (Fig. S8†). To quantitatively examine the S and Co content in the S/Z-CoS₂ composite, EDX spectral analysis was performed and the S to Co atomic ratio was calculated to be 6.7 : 1 based on the S and Co K-edges peak intensity ratio (the S/Co ratio of CoS₂ is 2 : 1) (Fig. S9†), indicating that a significant amount of elemental sulfur stays inside the CoS₂ cages after the heat treatment. This is critical and unique to our design, differing from the conventional strategy in which sulfur stays outside the host material, such as the ones in our previous studies of a porous metal oxide,²⁹ porous carbon,⁶⁷ and layered metal sulfide.⁶⁸ The homogenous encapsulation of sulfur in the matrix formed by CoS₂ and carbon can facilitate both electronic transport and the electrochemical utilization efficiency of the insulating sulfur.

The S/Z-CoS₂ composite was obtained by the unique strategy of enclosing sulfur into the ZIF-derived CoS₂ in the carbon framework. A common approach in the literature, to constrain elemental sulfur with a hollow^{37,69} or porous host material,^{29,51,55,70,71} is through a traditional sulfur melt-infusion method at 155 $^\circ\text{C}$ or sulfur vaporization at higher temperatures. Thus, in order to compare our method with the traditional strategy, a control group of hollow ZIF-67 was prepared (see Fig. 1 for an illustration of the detailed preparation). In this case, hollow ZIF-67 was obtained by etching solid ZIF-67 using tannic acid (see Fig. S1† for the color of hollow ZIF-67).⁵⁹ Subsequently, sulfur was infiltrated into the hollow structure under the same heat treatment used so that ZIF-67 was transformed to CoS₂ embedded in a carbon matrix, and sulfur would sublime and infiltrate into the hollow host material at the same time. The formed composite is denoted as S/H-CoS₂. Since the image intensity in ADF-STEM images is proportional to atomic number as well as atomic density, a lower intensity indicates a lower atomic density in the material with the same element. Based on this argument, Fig. 4a and b suggest that the hollowed

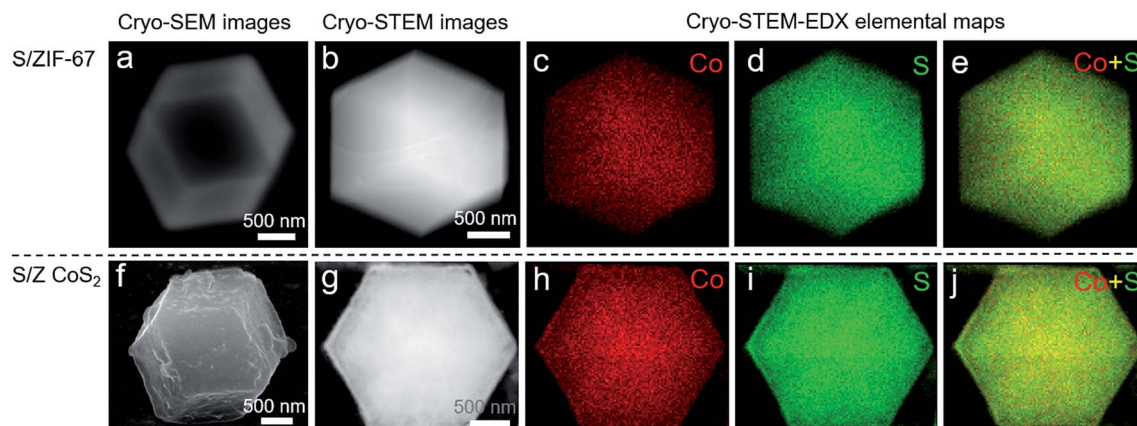


Fig. 3 Cryogenic electron microscopy (Cryo-EM) imaging and EDX elemental mapping. (a) Cryo-SEM image of S/ZIF-67 composite at $T = -165^\circ\text{C}$. (b) Cryo-STEM image of S/ZIF-67 at $T = -183^\circ\text{C}$. (c–e) STEM-EDX elemental maps of Co (red), S (green) and color overlay (yellow) of and Co and S, corresponding to the particle in (b). (f) Cryo-SEM image of S/Z-CoS₂. (g) Cryo-STEM image of S/Z-CoS₂. (h–j) Cryo-STEM-EDX elemental maps of Co (red), S (green) and color overlay (yellow) of and Co and S, corresponding to the particle in (g). EDX spectrum corresponding to the particle in (g) can be found in Fig. S9.† More examples of EDX maps of S/ZIF-67 and S/Z-CoS₂ can be found in Fig. S6 and S8,† respectively.

architecture was successfully obtained and μm -sized ZIF-67 precursors generated an inner void with a shell thickness of about 100 nm. A hollow ZIF-67 particle with a size of 2 μm and a shell thickness of 100 nm will result in a high theoretical void volume fraction of around 85% in the whole particle based on the geometry of a rhombic dodecahedron (volume, $V = \frac{16\sqrt{3}}{9}a^3$, where a is the edge length).

