

Rational design of sulfur-containing composites for high-performance lithium-sulfur batteries

Cite as: APL Mater. 7, 020904 (2019); doi: 10.1063/1.5081915

Submitted: 17 November 2018 • Accepted: 10 January 2019 •

Published Online: 13 February 2019



Jinhua Sun,¹ Junpeng Ma,² Jingbiao Fan,² Jeffrey Pyun,³ and Jianxin Geng^{2,a)} 

AFFILIATIONS

¹Department of Physics, Umeå University, SE-90187 Umeå, Sweden

²State Key Laboratory of Organic-Inorganic Composites, College of Energy, Beijing University of Chemical Technology, 15 North Third Ring East Road, Chaoyang District, Beijing 100029, China

³Department of Chemistry and Biochemistry, University of Arizona, 1306 East University Boulevard, Tucson, Arizona 85721, USA

^{a)}Email: jianxingeng@mail.buct.edu.cn. Tel.: +86-10-6443 7861.

ABSTRACT

Sulfur has received considerable attention as a cathode material for lithium-sulfur (Li-S) batteries due to its high theoretical energy density (2567 W h kg⁻¹), high earth abundance, and environmental benignity. However, the insulating nature of sulfur and the shuttle effect of soluble lithium polysulfides result in serious technical issues, such as low utilization rate of sulfur, reduced columbic efficiency, and poor cycling stability, which compromise the high theoretical performance of Li-S batteries. In the past years, various attempts have been made to achieve high specific capacity and reliable cycling stability of Li-S batteries. Incorporation of sulfur into functional host materials has been demonstrated to be effective to improve the electrochemical performance of sulfur-based cathodes via enhancing the electron and Li ion conductivities, immobilizing sulfur/lithium polysulfides in cathodes, and accommodating the volume changes in sulfur-based cathodes. Therefore, the rational design of sulfur-containing composites needs to be emphasized as key strategies to develop high-performance cathodes for Li-S batteries. In this perspective, after reviewing the achievements obtained in the design of sulfur-containing composites as cathodes for Li-S batteries, we propose the new issues that should be overcome to facilitate the practical application of Li-S batteries.

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Sulfur exhibits a high theoretical specific capacity (1675 mA h g⁻¹) and a high energy density (2567 W h kg⁻¹) as a cathode material for lithium-sulfur (Li-S) batteries with the advantages of environmental benignity, rich earth abundance, and low cost.¹ These values are roughly 6 and 9 times as that of the commercially intercalated cathode materials such as LiCoO₂ and LiFePO₄, respectively.² Theoretically, when used as the cathode in Li-S batteries, one S₈ molecule reacts in total with 16 lithium atoms to form 8 Li₂S (i.e., S₈ + 16Li ↔ 8Li₂S). The reaction involves a multielectron-transfer electrochemical process with two voltage plateaus located at 2.3 and 2.1 V versus Li/Li⁺, corresponding to the transformation from S₈ to soluble Li₂S₄ contributing about 25% of the total capacity (418 mA h g⁻¹) and the further reduction of Li₂S₄ to solid Li₂S accounting for 75% of the total capacity (1252 mA h g⁻¹),

respectively.^{3,4} Although the theoretical specific capacity and energy density of sulfur are much higher than those exhibited by commercially available cathode materials,⁵ making it possible to meet the energy and power requirements for next-generation energy storage devices, sulfur also suffers a series of limitations that thwart the high performance of Li-S batteries. First, the insulating features of sulfur (5 × 10⁻³⁰ S cm⁻¹ at 25 °C) and its reduced product (Li₂S/Li₂S₂) cause the sluggishness of electrochemical kinetics of sulfur cathodes and low utilization of sulfur. Second, dissolution of the intermediate lithium polysulfides, i.e., Li₂S_x (4 ≤ x ≤ 8), in an electrolyte, which leads to the shuttle effect because of the diffusion of lithium polysulfides from the cathode to anode, and results in low Coulombic efficiency and poor cycling stability. Third, large volume expansion (up to 80%) of sulfur

due to the different densities of Li_2S (1.66 g cm^{-3}) and sulfur (2.03 g cm^{-3}) leads to pulverization of the cathode, rapid capacity decay, and even safety problem.⁶ To overcome these limitations, a number of strategies have been proposed to prepare sulfur-based cathode materials by tuning the compositions and structures of cathode materials.^{4,7–14}

One of the most efficient and widely adopted strategies is incorporating sulfur into functionalized host materials.⁴ The host materials usually are designed with the following functions: first, a high accommodation capability for hosting sulfur; second, high electron and lithium ion conductivities for improving the electrochemical kinetics and increasing the utilization of sulfur; third, physical trapping and/or chemical immobilization of lithium polysulfides for improving the cycling stability; and fourth, structural stability for withstanding the huge volume changes in the cathode during the charge/discharge process.^{4,10} To develop the ideal host materials that meet all these requirements, extensive efforts were devoted either to modifying the existing materials or synthesizing new materials during the past years.^{15–19}

