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Review

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Recent advances in carbon-based sulfur host materials for lithium-sulfur batteries

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Abstract

Lithium-sulfur batteries (LSBs) have been brought into focus as the development direction of the next-generation power battery system due to their high energy density, eco-friendliness, and low cost, which has a broad application prospect in the field of energy storage. However, some problems are still unresolved in the sulfur cathode, e.g., poor electric conductivity, serious volume expansion of sulfur, shuttle effect caused by easy dissolution of lithium polysulfides in the electrolyte, and slow redox reaction kinetics of sulfur species. These issues lead to poor cycle stability and rate performance, making it hard to meet the requirement for LSBs in practical applications. Since the inherent nature of sulfur is the root cause of the above problems, reasonable design of functional sulfur hosts will be an effective way to break through the current bottlenecks of LSBs. The review covers the latest research progress on carbon-based sulfur host materials of LSBs, including structural design and functional optimization strategies, aiming to prepare multifunctional sulfur host materials by integrating physical confinement, chemical adsorption, and catalytic effect towards lithium polysulfides. The obstacles and future prospects of carbon-based sulfur hosts have also been brought forward, which provides in-depth guidance for practical application of LSBs.

Keywords: Carbon-based nanomaterials, sulfur host materials, functional modification, lithium-sulfur batteries

INTRODUCTION

The development of efficient, safe, and environmentally friendly energy storage systems is an enabler to improve the energy structure and promote low-carbon development and can effectively solve the contradiction between the continuity of energy demand and the discontinuity of renewable energy supply[1,2]. Among various energy storage systems, lithium-ion batteries (LIBs) consisting of $LiCoO_2$ cathodes and graphite anodes were successfully commercialized in 1991[3]. Due to their high discharge specific capacity, lightweight, long life, and high safety, LIBs have been widely used in energy applications, such as portable electronic devices, electric vehicles (EVs), and hybrid EVs (HEVs)[4,5]. However, with the further growth of energy demand, LIBs based on graphite anodes (theoretical specific capacity of 372 mA h g^{-1}) and transition metal oxide cathodes can no longer meet the demand for high-energy-density storage systems[6,7]. Therefore, it is urgent to develop new next-generation secondary batteries with the advantages of higher energy density, low cost, and environment friendliness[8].

Among the current energy storage systems, lithium-sulfur batteries (LSBs) consisting of sulfur cathodes and lithium metal anodes are attracting attention and developing very rapidly[9,10]. Unlike the intercalation and de-intercalation mechanism of Li^+ in conventional LIBs, the energy conversion mechanism of LSBs is a reaction of $S_8 + 16Li \rightarrow 8Li_2S$. Due to high theoretical energy density (2,600 Wh kg^{-1}) and specific capacity of sulfur cathodes (1,675 mAh g^{-1}), LSBs are considered as one of the directions for next-generation power battery systems[11,12]. Additionally, low toxicity and abundant resources of sulfur are very attractive in terms of mass production and sustainable development. If LSBs can be successfully commercialized, a battery pack with an actual energy density of 400-600 Wh kg^{-1} can significantly improve the cruising ability and effectively alleviate the problem of "mileage anxiety" of EVs[13,14].

In this review, as shown in Figure 1, a comprehensive overview of the latest research progress on carbon-based sulfur host materials of LSBs is provided, aiming to prepare multifunctional sulfur host materials by integrating physical confinement, chemical adsorption, and catalytic effect towards lithium polysulfides (LiPSs). The review mainly includes four aspects: (1) The latest development status and the reaction mechanism of LSBs; (2) Remaining problems of sulfur cathodes hindering the development of LSBs; (3) The research progress of carbon-based sulfur host materials in improving the electrochemical performance of LSBs; and (4) The future development direction of carbon-based sulfur host materials for LSBs. This review aims to inspire future research and development of innovative sulfur host materials by providing clear and concise information to ultimately achieve efficient sulfur cathodes.

Mechanism and challenges of LSBs

The configuration and operating mechanism of LSBs

LSBs are a class of secondary batteries that use the breaking and generation of sulfur-sulfur bonds to achieve the mutual conversion of chemical and electrical energy by applying sulfur or sulfur-containing compounds as the cathode and lithium or lithium-containing materials as the anode[15]. The structure of LSBs is schematically shown in Figure 2A, which mainly consists of four parts: a sulfur cathode, separators, electrolytes, and lithium metal anodes[16]. Among them, the sulfur cathode is usually composed of elemental sulfur (S_8), conductive carbon, and binders. For the typical "solid-liquid-solid" reaction mechanism of LSBs, ether-based electrolytes are usually used because the carbonate-based electrolyte will nucleophilically react with LiPS[17,18]. The formation of LiPS can be avoided by changing the "solid-liquid-solid" to a "solid-solid" reaction mechanism, thus making carbonate electrolytes possible[19,20].

A typical charge/discharge curve of an LSB in an ether electrolyte is shown in Figure 2B. During the discharge process, two voltage plateaus are typically observed, 2.1-2.4 and 1.6-2.1 V, respectively. In general, the first plateau is 2.1-2.4 V, corresponding to the conversion of S_8 to soluble Li_2S_x ($6 \leq x \leq 8$), which provides a specific capacity of 419 mA h g^{-1}, which accounts for 25% of theoretical capacity. The second

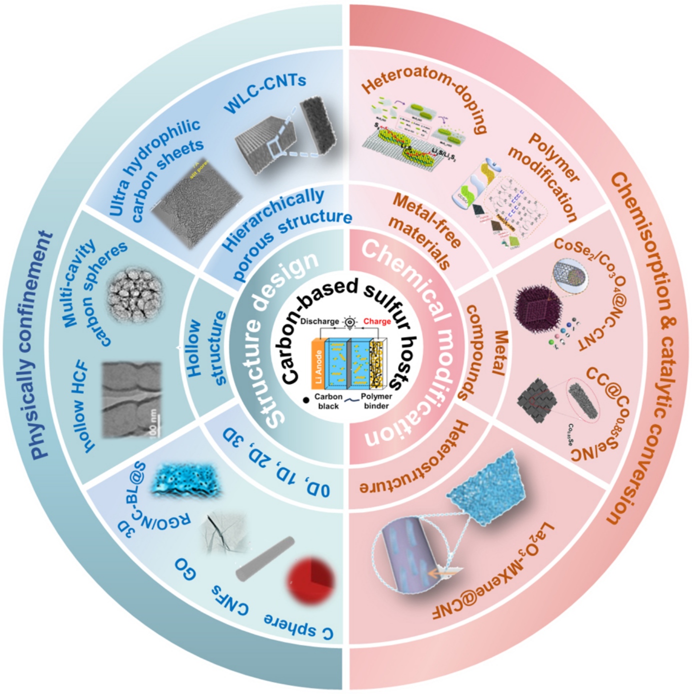

Figure 1. Schematic diagram of carbon-based sulfur host materials for LSBs.

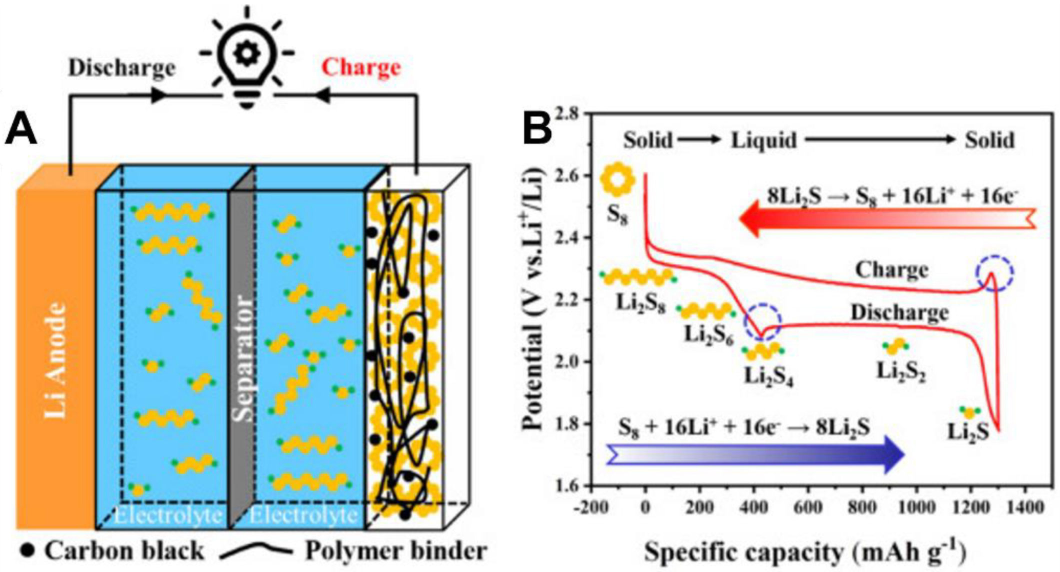

Figure 2. (A) Schematic diagram and (B) charge-discharge curves of LSBs[16]. Copyright Elsevier 2020.

plateau occurs at 1.6~2.1 V, mainly corresponding to the transformation of Li_2S_x to short-chain Li_2S_4 and insoluble Li_2S_2/Li_2S, providing a specific capacity of about 1,256 mA h g^{-1}, which accounts for 75% of theoretical capacity[21]. During the charging process, insoluble Li_2S/Li_2S_2 is transformed into LiPSs and eventually converted to elemental sulfur[22]. Recently, Zhou *et al*. observed directly the transformation of LiPSs on the electrode surface at the atomic scale by using *in situ* liquid-cell electrochemical transmission electron microscopy[23]. The introduction of surficial active centers of metal nanoclusters induces LiPSs aggregation and charge storage, resulting in a transient transition from LiPSs enriched phase to non-equilibrium Li_2S nanocrystals. This reaction pathway reveals a new transformation mechanism, which is different from the traditional electrochemical reaction in which LiPSs are gradually converted to Li_2S_2 and Li_2S, which depends on the basic understanding of LSBs[23].