The microstructure and chemical composition of S/H-CoS₂ composites were examined through Cryo-STEM-EDX mapping. EDX elemental maps of S/H-CoS₂ provide insights as to the local distribution of sulfur, both within as well as outside the hollow host (see STEM images in Fig. 4c–f). Analysis of the EDX spectrum, extracted from one particle in the white dashed box in Fig. 4f, suggests a S/Co atomic ratio of 9.5 : 1, which is larger than the theoretical S/Co ratio of 2 : 1 in CoS₂ (Fig. S10†). This indicates that a large amount of (likely) elemental sulfur stays within the region of the hollow ZIF-67 derived host. More importantly, an isolated μm -sized particle in bright green in Fig. 4f was ascribed to be a pure elemental sulfur particle outside of the Co-containing hollow host. This would suggest that sulfur coexists both in the elemental form as well as strongly associated with the ZIF-67 derived host, both in as well as outside. Further examination of four other regions in the S/H-CoS₂ clearly confirms that 2–5 μm pure elemental sulfur particles co-exist and remain external to the hollow host (Fig. S11†). Despite the fact that hollow ZIF-67 has a high void volume fraction of around 85%, a considerable amount of elemental sulfur remains outside as sulfur particles either in physical contact with or isolated from the hollow host, in a way that is similar to our previous study of a porous iron oxide.²⁹ S/

H-CoS₂ together with an integrated S/Z-CoS₂ composite will later be compared (*vide infra*) in battery tests, to explore the correlation between structural design and battery performance.

We posit that the polar sulfur host obtained, CoS₂ in a carbon matrix derived from ZIF-67 (Z-CoS₂), has a strong adsorption towards polar LiPSs (lithium polysulfides). To demonstrate/test the effectiveness of Z-CoS₂ as a host material for suppressing the diffusion of LiPSs, the adsorption ability of polar Z-CoS₂ towards LiPSs was tested. ZIF-67 derived CoS₂ in a carbon matrix without sulfur (Z-CoS₂), was obtained by subliming sulfur under high temperature (300 °C) for 6 hours in a flow furnace. Z-CoS₂ was then mixed with a 1 mM Li₂S₆ in DOL/DME (1 : 1, v/v) solution as a representative polysulfide. As shown in Fig. 5a, it is evident that the addition of Z-CoS₂ to the polysulfide solution turns the color of the Li₂S₆ from yellow to colorless (immediately), suggesting that Z-CoS₂ has a strong (and fast) adsorption affinity/capability for LiPSs. Thus, there would be the expectation that during cycling, Z-CoS₂ can help immobilize the LiPSs and greatly mitigate capacity fade. As a comparison, commercial CoS₂ and ZIF-67 were also added to the polysulfide solution. The commercial CoS₂ gave rise to a slight color change, indicating that CoS₂ is beneficial for constraining LiPSs, as previously reported.^{35,56,72} However, ZIF-67 did not cause any discoloration. Instead the solution changed to pinkish, suggesting that ZIF-67 lacks the ability to restrain the LiPSs from diffusing and, even worse, ZIF-67 is likely decomposing slightly with Co²⁺ diffusing into the electrolyte (giving rise to the pink coloration). UV-vis spectra (Fig. 5b) further indicated that Z-CoS₂ has a strong entrapment ability to polysulfides, due to both chemical