Generally, the reported host materials can be classified into several categories: (1) carbon materials (e.g., porous carbons,¹³ graphene,²⁰ carbon nanotubes,²¹ and carbon nanofibers²²), (2) organic materials (e.g., conductive polymers),^{12,23,24} and (3) inorganic materials (e.g., MnO_2 and TiO_2).^{14,17,25–27} These materials are usually modified to construct various structures with the aim of improving the utilization of sulfur and suppressing the shuttle effect.^{4,10,28} In this respect, various strategies have been reported: (1) incorporation of sulfur into porous structures such as micro-, meso-, and macropores;^{8,13,16,29} (2) encapsulation of sulfur/lithium polysulfides into core-shell structures;^{11,22,30} (3) adsorption of lithium polysulfides using polar-polar interactions;^{31,32} (4) covalent bonding of sulfur (e.g., C–S, O–S, and Mn–S);^{7,10,25,33,34} and (5) synthesis of sulfur polymers.^{12,15,23} A combination of two or several of the aforementioned strategies can also be used to solve the issues faced by sulfur-based cathodes.

Among all of the host materials, carbon-based materials are most intensively investigated because their structures and properties can readily be tailored for specifically addressing the issues of sulfur as the cathode for Li–S batteries.^{10,35,36} For example, carbon's conductive feature can be used to improve the electrical conductivity of sulfur cathodes; their nanostructures can be used to physically trap soluble lithium polysulfides, and their functionalized surfaces can be used to chemically immobilize the lithium polysulfides; their high specific surface areas and low densities allow them to be used to accommodate high quantities of sulfur.

Various carbon-based materials with different dimensions (0 dimensional nanospheres, 1D nanotubes and nanofibers, 2D graphene, and 3D hierarchical carbon) have been adopted to accommodate sulfur.^{17,22,28,32,35,37} The formed carbon/sulfur composites as cathodes usually exhibit enhanced electrochemical performance due to the increased electrical conductivity of cathode materials and the suppressed diffusion of lithium polysulfides. The first reported carbon material for hosting sulfur is CMK-3 (Fig. 1), which

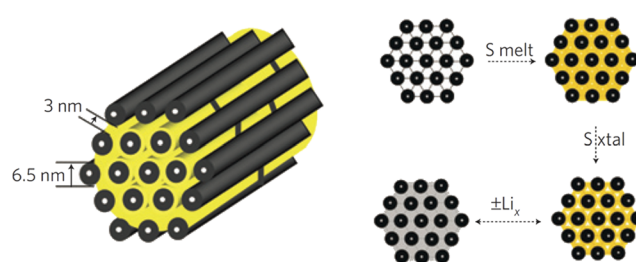


FIG. 1. A schematic diagram of the sulfur (yellow) confined in the interconnected porous structure of mesoporous CMK-3. Reproduced with permission from Ji *et al.*, *Nat. Mater.* **8**, 500 (2009). Copyright 2009 Springer Nature.

has highly ordered mesopores with a uniform pore diameter of 3.33 nm, a high pore volume of $2.1 \text{ cm}^3 \text{ g}^{-1}$, and a high electrical conductivity of 0.2 S cm^{-1} .⁹ The unique features of CMK-3 not only constrain sulfur into its channels but also offer essential electrical contact to the insulating sulfur. High specific capacities of up to 1320 mA h g^{-1} in the first cycle and 1100 mA h g^{-1} after 20 cycles were achieved. Following this pioneering research, a series of sulfur/porous carbon composites as cathodes had been developed.^{38,39} The results demonstrated that incorporation of carbon materials significantly enhanced the specific capacity of the sulfur-based cathode because the high conductivity and high surface area of the incorporated carbon enabled high-efficient utilization of sulfur. However, the specific capacity decayed quickly after the initial cycles due to the limited ability of the nonpolar carbon to entrap polar lithium polysulfides, leading to unsatisfactory cycling stabilities. Therefore, more efforts have recently been enforced to encapsulate sulfur and confine the lithium polysulfides into the cathode materials.