Main problems of sulfur cathodes for LSBs

The insulation and volume expansion of sulfur

Due to the different densities of sulfur and Li_2S (2.07 and 1.66 g cm^{-3}, respectively), the conversion from S_8 to Li_2S leads to a huge volume expansion of sulfur cathodes (~80%), which will inevitably pulverize the electrode after long cycles. In addition, electrically insulating sulfur has a low conductivity of about 5×10^{-30} S cm^{-1} at room temperature[24]. The electronic and ionic conductivity of Li_2S is also low, about 10^{-13} and 10^{-9} S cm^{-1}, respectively. Under high sulfur loading conditions, the actual capacity of LSBs decreases sharply due to low sulfur utilization and poor cycling stability. The incomplete conversion of solid/liquid phase products tends to accumulate excessively at the anode interface, leading to uncontrollable polarization of the electrode[25].

Shuttle effect

LiPS is an intermediate product formed by the reduction reaction of sulfur and has a high solubility in ether electrolytes[26]. It can act as an activator that can promote sulfur redox kinetics and contribute to forming a uniform dispersion of sulfur in the cathode to contact ions and electrons[27]. However, the good mobility of LiPS makes it irreversibly dissolve into the electrolyte and diffuse to the negative electrode due to the concentration gradient, which can be gradually reduced to Li_2S, resulting in a loss of active material. Dissolved LiPS can be further reoxidized to sulfur after the charging process. This free migration of LiPS back and forth in the electrolyte between the cathode and anode is called “shuttle effect”[28]. The shuttle effect causes the loss of sulfur easily, which mainly accounts for a capacity drop of LSBs. During the charging process, some migrated Li_2S will shuttle back to the cathode and redeposited unevenly in the sulfur region, which seriously affects the performance of LSBs[29].

Sluggish kinetics of sulfur conversion

Solid S_8 is converted to soluble long-chain LiPS and subsequently to solid Li_2S at the end of the discharge process. Then, unconverted Li_2S in the anode results in a lower discharge plateau and a higher overpotential, increasing the impedance of electron and ion transport[30]. After cycles, the reduction of sulfur species decreases the effective capacity and energy density of LSBs. Therefore, sulfur conversion kinetics will affect the overall performance of LSBs[31].

Advancements in carbon-based sulfur host materials for LSBs

Currently, reasonable design of sulfur hosts has been a primary breakthrough to solve the abovementioned problems. Porous carbon with high electronic conductivity, good mechanical stability, and an adjustable pore structure is an ideal host for loading sulfur[32]. Its porous structure can make sulfur dispersed uniformly, alleviate volume expansion of sulfur, and limit LiPS dissolution through physical confinement. Compared with physical confinement, chemisorption can trap LiPS more efficiently and improve the cycling stability of sulfur cathodes. Furthermore, catalysts can be introduced into sulfur hosts, which can regulate the deposition of Li_2S and accelerate LiPS redox kinetics as well, thus improving the electrochemical performance of LSBs[33]. Therefore, a design of multifunctional sulfur hosts to enhance the adsorption and sulfur redox kinetics by the triple synergistic effects of physical confinement, chemical adsorption, and catalytic conversion is expected to be an efficient strategy to break through existing bottlenecks of sulfur cathodes in LSBs[34].

Due to the poor conductivity of sulfur, it is difficult to directly obtain electrons from the external circuit, so sulfur needs to be combined with conductive materials to improve the conductivity of sulfur cathodes[35]. Porous carbon spheres with mesoporous/microporous structures are widely used as sulfur hosts due to their protective structural integrity. Thereinto, the porous carbon shell can prevent the outward diffusion of LiPS through the physical barrier, while the larger space inside can improve the sulfur loading and relieve the volume expansion of sulfur. In addition, multistage pores are also conducive to accelerating ion transport and limiting LiPS dissolution[36]. However, due to the weak physical force between the non-polar surface of carbon and polar LiPS, the shuttle effect is hard to inhibit. Therefore, by modifying non-polar carbon, S_8 and Li_2S can be evenly distributed on the surface of carbon through chemisorption and catalysis to ensure strong electric contact and relieve shuttle effect of LiPS[37]. Heteroatom-doping carbon materials, e.g., B, N, O, and S, can adsorb and enrich LiPS at the electrochemical interface through chemical bonding, enhancing the reaction kinetics[38]. Some transition metal compounds, including transition metal sulfides, nitride, and oxides, have strong interaction with LiPS, contributing to catalyzing the conversion of LiPS into Li_2S, which reduces LiPS accumulation in the electrolyte and alleviates shuttle effect[39,40]. When designing a functional sulfur host, multiple functions, such as physical confinement, chemisorption, and catalytic conversion, should be taken into consideration comprehensively to enhance the performance of LSBs[41].

Physically confined materials

Porous carbon has high electronic conductivity, good mechanical stability, and an adjustable pore structure, so it is an ideal host for sulfur loading. The stability of the sulfur cathode is improved mainly through physical confinement. In recent years, researchers have devoted themselves to developing nano-carbon materials with different morphologies and structures as sulfur hosts[42]. According to pore size (d), carbon materials can be divided into three types: (1) microporous carbon (d < 2 nm); (2) mesoporous carbon ($2 \leq d \leq 50$ nm); and (3) macroporous carbon (d > 50 nm)[43]. Rational structural design and surface modification of carbon materials as sulfur hosts are important means to improve the electrochemical performance of LSBs. Hierarchically porous carbon materials (HPC) containing microporous, mesoporous or macroporous structures are endowed with high S_{BET} and large V_{total}, which can achieve full utilization of active sulfur. On the one hand, conductive carbon materials can facilitate electron transport and improve sulfur utilization and reaction kinetics. On the other hand, micropores and small mesopores in HPC can provide high surface area for full contact of sulfur and carbon and offer abundant LiPS adsorption sites. Macromesopores and macropores can serve as containers for buffering volume changes of sulfur and as transport channels for Li^+. In addition, a hierarchically porous structure with outer micropores and inner mesoporous or large pores is reasonably designed, in which the outer micropores can block the dissolution of LiPS, and the inner mesoporous or large pores can increase the sulfur loading. Therefore, rationally designing the structure of HPC as sulfur hosts can effectively enhance sulfur utilization and electrochemical performance of LSBs. Ji *et al.* first proposed the mesoporous carbon (CMK-3) for sulfur loading[44], which not only provides rich storage space for sulfur and alleviates volume expansion of sulfur but also restricts LiPS dissolution by mesoporous structure, improving the stability of sulfur cathode. When the sulfur loading was 70 wt.%, CMK-3-S electrodes could remain at 800 mA h g^{-1} after 20 cycles at 0.1 C. The electrochemical performance of some physically confined materials as sulfur hosts for LSBs has been listed in Table 1.