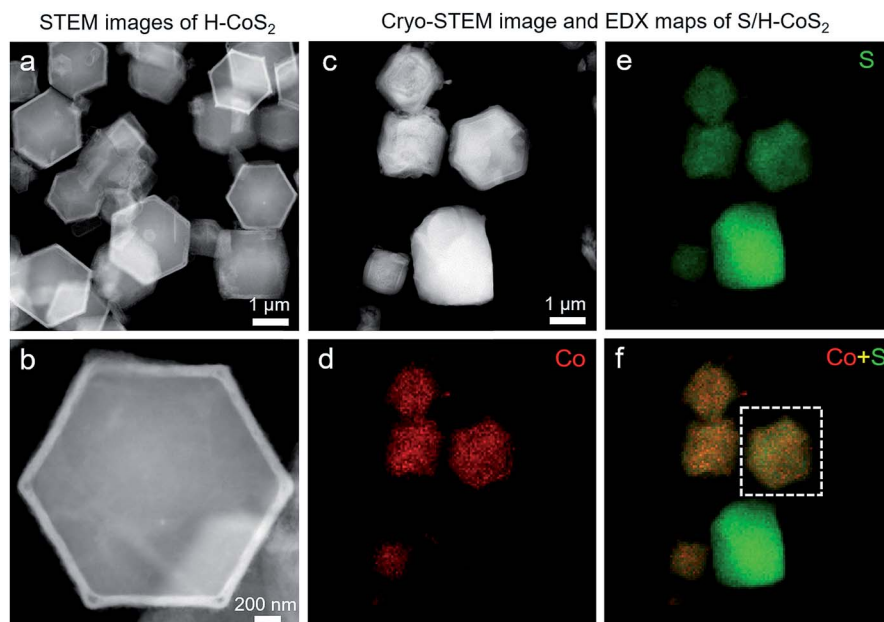


Fig. 4 (a) HAADF-STEM image of hollow ZIF-67 micrometer-sized particles. (b) STEM image of a specific hollow ZIF-67 particle. Lower image contrast in the middle of the particles clearly suggests a hollow structure. (c) Cryo-STEM image of S/H-CoS₂ composite particles. (d–f) Cryo-STEM-EDX elemental maps of Co (red), S (yellow) and color overlay of Co and S. Yellow suggests an overlay of Co and S elements while green indicates pure elemental sulfur. EDX spectrum of the composite particle in the dashed box can be found in Fig. S10.† More examples of EDX maps of S/H-CoS₂ can be found in Fig. S11.†

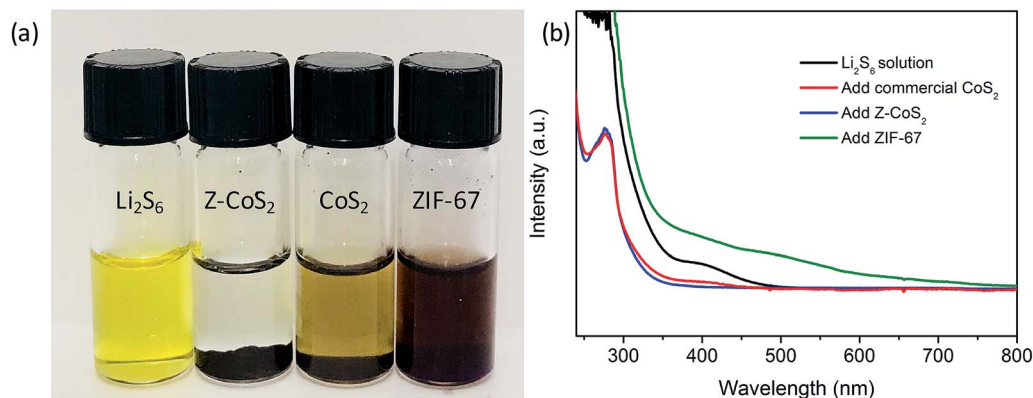


Fig. 5 (a) Photographs of Li_2S_6 solution and Li_2S_6 solutions after adding Z-CoS_2 , commercial CoS_2 and ZIF-67 powders. (b) UV/vis absorption spectra of lithium polysulfide (Li_2S_6) solution before and after adding Z-CoS_2 , commercial CoS_2 and ZIF-67 .

interactions and physical constraints. The strong and fast affinity of Z-CoS_2 for LiPSs could improve cycling stability of S/Z-CoS_2 composites.