Hollow carbon materials such as core-shell, yolk-shell, or multi-shell structures were demonstrated to be effective for hosting sulfur as the cathode for high-performance Li–S batteries [Figs. 2(a)–2(c)].^{8,40} The large inner hollow space not only allows a high loading of sulfur but also offers accommodation for the volumetric expansion of sulfur during the lithiation process. Highly graphitized hollow carbon spheres (HCS) were reported to suppress the diffusion of lithium polysulfides, leading to a high specific capacity of 1100 mA h g^{-1} after 100 cycles.³⁵ However, the outward diffusion of lithium polysulfides could not be completely avoided in long-term cycling. Regarding this, attempts to prepare double- and multi-shelled carbon were made to more effectively suppress the shuttle effect and withstand the volume changes in the active materials [Figs. 2(b) and 2(c)].^{24,30,40} For example, multi-shelled HCS with a high specific surface area of $1050 \text{ m}^2 \text{ g}^{-1}$ was synthesized by an aqueous emulsion approach [Fig. 2(d)].³⁰ After encapsulating sulfur, the composite delivered a high specific capacity of 1350 mA h g^{-1} at a current density of 0.1 C with significantly enhanced cycling stability. However, it was extremely difficult to impregnate a high quantity of sulfur into the multi-shelled HCS. Considering the trade-off between efficient confinement of lithium polysulfides inside the multi-shelled structures and high-quantity loading of sulfur into