According to their dimensions, carbon materials can be divided into zero-dimensional (0D), one-dimensional (1D), two-dimensional (2D), and three-dimensional (3D) structures. In the context of dimensionality, 0D usually refers to materials with all sizes in the nanoscale range, such as carbon nanospheres, quantum dots, fullerenes (C_{60}), *etc.*, which belong to the 0D structure. Hollow carbon spheres (HCSs) are regarded as ideal hosts for loading sulfur due to their unique structural characteristics of the large inner cavity and abundant outer porous shell. The carbon cavity inside can efficiently load sulfur to

Table 1. Summary of electrochemical performance of physically confined materials for LSBs

Sulfur hosts	S_{BET} (m^2 g^{-1})	V_{total} (cm^3 g^{-1})	Sulfur content (wt.%)	Sulfur loading (mg cm^{-2})	Initial capacity (mAh g^{-1})	Current density (C)	Cycles	Last capacity	Rate capacity	Refs.
CMK-3	1,976	2.1	70	/	1,000	0.1	20	800	/	[44]
MCC-8	761	1.33	71	1.5	1,143	0.5	200	869	943 (2 C)	[47]
C_{60}-S	/	/	75	4.0	1,121	0.2	350	691	530 (2 C)	[49]
NF@VG	760	/	70.1	7.0	738	1.0	600	609	783 (3 C)	[51]
3DRGO/NC-BL	/	/	57.1	/	920	0.5	500	~600	634 (5 C)	[56]
HCF/CNT	/	/	/	7.3	~1,100	0.2	60	945	876 (0.5 C)	[57]
WLC-CNTs	130.4	/	79	17.3	862	0.2	300	547	840 (0.5 C)	[58]

achieve high sulfur content, and the carbon shell can improve the conductivity of sulfur cathodes and prevent LiPS dissolution[45]. However, the size of sulfur particles in the single cavity is relatively large, and the sulfur in the central part cannot be well-exploited because gaining and losing electrons far from the carbon wall is difficult[46]. Meanwhile, the volume expansion of large sulfur particles will cause a breakage of HCS in the charging and discharging process, resulting in capacity decline and cycle deterioration. As shown in Figure 3A, Zhang *et al.* developed a surface energy-driven self-assembly method for the preparation of multi-cavity carbon nanospheres (MCC)[47]. The secondary structural units were spontaneously assembled to form multi-cavity aggregates with low surface energy. The internal large cavity of MCC is divided into many small cavities connected by porous carbon walls. The volume, connection, number, and size of the cavity can be adjustable. Thereinto, the size of the cavity can be further increased by employing "nanospace confined pyrolysis". When the MCC serves as the sulfur host, the sulfur content is up to 71 wt.%. A small cavity can reduce the size of sulfur particles, thus relieving volume expansion of sulfur cathodes. The interconnected carbon network improves sulfur utilization, which is conducive to the adsorption of LiPS produced in the charging-discharging process, thus improving the cyclic stability of MCC@S cathodes. The prepared MCC@S electrode can maintain a capacity of 869 mA h g^{-1} after 200 cycles at 0.5 C and reach a capacity of 943 mA h g^{-1} at 2 C. The cycle performance was significantly improved compared to the single cavity carbon sphere (with a low capacity of 636 mA h g^{-1} after 100 cycles at 0.5 C). The results show that MCC has high efficiency in sulfur fixation and utilization. Liu *et al.* prepared ZCO-QDs@HCS-S cathodes by *in situ* growing $ZnCo_2O_4$ quantum dots (ZCO-QDs) on HCS[48]. Thereinto, mesoporous HCS can improve the overall conductivity and sulfur loading of the cathode and facilitate the penetration of electrolytes and Li^+ diffusion. The sulfur electrode has excellent cycle stability, with a capacity decay rate of 0.057% after 1,000 cycles at 3 C. Xiang *et al.* reported a novel C_{60}-S supramolecular complex as the cathode for LSBs, in which 100% of C_{60} molecules provide active sites for the LiPS adsorption and promote LiPS conversion owing to the eutectic structure[49]. In addition, the lithiated C_{60} helps to accelerate the Li^+ transport in the sulfur cathode and improve the electrochemical performance in the lean electrolyte. When the electrolyte/sulfur (E/S) ratio is 5 μL mg^{-1} and sulfur loading is 4 mg cm^{-2}, the specific capacity of C_{60}-S electrodes is 606 mA h g^{-1} (2.4 mA h cm^{-2}) after 100 cycles at 0.2 C.

Carbon nanotubes (CNTs) and carbon nanofibers (CNFs), as 1D nanomaterials, have a high length-diameter ratio and good electrical conductivity, which are conducive to the construction of the conductive network in the electrode and the improvement of electronic conductivity of sulfur cathodes. Meanwhile, CNTs and CNFs are often taken as sulfur host materials due to their high mechanical strength, reducing the

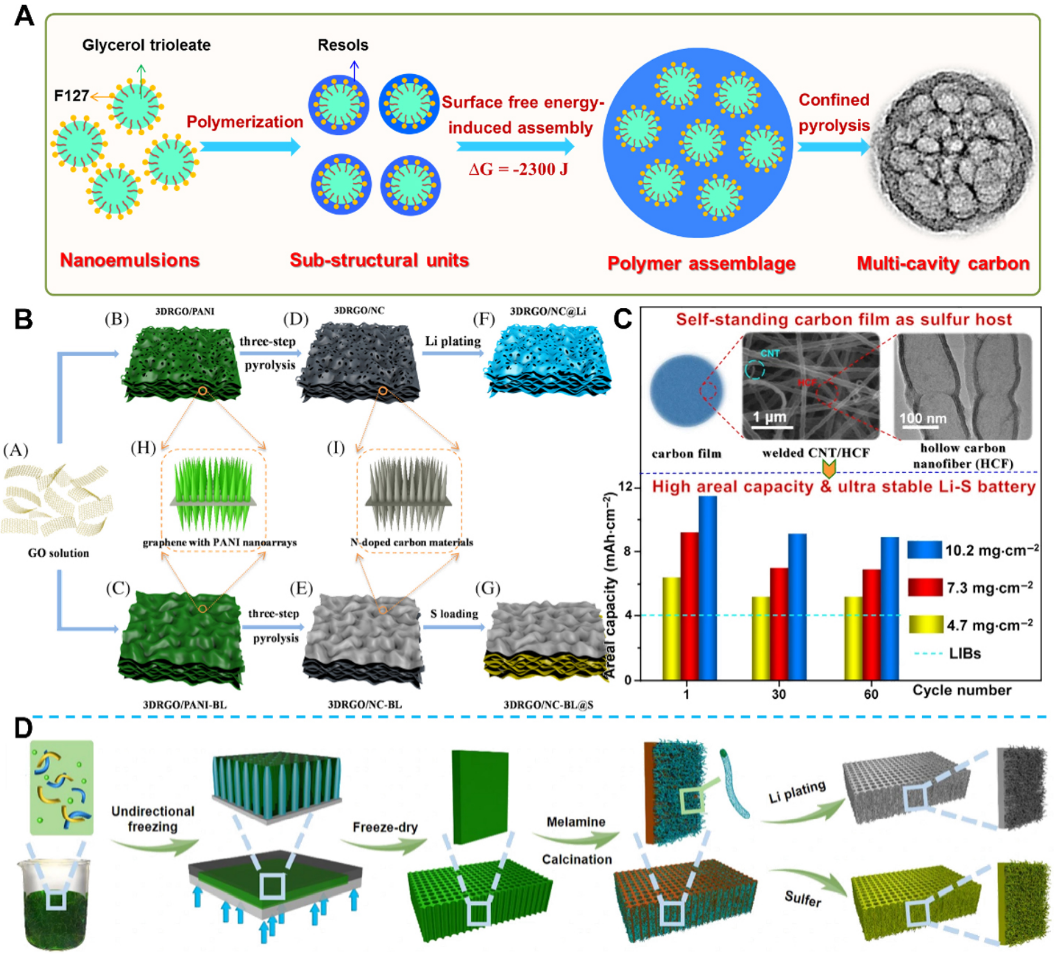

Figure 3. Illustration for the synthesis: (A) multi-cavity carbon spheres[47], Copyright John Wiley and Sons 2017. (B) 3DRGO/NC-BL@S cathode[56] Copyright John Wiley and Sons 2020. (C) CNT/HCF film[57], Copyright Springer Nature 2020 and (D) S@WLC-CNTs cathode[58]. Copyright Springer Nature 2021.

volume expansion of sulfur effectively. Fu *et al.* studied the electrochemical reaction of Li and S in narrow-diameter single-walled CNTs (SWNTs)[50]. The results show that the electrochemical performance can be significantly adjusted by changing the diameter of SWNTs and the size of solvated Li^+. The average diameter of HiPco-SWNTs is 1.0 nm prepared by the high-pressure carbon monoxide method, which is smaller than the size of solvated Li^+. Therefore, the Li reacts with S limited in HiPco-SWNTs through solid phase reaction, thus improving the electrochemical reaction activity. Lin *et al.* prepared a nitrogen-doped porous carbon fiber/vertical graphene (NF@VG) composite as a sulfur host[51]. The porous structure and nitrogen doping effectively enhance the adsorption effect for LiPS through physical limitation and chemisorption, while the VG network greatly promotes electron transfer and speeds up the LiPS conversion kinetics. Under the conditions of high sulfur loading (13 mg cm^{-2}), high sulfur content (81.6 wt.%), and low E/S (4.8 μL mg^{-1}), the areal capacity of the LSB is 11.2 mA h cm^{-2}, indicating that NF@VG sulfur hosts deliver excellent electrochemical performance. Graphene, as the representative 2D material, has been extensively investigated in the field of energy storage due to its high conductivity and large S_{BET}[52]. Researchers have proposed a vast array of strategies to decorate graphene to raise the ability to bind LiPS. A new type of sulfur electrode was prepared, in which the sulfur is sandwiched between two graphene membranes, with one side of that acting as a current collector and the other as a sandwich[53]. This lightweight and sandwich-like structure not only speeds up electron transport but also reduces volume expansion of sulfur, alleviating shuttle effect and increasing the energy density of LSBs.