Electrochemical performance

Coin cells with S/Z-CoS_2 , S/ZIF-67 and S/H-CoS_2 as cathode materials were prepared to evaluate their electrochemical performance. Cyclic voltammograms (CV) of these materials were obtained over the voltage range of 1.7–3.0 V at a scan rate of 0.1 mV s^{-1} (Fig. 6a–c). For S/Z-CoS_2 , two well-defined reduction peaks at 2.28 and 2.05 V were observed, corresponding to the reduction of sulfur to high-order lithium polysulfides Li_2S_x ($4 \leq x \leq 8$) as well as lithium polysulfides to solid-state $\text{Li}_2\text{S}_2/\text{Li}_2\text{S}$, respectively, while the anodic peak could be assigned to the oxidation of $\text{Li}_2\text{S}_2/\text{Li}_2\text{S}$ to S_8 . In the case of S/ZIF-67 , the two reduction peaks were found at lower potentials of 2.22 V and 1.98 V, respectively. The potential shifts are likely due to the low electronic conductivity of ZIF-67 , which results in slower redox kinetics. As mentioned previously, the heat treatment carbonizes the ZIF-67 material to produce CoS_2 in the carbon matrix. Benefitting from the generated carbon as well as CoS_2 , the overall conductivity of the composite material is enhanced, facilitating electronic transfer. Due to the similar reaction pathways, S/H-CoS_2 has higher conductivity than S/ZIF-67 , leading to a positive shift of the reduction peaks (2.23 and 2.01 V) compared to S/ZIF-67 . However, the external elemental sulfur on the surface of the host material impedes electron transfer between particles, so that the reaction kinetics are slower than for S/Z-CoS_2 . To compare the conductivity of the materials, electrochemical impedance spectra (EIS) of S/Z-CoS_2 , S/ZIF-67 and S/H-CoS_2 cathodes are presented in Fig. S12.† S/Z-CoS_2 exhibits the smallest semicircle diameter in the high-frequency region, suggesting that S/Z-CoS_2 has the faster charge transfer processes. In addition, Fig. 6a–c show that after 10 CV cycles, the peak positions and intensities were not changed for S/Z-CoS_2 , indicating the stable cycling stability of the material. In contrast, both S/ZIF-67 and S/H-CoS_2 exhibited dramatic shifts and decreased intensities, due to severe polysulfide shuttling.

The cycling performance of these three electrodes are compared at a current density of 0.2C (Fig. 6d). S/Z-CoS_2 , S/ZIF-67 and S/H-CoS_2 delivered initial capacities of 993, 900, and 970 mA h g^{-1} , respectively. However, after only 50 cycles, the discharge capacity of S/ZIF-67 dropped rapidly to 300 mA h g^{-1} , corresponding to a capacity retention of only 30%. The rapid capacity decay is due to the fast polysulfide dissolution, which is in agreement with Fig. 6c. The S/H-CoS_2 electrode delivered a somewhat higher capacity with slightly better capacity retention than S/ZIF-67 because of the increased electrical conductivity, caused by heat treatment, and chemical interactions between CoS_2 and LiPSs during cycling. However, with minimal chemical adsorption effects, the capacity fade was still severe with only 28% retention after 200 cycles. In contrast, S/Z-CoS_2 electrodes exhibited a significantly enhanced cycling stability. A much higher capacity of 750 mA h g^{-1} was achieved with an excellent capacity retention of 76% after 200 cycles. The improved stability is likely due to the increased conductivity of the material, compared to S/ZIF-67 , and mitigated loss of active material, through LiPSs dissolution, by both physical confinement and the chemical interactions of LiPSs with CoS_2 in the carbon matrix. The capacity values obtained based on the mass of the composite are shown in Fig. S13.† The prolonged cycling stability of the materials was further tested at 1C (Fig. 6e). S/Z-CoS_2 exhibited a highly stabilized capacity of 440 mA h g^{-1} after 1000 cycles, corresponding to a low average capacity drop rate of 0.04% per cycle.

The rate capabilities and the electrode kinetics were investigated at various current densities (Fig. 7a). As the current density was increased stepwise from 0.1 to 5C, the S/Z-CoS_2 delivered high capacity values of 1100, 910, 740, 640, 580, 490 and 430 mA h g^{-1} , respectively. When the current density was decreased back to 0.1C, a capacity of 930 mA h g^{-1} was obtained, indicating a high structural stability, even at high C-rates. Compared with S/Z-CoS_2 , the S/ZIF-67 shows much lower discharge capacities at various current densities, and almost no capacity at current densities higher than 2C. The dramatically low capacities are caused, at least in part, by the low conductivity of the composite material (Fig. S12†). Owing to