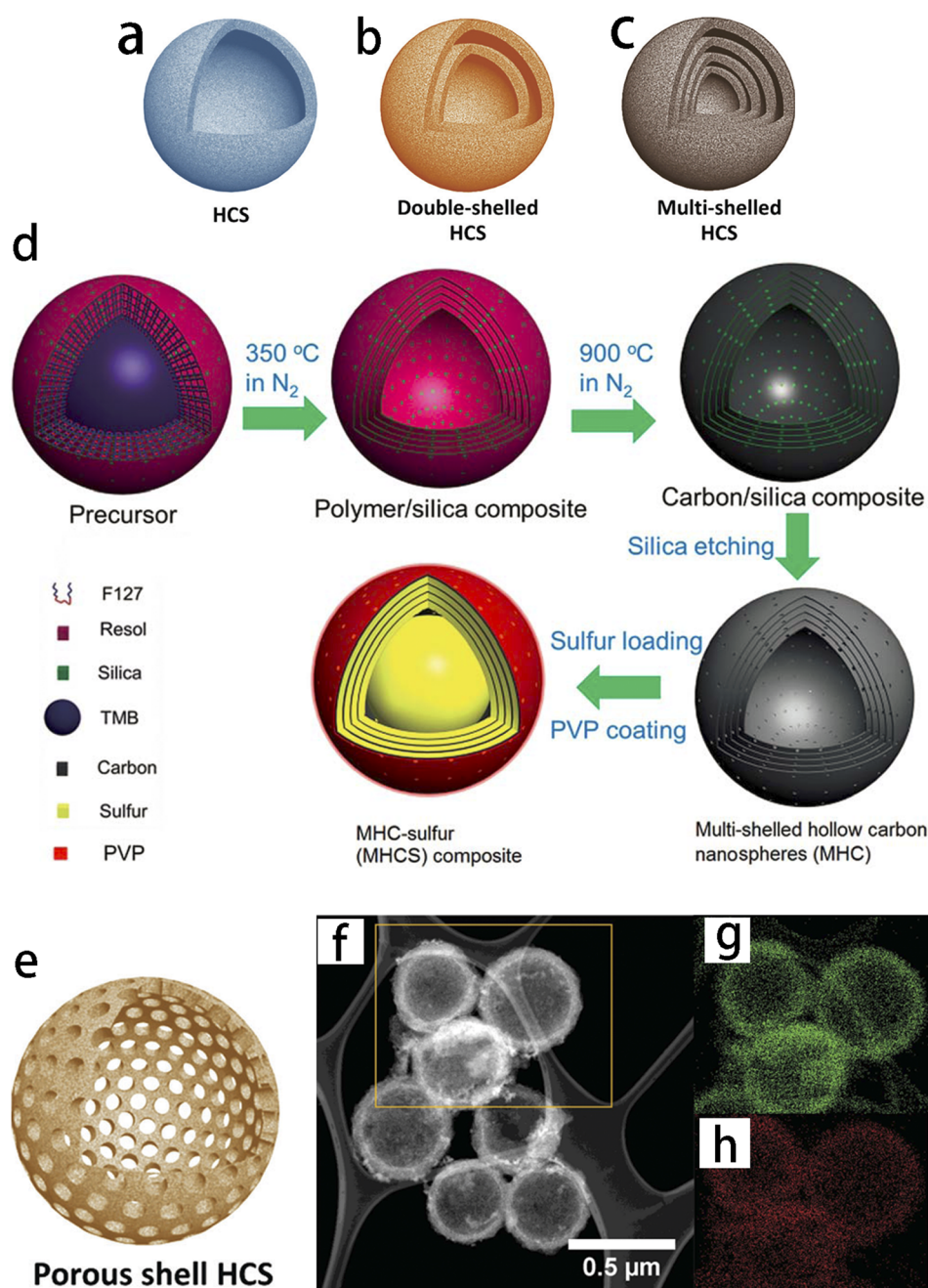


FIG. 2. [(a)–(c)] Schematic illustrations of various hollow carbon structures to host sulfur: (a) HCS, (b) double-shelled HCS, (c) and multi-shelled HCS. (d) The synthesis of multi-shelled HCS-encapsulated sulfur composites. (e) HCS with tailored porosity. [(f)–(h)] The STEM image and elemental mappings of nitrogen-doped mesoporous-HCS-3-S composites. [(a)–(c) and (e)] Reproduced with permission from Li *et al.*, *Energy Environ. Sci.* **9**, 3061 (2016). Copyright 2016 The Royal Society of Chemistry; (d) Reproduced with permission from Chen *et al.*, *J. Mater. Chem. A* **2**, 16199 (2014). Copyright 2014 The Royal Society of Chemistry; [(f)–(h)] Reproduced with permission from Zhou *et al.*, *Adv. Energy Mater.* **5**, 1401752 (2015). Copyright 2015 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

the structures, it is important to explore simple and reliable techniques to synthesize materials with desired structures for hosting sulfur.

Creation of porous structures with tailored sizes in carbon shells was proposed as an effective approach to improve the performance of sulfur-based cathodes [Fig. 2(e)].^{39,41} The carbon shells with well-defined porous structures show a number of functions. Along with the physical barrier to

prevent the diffusion of lithium polysulfides, the carbon shells with micro- and mesopores also provide a capillary force for impregnation of sulfur and act as channels for electrolyte penetration. It has been demonstrated that carbon shells containing deliberately created porosity and carefully controlled pore sizes enhance the loading and utilization of sulfur [Figs. 2(f)–2(h)].^{39,41} However, simple physical entrapment is not sufficient to completely inhibit the shuttle effect of

lithium polysulfides over long-term cycling because interactions between polar lithium polysulfides and nonpolar surface of carbon are weak.⁴² Therefore, more effective strategies should be explored to further suppress the shuttle effect of lithium polysulfides.

Creation of chemical interactions between host materials and sulfur/lithium polysulfides is efficient to confine lithium polysulfides.^{7,33,36,43–46} The chemical interactions usually take place at the interfaces of host materials and lithium polysulfides. Therefore, this strategy is based on the interface phenomenon rather than spatial confinement. To fulfill the strategy, host materials need to be carefully chosen with intrinsic features or designed with required functionalities, which offer them with diverse chemical mechanisms to suppress the shuttle effect of lithium polysulfides. In general, the chemical strategies can be categorized into the following types: (1) chemical affinity (i.e., polar–polar interactions between the polar surfaces of host materials and polar lithium polysulfides) and (2) covalent bonds (i.e., sulfur is covalently bonded to functional groups/atoms of the hosts via covalent bonds such as C–S, O–S, and Mn–S).³³

The polar–polar interactions have been demonstrated to be efficient for adsorbing lithium polysulfides. Although carbon materials are featured with hydrophobic surfaces, their surface chemical properties can be modified via a variety of methods. For example, boron doping endowed the carbon host with a positively polarized surface and allowed chemisorption of sulfur and lithium polysulfides. The resulting sulfur/B-doped carbon cathode delivered a higher initial capacity (1300 mA h g^{−1}) and much improved cyclic stability as compared with the cathode prepared from non-doped porous carbon.⁴³ An electronegative N atom as a popular dopant can be doped into carbon to induce asymmetric charge distribution. Although it does not provide active sites for adsorption of sulfur, nitrogen doping promotes the adsorption of sulfur on oxygenated functional groups, as proved by both experimental data and theoretical calculations.⁴⁴ Most recently, Geng *et al.* created the complex of polythiophene and polysulfide molecules using Fe in a macroporous conjugated polymer structure.⁴⁷ Electrochemical characterization demonstrated that formation of the complex not only reduces the polarization and enhances the specific capacity but also improves the cycling stability of the