When 3D porous carbon served as a sulfur host, the performance of sulfur cathodes can be enhanced owing to the advantages of mesoporous and microporous structures[54,55]. Therefore, a self-standing 3D hierarchical graphene host modified with N-doped nanoarrays (3DRGO/NC-BL) was constructed [Figure 3B][56]. Due to high conductivity, strong affinity, and optimized Li^+ transport path, 3DRGO/NC-BL can effectively promote the uniform Li^+ deposition and sulfur conversion. In particular, the extra graphene layer can effectively inhibit shuttle effect of sulfur cathodes. Therefore, the S cathode shows a high specific capacity and ultrahigh capacity retention. More importantly, an integrated LSB exhibits long-cycle stability and good flexibility. When the sulfur loading is high, shuttle effect is more serious and S_8/Li_2S deposition will not be uniform, which aggravates the capacity attenuation of the battery.

How to develop high sulfur loading and areal capacity is of great significance for the construction of high energy density LSBs. He *et al*. prepared a self-standing carbon film (HCF/CNT) in which CNTs and N, O co-doped hollow carbon fibers (HCF) are "welded" with each other by a chemical vapor deposition method [Figure 3C][57]. The HCF/CNT-S film shows a high areal capacity and cycling stability. When the sulfur loading is 10.2 $mg{\cdot}cm^{-2}$, the areal specific capacity is 8.9 mAh cm^{-2} after 60 cycles at 0.2 C. The HCF/CNT film shows that the contact resistance of CNTs and HCF is reduced by welding together through the carbon layer, which can significantly improve the conductivity of the carbon film and sulfur utilization. Meanwhile, the cavity of HCF can encapsulate a large amount of sulfur and realize high sulfur loading. N and O doping can enhance LiPS adsorption and improve the cyclic stability of the sulfur cathode. In addition, CNTs and HCF are interwoven into large pores, which can provide a channel for rapid electrolyte transfer. This study puts forward an original idea on construction of high-areal-capacity sulfur hosts. The traditional electrode with high areal specific capacity is prepared by casting slurry on the current collector. However, due to the large shrinkage of slurry in the drying process, the active electrode material will fracture and crack, resulting in poor mechanical stability. The binder is an electrical insulation that blocks the path of electrons and reduces the conductivity of the electrode, especially for thick electrodes.

Additionally, the increase in electrode thickness leads to the deteriorative charge transfer kinetics. As shown in Figure 3D, a wood-like carbon with a forest of CNTs (S@WLC-CNTs) is prepared by an ice template method and catalytic tip growth method as the skeleton in the sulfur cathode, which has high electrical conductivity and strong wood structural characteristics[58]. This unique S@WLC-CNTs electrode has microchannels of low curvature that reduce charge diffusion paths of ions and electrons, allow the electrolyte to move freely within the electrode, and mitigate volume changes of sulfur cathodes. In addition, electron-rich CNT forest can effectively capture soluble LiPS through non-polar interactions and catalyze the redox kinetics of LiPS conversion in the electrode.

Chemisorption and catalytic conversion materials

Since the sulfur cathode of LSBs is difficult to meet the demand of practical application, the primary breakthrough to solve the above problems is to design the sulfur host materials reasonably[59]. Compared to physical limiting effect, chemisorption can anchor LiPS more effectively and enhance cycle stability of sulfur cathodes. Then, a variety of catalytic catalysts have been introduced into sulfur hosts, which can regulate Li_2S deposition and accelerate LiPS transformation. Accelerated sulfur redox kinetics and Li^+ diffusion can reduce the internal resistance and improve the electrochemical performance of LSBs. For this purpose, a multifunctional sulfur host material should be designed with the triple coordination of physical confinement, chemisorption and catalytic conversion, enhancing the adsorption and catalytic conversion of

LiPS and improving sulfur utilization. The chemisorption materials are used to firmly trap the LiPS, and then the catalytic material is used to speed up the LiPS conversion, to achieve a stable "trap-diffusion-catalytic conversion" process of LiPS on the surface of the electrode, and finally obtain LSBs with long-period and high rate performance. Therefore, chemisorption and catalytic conversion materials composed of highly efficient adsorption materials and highly catalytic active ingredients need to be constructed.

Metal-free materials

(1) Heteroatom-doping carbon

According to surface chemistry, carbon materials can be divided into heteroatom-doping and functional groups. For non-polar carbon, heteroatom-doping can be a straightforward method to achieve surface functionalization of carbon materials. Heteroatom-doped porous carbon has a high specific surface area, which makes the sulfur disperse evenly[60]. The porous structure restricts the LiPS dissolution by physical confinement[61]. The heteroatoms can act as anchoring sites to chemically adsorb LiPS, which is conducive to the preparation of high-performance sulfur cathode materials[62]. Graphene oxide (GO) can be considered as an oxygen-doped graphene due to a large number of oxygen-containing groups, e.g., epoxide and -OH groups. This oxygen-doping graphene shows high affinity with LiPS, thus effectively inhibiting LiPS diffusion[63]. However, excessive oxygen functional groups can impair the high conductivity of carbon materials. GO is prone to partial reduction at high temperatures to form reduced GO (rGO), which has high conductivity and residual oxygen groups, offering sites for LiPS adsorption[64]. An all-graphene electrode formed by a graphene current collector with high conductivity and partial GO was proposed, showing good cyclic stability even under high sulfur loading, where GO as a polar component to inhibit LiPS dissolution[65].

Nitrogen-doping graphene can be conductive skeletons and LiPS adsorbents as well. Song *et al*. synthesized graphene sheets with large S_{BET} and abundant N-containing groups (NG)[66]. Transmission electron microscope (TEM) images of NG are shown in Figure 4A. This NG-S electrode provided a high areal specific capacity of 5 mA h cm^{-2} when the sulfur loading reached 5 mg cm^{-2}, demonstrating good cyclic stability. Nitrogen-doping carbon nanospheres (NCSs) as sulfur hosts have been synthesized with a sulfur loading of 5 mg cm^{-2}[67]. In addition, NCSs have polar sites, which can form Li-N bonds with LiPS and combine with the micropore restriction effect to further enhance the adsorption towards LiPS, thus achieving good cyclic stability. The electrochemical performance of some chemisorption and catalytic conversion materials as sulfur hosts for LSBs has been summarized in Table 2.

To learn the interaction between LiPS and heteroatomic doping sites, ^7Li nuclear magnetic resonance (NMR) spectra have been conducted, combined with Density Functional Theory (DFT) calculations and experimental data[68]. It was found that pyridine N composed of lone pair electrons has a strong interaction with Li^+.

Xu *et al*. used P_2O_5 as a sacrificial template to synthesize phosphorus and oxygen-doping porous carbon sheets[69]. Phosphorus-doping porous carbon has been prepared by heating phosphorous compounds reduced by carbon at high temperatures. The X-ray photoelectron spectroscopy (XPS) spectra of P-doping carbon changed before and after the Li_2S_6 adsorption, indicating the strong binding effect with LiPS. Therefore, P-doping carbon as a sulfur host delivers relatively stable cycling performance with an average capacity decay of 0.025% after 1,000 cycles at 1 C.