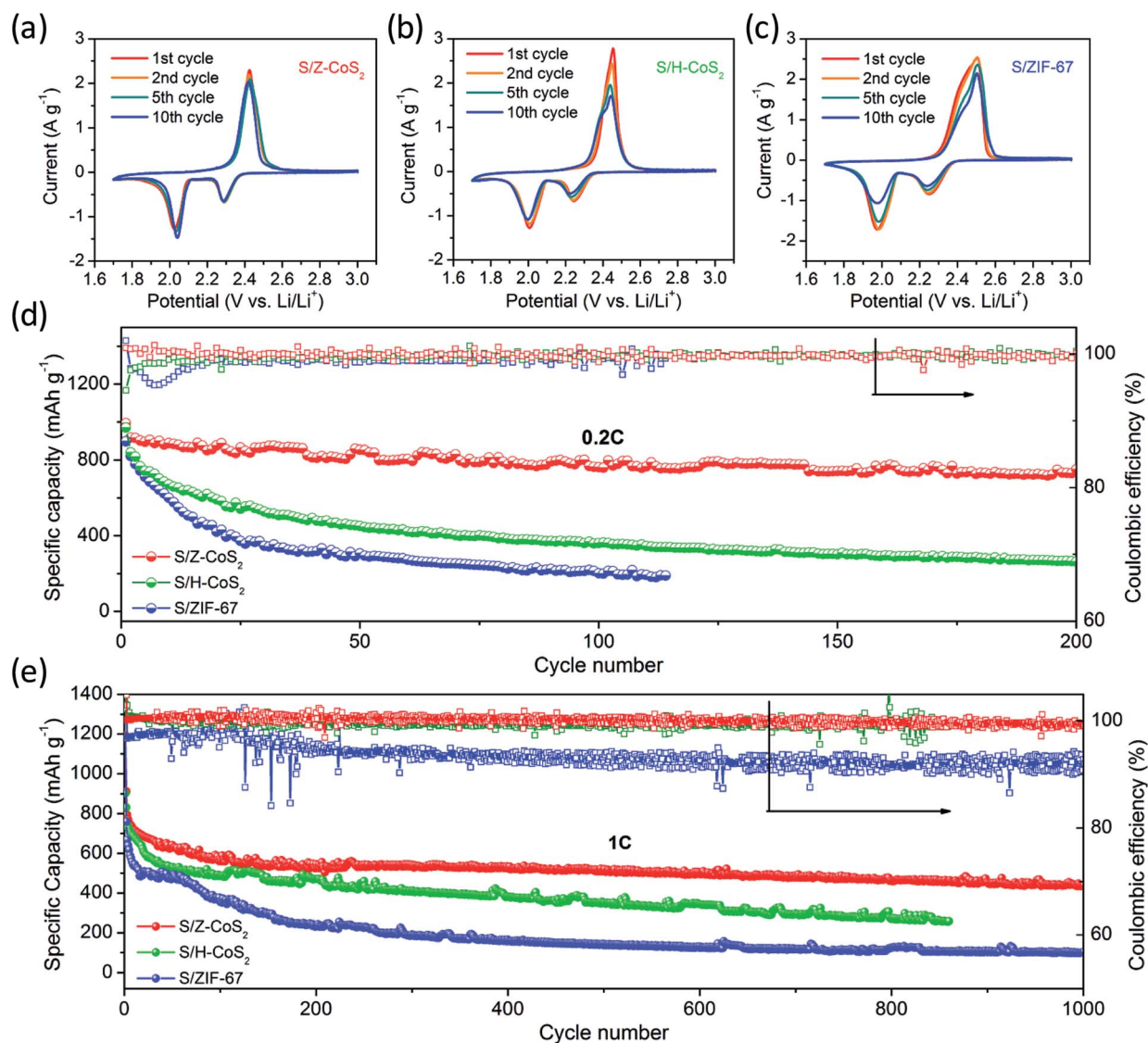


Fig. 6 CV profiles of (a) S/Z-CoS₂, (b) S/H-CoS₂, and (c) S/ZIF-67 for 10 cycles at a scan rate of 0.1 mV s⁻¹. (d) Cycling performance of S/Z-CoS₂, S/H-CoS₂, and S/ZIF-67 at 0.2C for 200 cycles. (e) Long-term cycling of S/Z-CoS₂, S/H-CoS₂, and S/ZIF-67 at 1C for 1000 cycles.

the higher conductivity of H-CoS₂, the rate capability of S/H-CoS₂ is better than S/ZIF-67 at high current densities. However, without efficient physical constraint, the ineffective LiPSs confinement of H-CoS₂ results in relatively low capacities at low C-rates. It is worth noting that S/H-CoS₂ and S/Z-CoS₂ have similarly high capacities at high current densities. This could be due to CoS₂, serving as an electrocatalyst, could favorably affect the redox reactions.^{56,72} Ascribed to the improved conductivity and efficient LiPSs entrapment by both physical confinement and chemical adsorption effects, S/Z-CoS₂ exhibited the best performance in terms of redox kinetics and cycling stability.