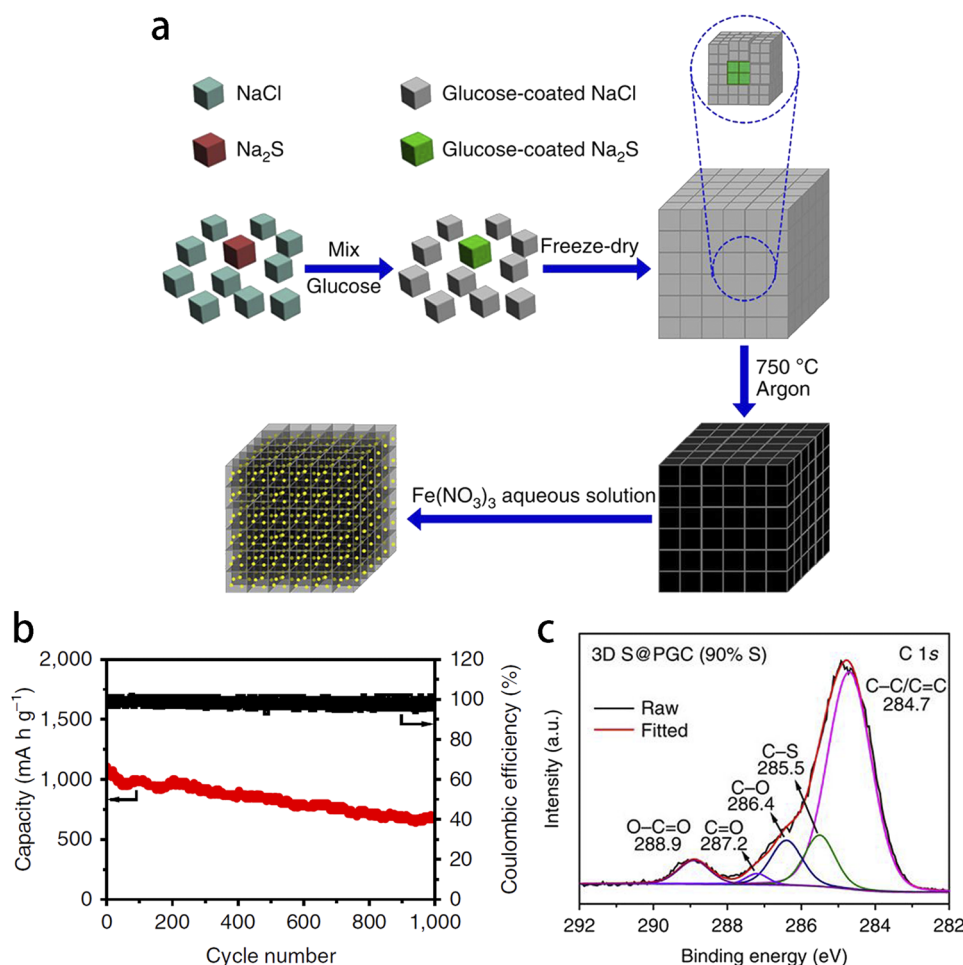


FIG. 3. (a) Schematic illustration of *in situ* synthesis of sulfur nanoparticles via oxidation of Na₂S by Fe(NO₃)₃ for the preparation of the 3D S@PGC composite. (b) Cycling performance of the 3D S@PGC cathode over 1000 cycles at a charge/discharge rate of 2 C. (c) C 1s XPS spectrum of the 3D S@PGC (90% S) composite. Reproduced with permission from Li *et al.*, Nat. Commun. 7, 10601 (2016). Copyright 2016 Springer Nature.

Li–S batteries prepared using the aforementioned structure as the cathode framework for hosting sulfur.

Covalent bonds between the host materials and sulfur/lithium polysulfides have been intensively investigated during the past years. Unlike the physical interactions such as van der Waals forces, the covalent bonds can firmly hold the soluble lithium polysulfides within the cathode and the shuttle effect can be effectively eliminated. So far, the elements that have been utilized to form covalent bonds with sulfur include C, O, Ti, Mn, etc. For example, Geng *et al.* recently proposed a facile strategy for *in situ* synthesis of sulfur nanoparticles via oxidation of Na_2S by $\text{Fe}(\text{NO}_3)_3$ in 3D porous graphitic carbon (3D S@PGC) [Fig. 3(a)].¹³ The *in situ* strategy for synthesis of sulfur resulted in the formation of C–S covalent bonds due to the addition of various reactive intermediates to the unsaturated C=C of the PGC as well as the nucleophilic attack of transient negatively charged polysulfides with residual oxygen-containing functional groups present in the PGC. In addition, the sulfur content of the composite could be tuned up to 90% and the loaded sulfur showed a high utilization rate (82.5% at 0.5 C). As a result, the Li–S batteries prepared using 3D S@PGC as the cathode exhibited high specific capacities (1382, 1242, and 1115 mA h g^{-1} at 0.5, 1, and 2 C, respectively) and long cycling life (small capacity decay of 0.039% per cycle over 1000 cycles at 2 C) [Fig. 3(b)]. Such excellent cycling stability of 3D S@PGC was attributed to the presence of C–S covalent bonds between the sulfur nanoparticles and PGC.¹³ The presence of C–S bonds was confirmed by X-ray photoelectron spectroscopy (XPS), and Fourier-transform infrared spectroscopy [Fig. 3(c)]. During charging/discharging processes, the covalent bonding between sulfur nanoparticles and the PGC framework played an important role in effectively preventing the loss of active materials, suppressing the shuttle effect, and stabilizing the cycling life of the corresponding Li–S batteries. More recently, Geng *et al.* covalently immobilized nanoscale sulfur particles onto the surfaces of unzipped multiwalled carbon nanotubes (UMWNTs) via ball milling of sulfur and UMWNTs (S@UMWNTs).⁴⁸ The radicals generated upon mechanically induced scission of the weak S–S bonds react with the C=C bonds and/or the oxygen-containing functional groups on the UMWNTs, leading to the formation of C–S bonds. As a result, the Li–S batteries prepared using S@UMWNTs as the cathode material exhibit improved electrochemical performance, especially the long-term cycling stability (e.g., a small capacity decay of 0.09% per cycle was achieved over 500 cycles at 1 C).