Table 2. Summary of electrochemical performance of chemisorption and catalytic conversion materials for LSBs

Sulfur hosts	Sulfur content (wt.%)	Sulfur loading (mg cm^{-2})	Initial capacity (mAh g^{-1})	Current density (C)	Cycles	Last capacity	Rate capacity	Refs.
NG	90	1.5	1,082	0.5	200	833	950 (1 C)	[66]
UHCS	/	/	930	0.5	200	675	630 (2 C)	[70]
CC/poly(Li_2S_6-r-DIB)	43	/	1,200	2 A g^{-1}	120	934	727 (2 A g^{-1})	[82]
CNG	50	/	1,280	/	280	700	/	[89]
$CoSe_2/Co_3O_4$@NC-CNT	~ 75	2.0	780	1.0	500	602	688 (5 C)	[102]
CC@$Co_{0.85}Se$/NC	/	1.0	953	1.0	400	799	/	[107]
Co_9S_8/C	77	1.5	1,020	0.5	200	790	810 (3 C)	[108]
MoS_{2-X}/rGO	75	1.5	~1,251	0.5	600	628.2	690 (3 C)	[110]
MoP/GO	73	1.0	~739	1.0	11,566	597	656 (2 C)	[115]
TiO_2-TiN	80	1.2	~790	1.0	2,000	704	682 (2 C)	[125]
La_2O_3-MXene@CNF	75.24	1.0	992.6	0.2	400	846	747.7 (3 C)	[128]

Besides the introduction of external heteroatomic precursors, heteroatom-doping carbon materials can also be prepared by using a precursor composed of heteroatomic groups. Metal-organic frameworks (MOF) containing organic ligands and rich functional groups can serve as precursors for the synthesis of heteroatom-doping carbon skeletons. That helps the carbon skeleton achieve heteroatomic self-doping through an easy step. As shown in Figure 4B, Hao *et al*. prepared ultra-hydrophilic carbon nanosheets (UHCS) by a thermal stripping MOF precursor (4,4′-bipyridine copper)[70]. The MOF is a 2D layered structure that interacts with other molecules through π-π bonds. Several merits of carbon nanosheets prepared by using the exfoliated MOF are listed: (1) UHCS are composed of centrally distributed micropores (~0.7 nm); (2) There are abundant functional groups in a MOF precursor. After carbonization at 500 and 900 °C, the heteroatom-doping content of UHCS is as high as 30 and 24 at.%, respectively. Therefore, the surface of carbon nanosheets is polar and highly hydrophilic. As a sulfur host, it provides abundant polar sites for LiPS adsorption so that the sulfur cathode has a stable cycling performance. To solve the poor conversion kinetics of sulfur species and Li^+ transport, Liu designed a bridging structure of the MOF-carbon interface to achieve catalytic acceleration of Li^+ desolvation and sulfur conversion processes[71]. At the interface conferring ion-electron double conductance, the active C-N bridging bonds in the MOF@CC structure serve as the adsorption and catalytic sites, which reduces the binding effect between solvent molecules and Li^+ and enables the highly active Li^+ that are free from the solvent shell to conduct to the site more quickly, and the electron exchange reaction occurs when they contact with LiPS. Based on the designed MOF@CC separator, the LSB delivers excellent reversibility (0.5 C, 1,063 mA h g^{-1}) and rate performance (5 C, 765 mA h g^{-1}).

(2) Polymers modified carbon

Functional groups that provide additional lone pair electrons can coordinate with Li^+, resulting in interacting strongly with LiPS[72]. Therefore, the combination of carbon-based materials and functional groups can exert their superiorities to enhance cycle performance of the sulfur electrode[73,74]. Polymers, such

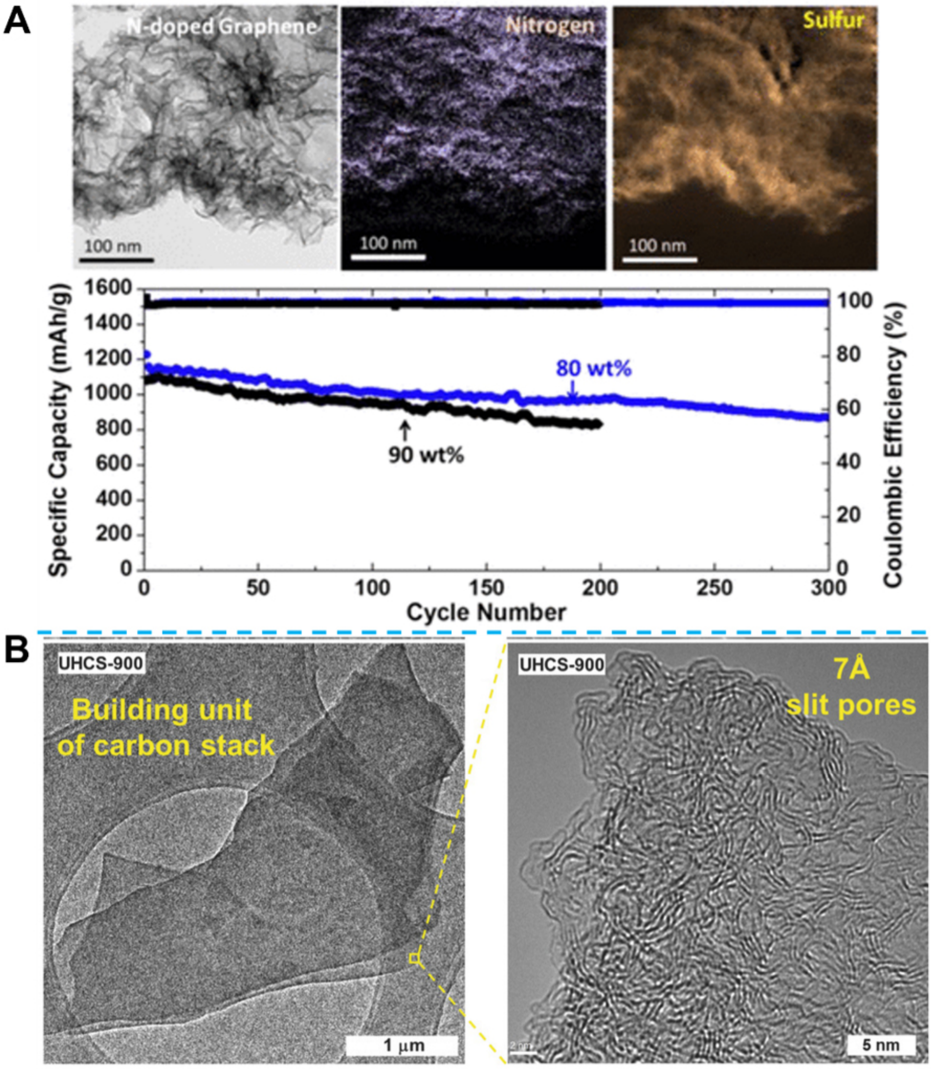

Figure 4. (A) TEM images and cycle performance of nitrogen-doped graphene/sulfur[66]. Copyright American Chemical Society 2016. (B) TEM images of ultra hydrophilic carbon sheets[70]. Copyright John Wiley and Sons 2017.

as polyvinylpyrrolidone (PVP)[75], polyimide (PI)[76], poly (3,4-vinyldioxythiophene) (PEDOT)[77] and polyaniline (PAN)[78], some of which have good electronic conductivity and positively charged amino groups, can attract negatively charged polysulfide anions through static electricity[79]. Therefore, it can be directly applied or modified as a sulfur host to improve the cyclic stability of the sulfur electrode. The PAN-coated S-C cathode (a sulfur content of 73 wt.%) was prepared [Figure 5A][80]. After cycling 2,500 times at 5 C, the capacity decay is as low as 0.01%, which shows good cycle stability. PAN is commonly taken as a coating for sulfur due to the abundance of nitrogen-containing groups on the skeleton. To improve the chemisorption effect, Chen *et al*. grafted phytic acid (PA) containing P onto the -NH- group on the main chain of PAN to prepare N and P rich in quinone imide ($-NH^+=/-N=$) polymer [Figure 5B][81] Quinone imide-doped GO was prepared by coating the polymer on GO as a sulfur host, which can adsorb Li_2S_8 and speed up sulfur redox reaction. When the sulfur loading is 3.3 mg cm^{-2}, the areal specific capacity is 3.72 mAh cm^{-2}.