High sulfur loading of the electrode composite is of great significance for the practical use of Li-S batteries. Thus, S/Z-CoS₂ electrodes with high areal sulfur loadings of 2.5–2.9 mg cm⁻² were further tested. Fig. 7c presents cycling performance of the high-loading electrodes cycled at 0.2C for 150 cycles. An initial discharge capacity of 1030 mA h g⁻¹ was achieved,

corresponding to an areal capacity of 3 mA h cm⁻². After 150 cycles, a high and stabilized specific capacity of 750 mA h g⁻¹, corresponding to 2.2 mA h cm⁻², was obtained. The stable cycling performance of high-loading sulfur electrodes of S/Z-CoS₂ is ascribed to the high conductivity of S/Z-CoS₂ and efficient confinement of LiPSs by both physical and chemical entrapment. The rate performance of high-loading electrodes in Fig. 7b shows that the S/Z-CoS₂ electrode can provide a high areal capacity of 1.5 mA h cm⁻² even at a high C rate of 1C. Two well-defined discharge plateaus were observed at various current densities (Fig. S14†), illustrating the fast redox kinetics of the electrodes.

Furthermore, to study the reaction kinetics of the electrodes, the galvanostatic intermittent titration technique (GITT) was employed by discharging/charging the cell for 30 min at 0.1C followed by a 10 hour rest period. The lithium ion diffusion coefficient at different states of charge (SOC), could be

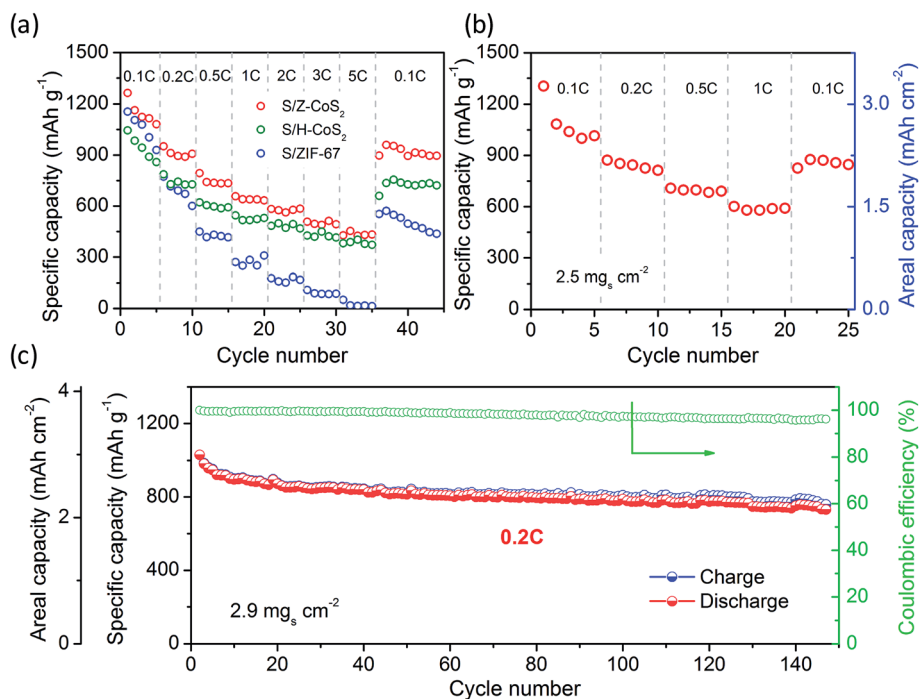


Fig. 7 (a) Rate performance of S/Z-CoS₂, S/H-CoS₂, and S/ZIF-67 at C rates from 0.1C to 5.0C. (b) Rate performance of high sulfur loading electrodes of S/Z-CoS₂. (c) Cycling performance of S/Z-CoS₂ with high sulfur loading at 0.2C rate.