Graphene oxide (GO) has abundant oxygen-containing functional groups which have been demonstrated to exhibit exceptional ability for trapping lithium polysulfides. The formation of O–S bonds in the GO/S composites was confirmed by the XPS and K edge X-ray absorption spectroscopy.^{32,34} The interactions between S_3^{2-} (or S_3^-) and reduced GO (RGO) were verified by first-principle calculations, and charge transfer between lithium polysulfides and graphene was also observed.¹⁸ However, presence of the abundant oxygen-containing functional groups may reduce the electrical conductivity of the resulting composites.⁴⁹

Therefore, it is required to optimize the quantity of oxygen-containing functional groups to balance the anchoring of lithium polysulfides and reservation of the high electrical conductivity of the resulting composites.²⁸ Instead of using GO as starting materials, graphene can also be directly functionalized with organic molecules by electrochemical or mechanical methods.^{50–54} The direct functionalization of graphene not only preserves its high electrical conductivity but also offers functionalities for trapping lithium polysulfides.^{51,55}

Metals (e.g., Cu and Co) and metal oxides (e.g., MnO_2 and TiO_2) incorporated into the carbon can also be used for trapping lithium polysulfides via chemical interactions.^{6,14,17,19,25,27,31,33} Metal-organic framework (MOF)-derived metal/carbon composites are good examples to elucidate the function of metal–sulfur bonds in immobilization of lithium polysulfides.⁵⁶ Co-doped graphitic carbon and Ni-doped graphitic carbon prepared from ZIF-67 have been demonstrated as an excellent host for immobilizing lithium polysulfides due to the chemical interactions between the doped metals and lithium polysulfides.^{19,45,56} Metal oxides, which can provide more binding sites and exhibit stronger adsorption of lithium polysulfides, were also used to

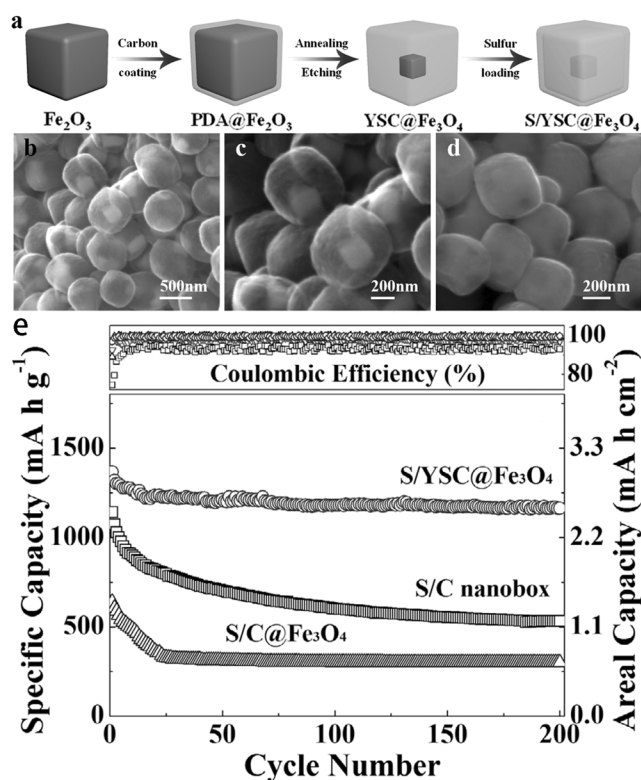


FIG. 4. (a) Schematic illustration of the synthesis of the S/YSC@ Fe_3O_4 composite. [(b) and (c)] SEM images of YSC@ Fe_3O_4 . (d) An SEM image of S/YSC@ Fe_3O_4 . (e) Cyclic stability of the S/C@ Fe_3O_4 , S/YSC@ Fe_3O_4 , and S/C nanobox cathodes at C/10 rate for 200 cycles. Reproduced with permission from He *et al.*, Adv. Mater. **29**, 1702707 (2017). Copyright 2017 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