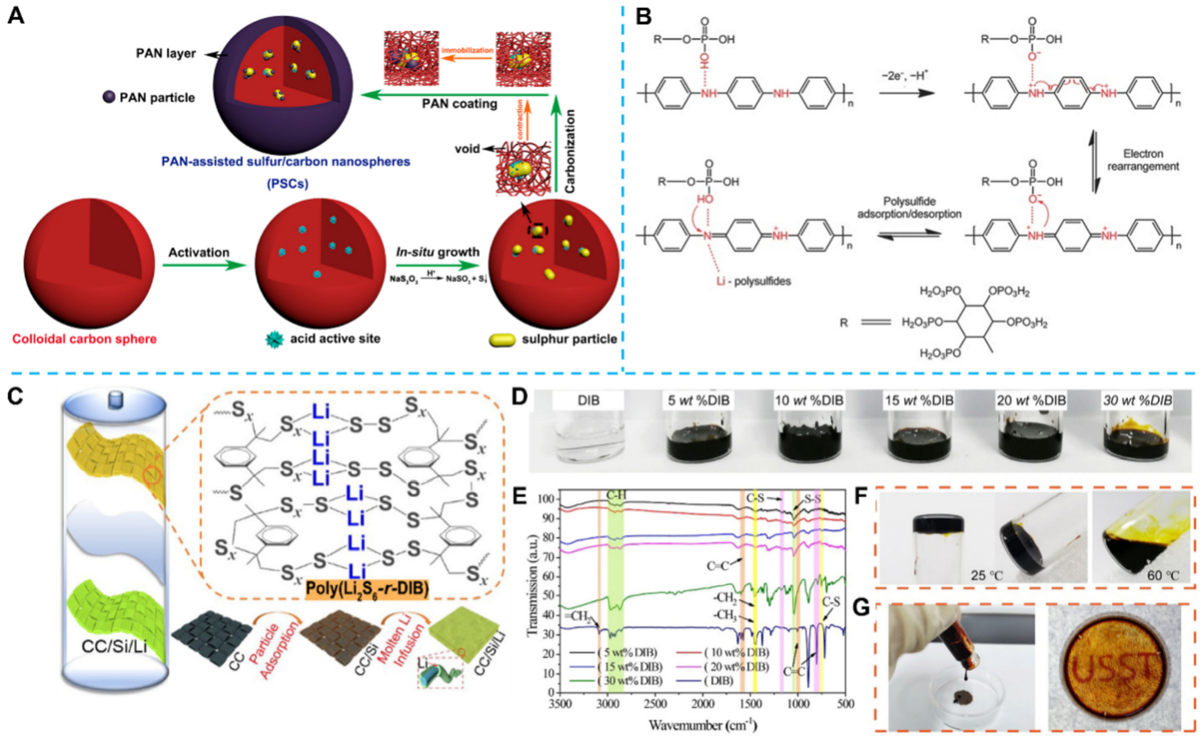

Figure 5. (A) Schematic of synthetic procedure for PAN-assisted S/C nanospheres[80]. Copyright American Chemical Society 2015. (B) Schematic illustrating the stabilization and enrichment of quinonoid imines by PA[81]. Copyright John Wiley and Sons 2017. (C) Synthetic schematics of the Li-rich sulfur-incorporated polymeric cathodes, (D) digital photographs, (E) IR absorption characterization of the poly(Li_2S_6-r-DIB) copolymers, (F) digital images of poly(Li_2S_6-r-10 wt.% DIB) before and after tilting the vial at room temperature and 60 °C, and (G) digital images of poly(Li_2S_6-r-10 wt.% DIB) transparent films cast in a glass dish[82]. Copyright American Chemical Society 2021.

It is essential to construct a hierarchical channel structure with high pore volume to store sulfur and introduce strong polar segments and catalytic sites to promote the catalytic conversion of LiPS. A copolymer poly (Li_2S_6-r-DIB) was prepared by covalent polymerization of Li_2S_6 to 1,3-diisopropenylbenzene (DIB), as shown in Figure 5C-G[82]. The LiPS dissolution was effectively inhibited by reinforcing the chemical restriction of Li_2S_6 by a conjugated polymer framework. During the discharging-charging process, π electron in poly (Li_2S_6-r-DIB) promotes rapid electron migration, and the extra Li^+ compensates for Li loss and promotes the redox kinetics of Li^+, which improves the sulfur utilization and Coulombic efficiency of the battery. In addition, by using the thermoplastic properties, poly (Li_2S_6-r-DIB) is directly coated on the flexible conductive carbon cloth to prepare a flexible sulfur electrode. The gap space of the carbon cloth is conducive to buffering the volume expansion of sulfur to obtain stable long-term cycling performance. On this basis, the flexible LSB was assembled by matching the modified carbon cloth/Si/Li flexible anode, which showed stable electrochemical performance under different folding conditions.

A semi-fixed molecular catalyst was designed, in which porphyrins were covalently grafted on conductive and flexible polymer chains as the active sites so that they had both homogeneous and heterogeneous catalytic functions[83]. Semi-fixed molecular catalysts play a key part in accelerating electrochemical reaction and regulating deposition behavior of reactants in heterogeneous reactions. Meanwhile, the actual energy density of the 1.5 Ah soft pack battery can reach 343 Wh kg^{-1}.

(3) Other metal-free materials

According to literature reports, many non-metallic materials (silicene, phosphorene, 2D borides, nitrogen carbide, boron nitride[84], and other low-dimensional materials) have catalytic activity mediated by p orbitals[85], which can be used as electrocatalysts to promote the conversion of soluble LiPS to insoluble Li_2S[86]. Phosphorene is a thin nanosheet similar to graphene[87], in which each P atom combines with three adjacent atoms to form a wrinkled honeycomb structure. As shown in Figure 6A-D, Li *et al*. prepared a few layers of phosphorene (FLP) nanosheets loaded on carbon fibers (FLP-CNF) as a sulfur host and Li_2S_6 as an active substance[88]. Due to high conductivity (450 S m^{-1}) and strong affinity for LiPS, FLP can be an effective electrocatalyst and LiPS adsorbent to reduce the electrochemical polarization, accelerate the redox reaction between sulfur species, and further improve the cycle stability of the battery. As shown in Figure 6E-H, proton-type carbon nitride (p-C_3N_4) has a layered structure and abundant nitrogen atoms, which has been confirmed to have a strong affinity for LiPS[89]. p-C_3N_4 can overcome the redox barrier effectively by changing the molecular structure of LiPS. In addition, p-C_3N_4 can reduce the electrochemical impedance of the electrode and promote the kinetics of LiPS conversion. Therefore, a p-C_3N_4/graphene (CNG)-S electrode exhibits better electrochemical performance compared to pure graphene.

Metal-based materials

(1) Metal

Compared with non-metallic materials, metal-based materials have higher electronic conductivity. They not only have a stronger chemisorption effect on LiPS but also serve as catalysts to accelerate redox reaction of LiPS[90,91]. A unique multifunctional double-layer carbon structure with micron-scale physical limitation is proposed; that is, metal Co and CNTs constitute a fluffy porous inner carbon skeleton, which can accelerate electron transport and provide sufficient space for LiPS conversion[92]. The outer carbon is composed of a micron-thick graphene nanoflower layer (GF), which efficiently limits the diffusion of soluble LiPS, playing an important role in physically inhibiting the shuttle effect. Meanwhile, metal Co serves as a chemical adsorption site and an electrocatalyst, which can chemically trap LiPS and accelerate LiPS transformation[93]. After 200 cycles at 2 C, the capacity of Co/CNT@GF-S electrodes remains at 799 mAh g^{-1}. Under a sulfur loading of 8.1 mg cm^{-2}, the battery can deliver an areal capacity of 5.0 mAh cm^{-2} after 100 cycles at 0.1 C. The result shows that the electrochemical performance of the Co/CNT@GF-S cathode is greatly improved through the synergistic effect of the porous carbon structure with the chemisorption and catalytic activity of metal Co.

(2) Metal oxides

Due to the presence of oxygen ions, metal oxides have strong polar surfaces[94]. Therefore, owing to abundant polar active sites, metal oxides have strong chemisorption on LiPS, which greatly promotes the sulfur redox reaction[95]. Different morphologies of titanium dioxide (TiO_2), such as nanospheres, nanotubes, and nanosheets, can prevent the diffusion of LiPS through chemisorption. Early, TiO_2 shells were taken to suppress the volume expansion of sulfur[96]. A TiO_2 layer is a coating on the sulfur core to form a yolk-shell structure so that it can maintain a complete shell structure during the process inhibiting the volume expansion of sulfur. In the sulfur electrode, the combination of carbon and TiO_2 contributes to accelerating charge transfer kinetics. Moreover, a TiO_2 atomic layer was deposited on the NG-S electrode to prepare a TiO_2/NG-S electrode[97]. TiO_2 has strong chemical adsorption towards LiPS, which slows down the shuttle effect of LiPS and significantly improves the performance of LSBs. The initial specific capacity of the TiO_2/NG-S electrode reached about 1,069 mA h g^{-1} at 1 C and maintained 919 mA h g^{-1} after 500 cycles.