calculated from the transient voltage response using the expression developed by Weppner and Huggins.⁷³ The lithium ion diffusion coefficients calculated using this equation at different SOC are plotted in Fig. S15a and b.† The values are found to be higher at the first discharge plateau than those at the second plateau, confirming that the reaction of S₈ to Li₂S₄ is faster than the transformation of Li₂S₄ to Li₂S, so the liquid-solid reaction is the rate-determining step in the sulfur reduction. Moreover, CV tests at different scan rates were further conducted to study the reaction kinetics of the electrodes (Fig. 8a–c). At higher sweep rates, the potentials of the reduction peaks of S/Z-CoS₂ are the highest while those of the oxidation peaks are the lowest among three samples of S/Z-CoS₂, S/ZIF-67 and S/H-CoS₂, further indicating that the S/Z-CoS₂ composites have the fastest kinetics for the reaction between Li₂S and S₈. The Li⁺ diffusion coefficient can be derived by analyzing the CV data at different scan rates according to the Randles-Sevcik equation:

$$I_p = 2.69 \times 10^5 n^{3/2} A D^{1/2} C \nu^{1/2}$$

where I_p is the peak current, n is the charge transfer number, A is the geometric area of the active electrode, D is the lithium ion diffusion coefficient, C is the concentration of Li⁺, and ν is the potential scan rate. The lithium ion diffusion coefficients can be determined by plotting the current density I_p , versus the square root of the scan rate $\nu^{1/2}$ (Fig. 8d–f). The linear relationship of I_p versus $\nu^{1/2}$ indicates that the reaction is a diffusion-controlled process. For Z-CoS₂ encapsulating sulfur electrode, the slopes are the highest among the three samples. For peak C1 (Fig. 8d), the diffusion rate increased by 29% and 34% for peak C2,

respectively (Fig. 8e), compared to S/ZIF-67 electrodes. These results suggest that ZIF-67 derived CoS₂ embedded in carbon framework could significantly enhance the redox reaction kinetics, especially for the transformation from Li₂S₄ to Li₂S.

All of these results indicate that S/Z-CoS₂ is a promising sulfur cathode material for high energy density Li-S batteries with stable cycling life and outstanding rate performance. By comparing with other cathodes based on carbon, metal sulfides/oxides or MOF materials as hosts (Table S1†), it is evident that our S/Z-CoS₂ exhibits highly enhanced rate capability and outstanding cycling stability. The significantly improved performance is ascribed to various reasons. First, the heat treatment, which produced a carbon framework, significantly increased the conductivity of the composite (Fig. S12†), increasing the utilization of active material during cycling and lowering the polarization in the coin cells. Second, the polar CoS₂ embedded in the carbon framework can provide strong adsorption to LiPSs, enriching the LiPSs concentration on the conductive host surface, thus accelerating the redox reaction. This has been verified by the adsorption test (Fig. 5). Third, *in situ* encapsulation of sulfur particles gives rise to an intimate contact between the host material and sulfur particles, and at the same time, provides a protective cage for physically restraining the LiPSs from diffusing into the electrolyte. The combined effects of physical confinement and chemical interactions give rise to the enhanced cycling stability. In addition to the physical and chemical entrapment of LiPSs, CoS₂ also serves as an electrocatalyst which can accelerate the polysulfides redox kinetics, especially for the liquid-solid state reaction, as manifested by the kinetic analysis (Fig. 8). It is also proposed that