chemically trap lithium polysulfides.^{25,57} Most importantly, the discharged products ($\text{Li}_2\text{S}/\text{Li}_2\text{S}_2$) are preferentially deposited on the surface of metal oxides, leading to better cycling stability and improved utilization of sulfur. Nazar *et al.* proposed the use of MnO_2 to trap lithium polysulfides in the cathode via a chemical process.²⁷ In the sulfur/ MnO_2 composite cathode, MnO_2 nanosheets as a host react with initially formed lithium polysulfides to form surface-bound intermediates, which then function as a redox medium to bind higher-ordered lithium polysulfides and convert them to insoluble $\text{Li}_2\text{S}/\text{Li}_2\text{S}_2$. As a result, the Li–S batteries prepared using the sulfur/ MnO_2 composite as the cathode show a superior cycling stability, with a fade rate of only 0.036% per cycle over 2000 cycles.

The goal of synthesizing host materials with rational structures, high conductivity, and strong interactions with

sulfur is to offer the sulfur cathodes high specific capacity, long cycling stability, high Coulombic efficiency, and excellent rate capability. To achieve this goal, the advantages of different materials can be integrated into a dual/multi-functional hybrid for hosting sulfur. For example, yolk-shelled $\text{C}@\text{Fe}_3\text{O}_4$ nanoboxes ($\text{YSC}@\text{Fe}_3\text{O}_4$) were synthesized for hosting sulfur as the cathode of high-performance Li–S batteries [Figs. 4(a)–4(d)].¹⁴ The $\text{C}@\text{Fe}_3\text{O}_4$ nanoboxes remarkably immobilize the lithium polysulfides through the combined effects of the physical trapping by the core-shell structure and the chemical interactions between Fe_3O_4 and lithium polysulfides. The combined effects of the $\text{C}@\text{Fe}_3\text{O}_4$ nanoboxes enable a high sulfur loading (up to 5.5 mg cm^{-2}) in the cathode, along with excellent rate performance, high specific capacity, and long cycling life [Fig. 4(e)]. Another example to integrate the advantages of different materials is a 3D NiS_2 -RGO framework,