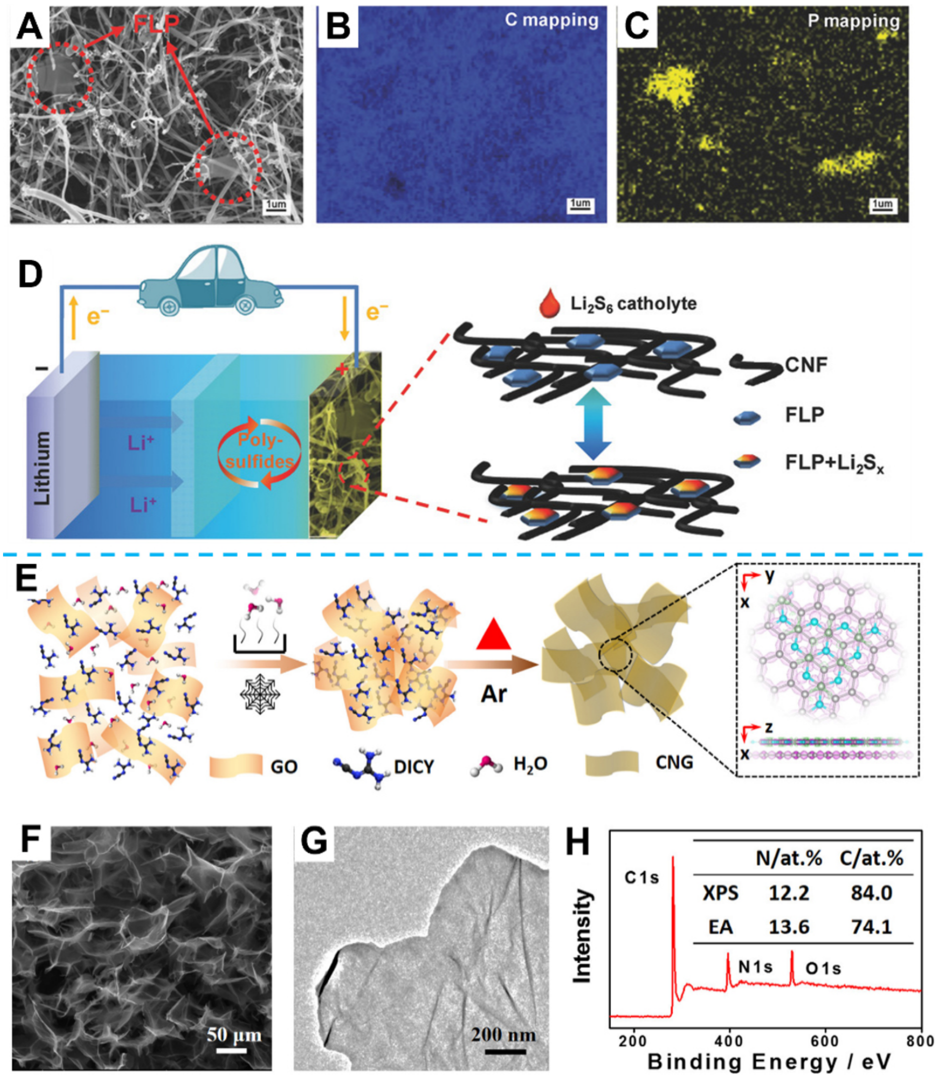

Figure 6. (A-D) Morphology and schematic of FLP-CNF electrode[88]. Copyright John Wiley and Sons 2017. (E-H) Illustration of synthesis, SEM, TEM images and XPS survey of CNG[89]. Copyright American Chemical Society 2016.

Fang *et al*. prepared TiO_2 sandwiched between HCSs (C@TiO_2@C) as a sulfur host[98]. The TiO_2 layer anchors the LiPS through chemisorption, while the double-layer carbon shell provides electron transport paths and acts as a physical blocking in space to limit LiPS dissolution. Additionally, a hollow structure mitigates the volume expansion of sulfur during the lithiation process. When the sulfur content is 76.4 wt.%, a C@TiO_2@C-S electrode exhibits a specific capacity of over 1,200 mA h g^{-1} at 0.2 C.

MnO_2 has strong adsorption towards LiPS, but the conductivity of the S-MnO_2 electrode is low. Rehman *et al*. wrapped MnO_2 nanosheets with hollow carbon nanoboxes (HCB)[99], capturing LiPS mainly through physical limitation and chemisorption. MnO_2@HCB/S electrodes deliver a capacity of 1,042 mA h g^{-1} at 1 A g^{-1}. The advantages of MnO_2@HCB as a sulfur host are as follows: (1) MnO_2 nanosheets in HCB have strong chemisorption towards LiPS; (2) HCB can guarantee high sulfur loading, reduce volume expansion of sulfur, and physically limit LiPS dissolution; and (3) Hierarchical porous carbon layers are beneficial to accelerate electrochemical charge transfer kinetics. In addition, a MnO_2 adsorption mechanism for LiPS was proposed. That is, MnO_2 can oxidize LiPS *in situ* to produce thiosulfate, and the resultant LiPSs are absorbed by thiosulfate and converted into polysulfate complex, mediating the LiPS conversion. Therefore, the polysulfate complex has an important effect on the adsorption and transformation of LiPS.

Co_3O_4 nanoparticles could improve the affinity towards LiPS[100]. Zhou *et al.* prepared Co_3O_4/C bivalve nanocages using ZIF-67 as a template and dopamine as a carbon source[101]. The prepared S@Co_3O_4/C electrode has a low capacity decay of 0.083% after 500 cycles at 1 C, which is mainly attributed to: (1) The highly conductive carbon shell not only speeds up the charge transfer kinetics but also physically restricts the diffusion of LiPS; and (2) The inner Co_3O_4 nanoparticles has strong chemisorption for LiPS.

It is still a challenge to design electrodes with high conductivity, high capacity, and strong affinity for LiPSs to meet the requirements of LSBs with high S content and long-term cycle stability. Three-phase interface heterostructures ($CoSe_2$/Co_3O_4@NC-CNT) with high S_{BET}, chemical adsorption capacity, and high catalytic activity were designed by a coaxial self-template growth and selenization [Figure 7A][102]. The $CoSe_2$/Co_3O_4@NC-CNT electrode can achieve high S loading and attenuate LiPS shuttle, showing a specific capacity of 688 mA h g^{-1} (5 C) and high stability (a capacity retention of 77.2% after 500 cycles at 2 C). It is of great significance to design a multifunctional material with high porosity, multiple active sites, high catalytic efficiency, and strong chemisorption.

(3) Metal sulfides/selenides

For metal sulfides, metal ions and S_2^{2-} give metal atoms high valence electron density, thus generating binding sites for non-intrinsic adsorbents[103]. In addition, the soft base S_2^{2-} is highly polarizable, thus giving the metal sulfides high conductivity. Therefore, the metal sulfides can reduce the decomposition barrier and enhance the redox reaction kinetics of LiPS by chemisorption[104]. By observing the color changes of Li_2S_6 and 1,2-dimethoxyethane (DME) solution and the DFT calculation, it can be verified that the adsorption ability for Li_2S_6 by metal sulfides is strongly linked to the kinds of metal ions. To study the adsorption behavior of Li_2S_6 on surfaces of metal sulfides, Ni_3S_2, SnS_2, FeS, CoS_2, VS_2, and TiS_2 were added to Li_2S_6/DME solutions[105]. It was found that the color of solution became lighter or transparent, indicating that metal sulfides had an excellent ability to adsorb LiPS. The color change is correlated to the binding energy of metal sulfides and Li_2S_6, where VS_2 has the strongest interaction with Li_2S_6 (1.04 eV). The specific discharge capacity of VS_2/S cathodes at 2 C is 1,093 mA h g^{-1}, and the capacity decay is 0.07%, which is better than that of other metal sulfides.

Cobalt-based sulfides/selenides are commonly used as sulfur hosts due to their excellent room temperature conductivity (1.36×10^5 S m^{-1} for Co_9S_8, 6.7×10^5 S m^{-1} for CoS_2, and 3.3×10^5 S m^{-1} for Co_3S_4)[106]. As shown in Figure 7B-E, a MOF-derived bi-functional $Co_{0.85}$Se nanoparticle embedded in 2D N-doped carbon nanosheets ($Co_{0.85Se}$/NC) was developed as an efficient sulfur host for LSBs[107]. The interleaved NC grown on carbon fibers can provide accommodation space and reactive sites for LiPSs, which play a role in physical limitation and alleviating volume expansion. Polar $Co_{0.85}$Se nanoparticles modified by NC can form strong chemical bonds with LiPSs and accelerate LiPS conversion kinetics. The specific discharge capacity of the $Co_{0.85}$Se/NC-S electrode reaches a capacity of 1,361, 1,001, and 810 mA h g^{-1} at 0.1, 1, and 3 C, respectively. After 400 cycles at 1 C, the capacity of $Co_{0.85}$Se/NC-S electrodes reaches 799 mA h g^{-1}, and the attenuation is ~0.04% per cycle.