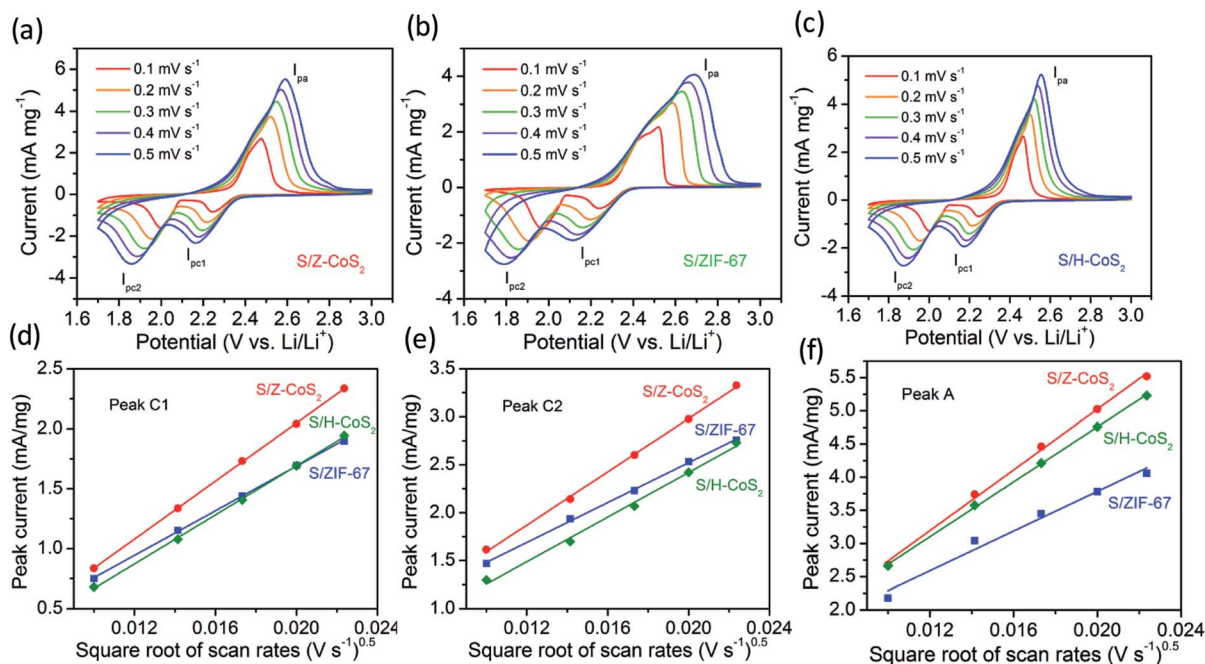


Fig. 8 CV profiles of (a) S/Z-CoS₂, (b) S/H-CoS₂, and (c) S/ZIF-67 at various scan rates from 0.1 mV s⁻¹ to 0.5 mV s⁻¹. Plots of S/Z-CoS₂, S/H-CoS₂, and S/ZIF-67 peak current vs. square root of scan rates for (d) cathodic peak 1, (e) cathodic peak 2, and (f) anodic peak 1.

CoS₂ could control the precipitation of insoluble Li₂S. The SEM images of a fully discharged cell after 20 cycles displayed in Fig. S16† indicate that there are no bulk Li₂S particles present on the surface and the morphology of the composite has no noticeable changes, indicating the controlled precipitation and stable encapsulation of the active material. Recent pioneering work has also demonstrated the effectiveness of introducing a conductive interlayer to improve the cycling performance and rate capability of Li-S batteries.⁴⁰ We believe that optimizing the composite composition ratio and other components in the cell, such as introduction of an interlayer or separator modification, will likely further enhance electrochemical performance.

Conclusions

In summary, a facile and scalable method was developed to synthesize S/Z-CoS₂ composites *via in situ* encapsulation followed by heat treatment. The annealing process transformed ZIF-67 to CoS₂ embedded in a carbon framework. The formation of CoS₂ embedded in a carbon framework was confirmed by XAS and Cryo-TEM. The successful encapsulation of sulfur by ZIF-derived CoS₂ in a carbon matrix was examined through Cryo-S/TEM imaging together with EDX elemental mapping. We have demonstrated that the encapsulation of sulfur particles by CoS₂ embedded in a carbon framework is beneficial for preventing/precluding the LiPSs from diffusing into the electrolyte during cycling and can also accelerate the redox reactions. Benefitting from the improved conductivity, both physical entrapment of LiPSs and their chemical binding to CoS₂, and more importantly, accelerated redox kinetics induced by CoS₂ as an electrocatalyst, the resulting S/Z-CoS₂ could

achieve a high areal capacity, excellent cycling stability and enhanced rate performance. This work provides valuable insights for novel and cost-effective sulfur host materials design for the future practical application of high-energy, high-power and long-life Li-S batteries.

Author contributions

N. Z. synthesized the materials, conducted the electrochemical study and wrote the manuscript. Y. Y. performed the cryogenic S/TEM imaging and EDX elemental mapping and wrote the corresponding analysis. X. F. conducted the XANES and EXAFS measurements and wrote the corresponding analysis. S.-H. Y., J. S. helped perform the experiment.

Conflicts of interest

There are no conflicts to declare.

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