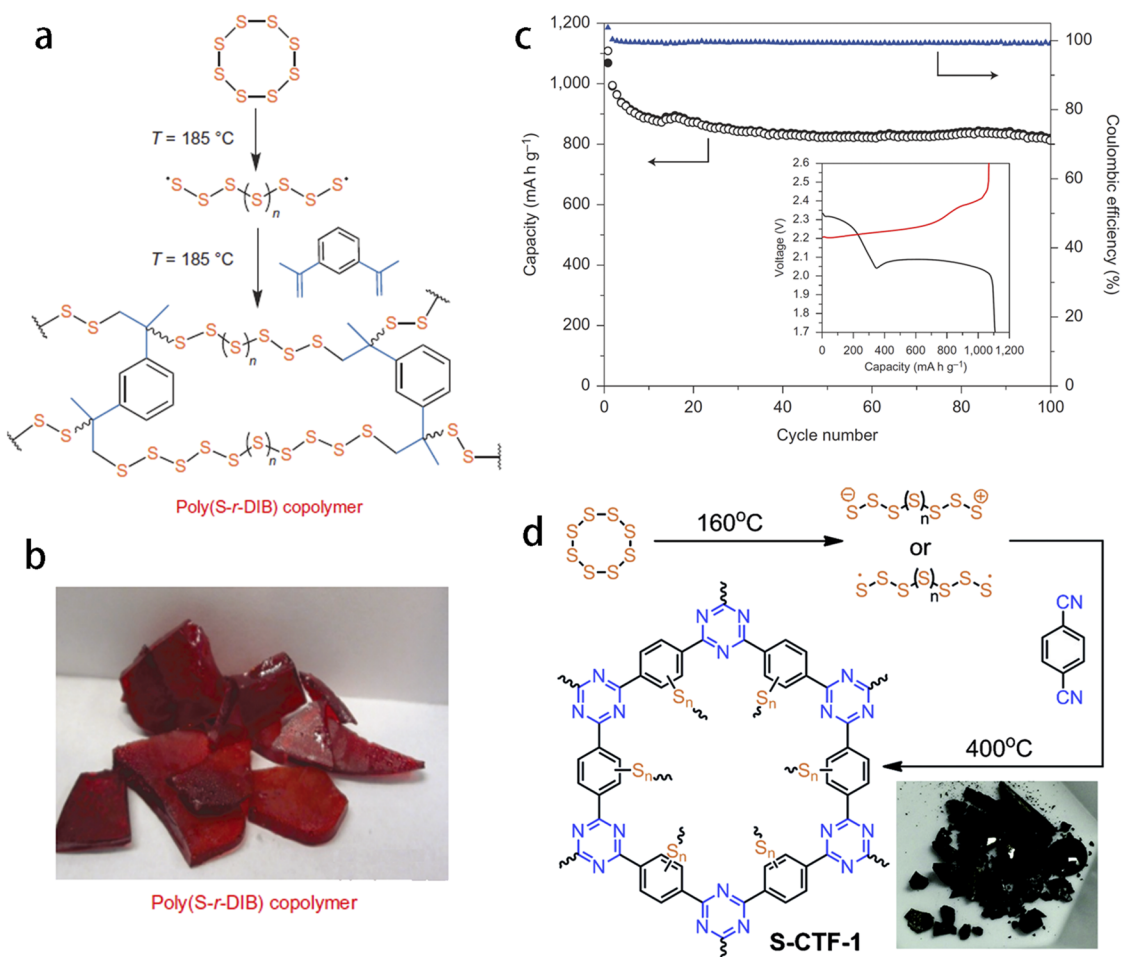


FIG. 5. (a) Schematic illustration of the synthesis of poly(S-r-DIB) via the copolymerization of S_8 and DIB. (b) Optical images of poly(S-r-DIB) having 30 wt. % DIB. (c) Cycling stability of a Li–S cell prepared using poly(S-r-DIB) containing 10 wt. % DIB as the cathode. (d) Synthesis route of S-CTF-1. [(a)–(c)] Reproduced with permission from Chung *et al.*, Nat. Chem. **5**, 518 (2013). Copyright 2013 Springer Nature; (d) Reproduced with permission from Talapaneni *et al.*, Angew. Chem., Int. Ed. **55**, 3106 (2016). Copyright 2016 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

which was reported as a reservoir of lithium polysulfides.⁵⁸ An optimized amount of NiS₂ (18 wt.%) anchored on RGO sheets provides abundant active sites to adsorb lithium polysulfides. In the 3D hybrid frameworks, the conductive RGO framework offers a 3D electron pathway to facilitate charge transfer toward the NiS₂-lithium polysulfide interface, resulting in a fast redox kinetics of lithium polysulfide conversion and excellent rate performance.

Synthesis of sulfur polymers is another strategy for suppressing the shuttle effect of lithium polysulfides. Sulfur polymers can be synthesized by copolymerizing elemental sulfur (i.e., S₈) with an unsaturated monomer. Sulfur chains are chemically bonded to the organic monomers, forming a uniform and highly cross-linked polymer network. The first sulfur polymer was synthesized via the free radical copolymerization of S₈ with 1,3-diisopropenylbenzene by Pyun *et al.* [Figs. 5(a) and 5(b)].²³ The sulfur polymer was designated as poly(S-*r*-DIB) and turned out to exhibit great potential as a cathode material for Li-S batteries [Fig. 5(c)]. However, the electrical and ion conductivities of these polymers are low, leading to low energy and power densities of the resulting batteries.^{10,59} Later, Li ion transport was improved by the synthesis of 3D interconnected porous sulfur polymers.¹² Furthermore, incorporation of sulfur polymers into covalent triazine framework (S-CTF-1) not only firmly binds sulfur with the polymer matrices but also effectively improves the electrical conductivity of the sulfur polymers [Fig. 5(d)].¹⁵

Based on the summary of the achievements on the cathode materials of Li-S batteries, one can undoubtedly conclude that the design of cathode materials plays the decisive role in overcoming the intrinsic drawbacks of sulfur as cathode materials for Li-S batteries. Most of these strategies focus on the following issues: low electrical/Li⁺ conductivity of sulfur and Li₂S/Li₂S₂, the shuttle effect of lithium polysulfides, and volume expansion of sulfur-based electrode materials. Although these issues have been resolved in a certain extent, there are still a number of challenges to overcome before Li-S batteries can be practically used. These challenges may include (1) pursuing high loadings and high utilization rates of sulfur, (2) achieving high specific capacities and high energy densities as close to the theoretical values, (3) obtaining reliable long-term cycling stabilities, and (4) realizing safe operation. To overcome these challenges, which are related to academic issues and/or technical ones, more efforts should be enforced to develop new materials, to design novel structures, to investigate the underlying mechanisms, and to solve the technical problems. We hope that this perspective would inspire people to explore new cathode materials to achieve the goal of fabricating high-performance Li-S batteries.

This work was supported by the “National High Level Talents Special Support Plan” of China, the National Natural Science Foundation of China (No. 51773211), Beijing Advanced Innovation Center for Soft Matter Science and Engineering, and Beijing Municipal Science and Technology Commission.

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