Chen *et al.* synthesized Co_9S_8 nanoparticles embedded in hollow nano polyhedral carbon (Co_9S_8/C) by a template and vulcanization method[108], as shown in Figure 8A. Co_9S_8/C composites have many advantages:

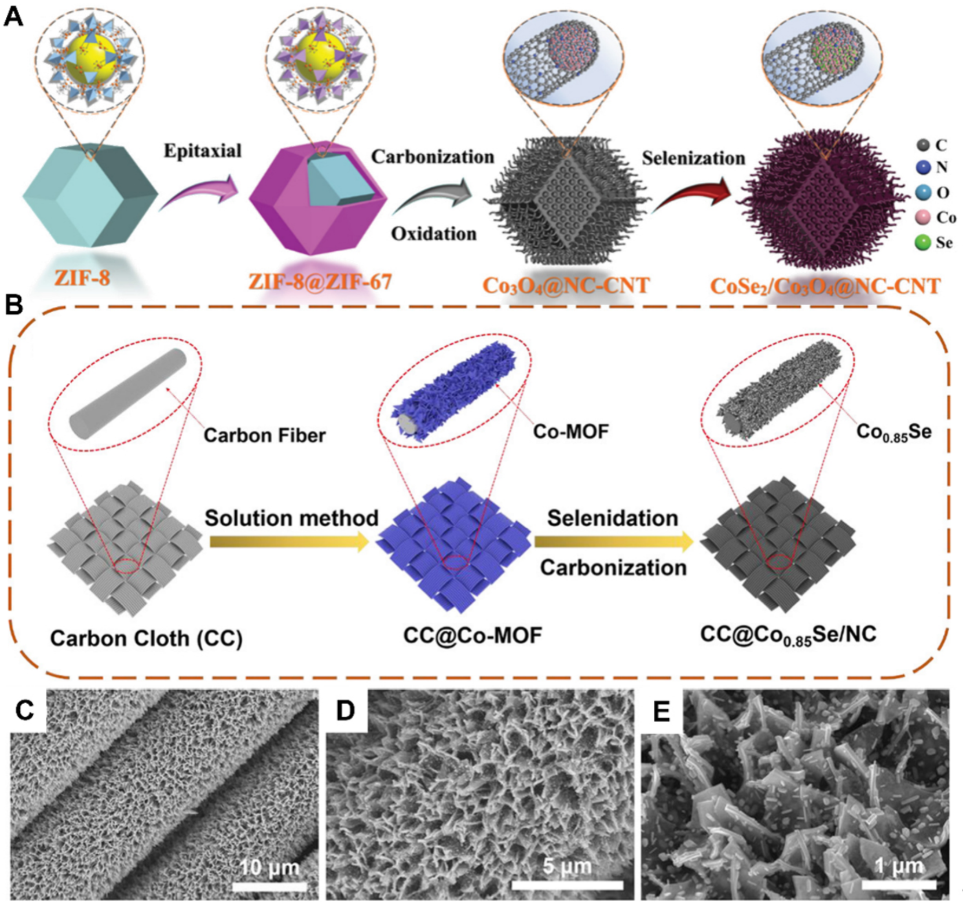

Figure 7. (A) Schematic diagram illustration of the synthesis procedure of the $CoSe_2/Co_3O_4$@NC-CNT heterostructure[102]. Copyright John Wiley and Sons 2022. (B) Schematic illustration of the fabrication process for CC@$Co_{0.85}$Se/NC, and (C-E) SEM images of CC@$Co_{0.85}$Se/NC[107]. Copyright American Chemical Society 2021.

(1) Large internal cavity can contain high content of sulfur, easing the volume expansion of sulfur; (2) The embedded Co_9S_8 nanoparticles can effectively adsorb LiPS and inhibit the shuttle effect; and (3) a 3D conducting network provides a fast electron transfer path. DFT calculation showed that the adsorption energy of Co_9S_8 nanoparticles for different sulfur species ranged from 2.97 to 6.08 eV, indicating that Co_9S_8 nanoparticles had strong chemisorption capacity. The chemical interaction between sulfur and Co_9S_8 is mainly due to the formation of Co-S and Li-S bonds. The specific capacity of the Co_9S_8/C-S electrode was 560 mA h g^{-1} after 1,000 cycles at 2 C.

Molybdenum disulfide (MoS_2) exhibits a 2D layered structure with good electrocatalytic activity[109]. As shown in Figure 8B-E, Lin *et al.* prepared sulfur-rich defective MoS_2 nanosheets modified with rGO (MoS_{2-x}/rGO) as a sulfur host[110]. Due to abundant sulfur defects, MoS_{2-x}/rGO shows a strong affinity towards LiPS and promotes LiPS redox reaction, thus enhancing sulfur utilization. Similarly, You *et al.* prepared a 3D sulfur host (MoS_2/rGO) by combining MoS_2 nanosheets with rGO foam[111]. Hu *et al.* prepared HCS with nanobubbles by using Ni-MOF as a precursor[112]. A layer of MoS_2 nanosheets was then coated on the surface of HCS by a solvothermal method. The results show that the specific capacity of the S/MoS_2@HCS electrode is 1,048 mAh g^{-1} at 0.2 C. Good electrochemical performance of S/MoS_2@HCS electrodes is mainly owing to: (1) Hollow nanobubbles provide enough space for sulfur loading and reduce the volume expansion of sulfur; (2) High conductivity ensures fast electron transmission and improves the sulfur

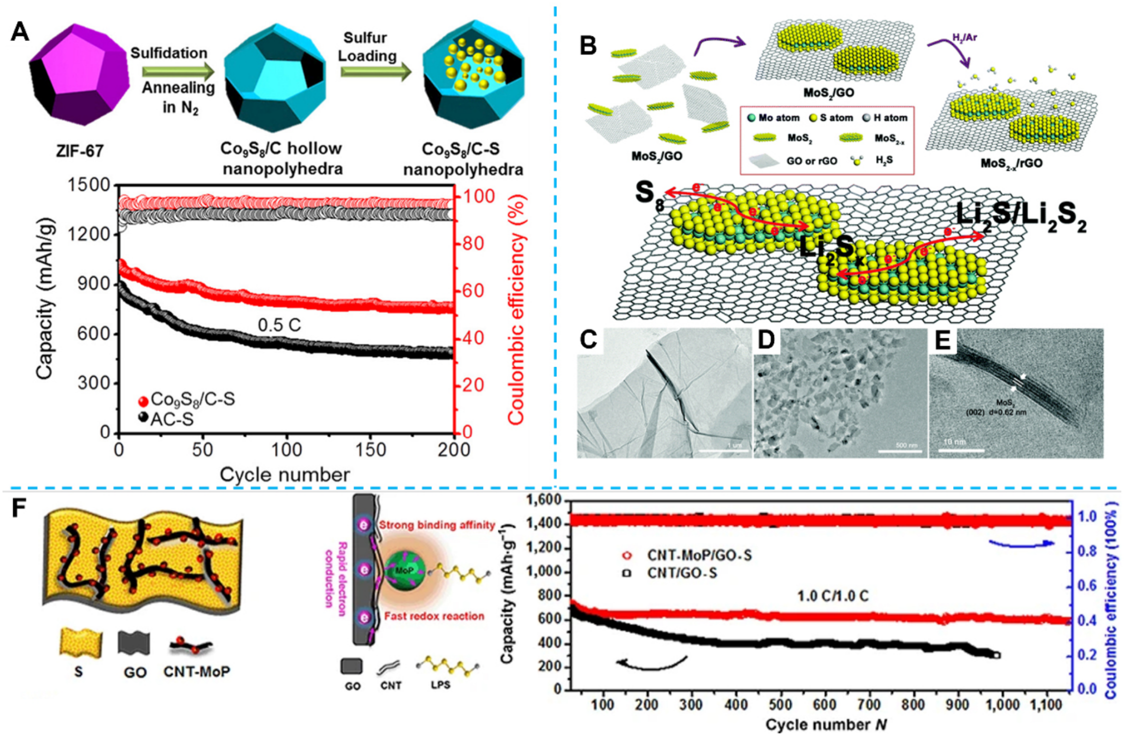

Figure 8. (A) Schematic illustration of the synthesis process and cycle performance of Co_9S_8/C-S nanopolyhedra[108]. Copyright Elsevier 2017. (B) Schematic of the synthesis of the MoS_{2-x}/rGO composite; TEM images of (C) GO and (D and E) MoS_2 nanoflakes[110] Copyright RSC Publishing 2017. (F) Schematic structure and long-term cycle performance of CNT-MoP/GO-S[116]. Copyright Springer Nature 2017.

utilization; (3) MoS_2 nanosheets coated on the surface of HCS effectively limited LiPS diffusion through chemisorption; and (4) MoS_2 nanosheets, as an electrocatalyst, promote the reversible conversion of LiPS to Li_2S.

(4) Metal phosphides

For metal phosphides, because P atoms can obtain electrons from metal atoms and serve as Lewis bases to capture positively charged species, metal phosphides show chemical adsorption towards LiPS and catalytic activity to accelerate LiPS redox reaction[113,114]. Transition metal phosphides possess metallic properties when the atomic ratio of metal to P is appropriate. Therefore, metal phosphides are often taken as LiPS adsorbents and catalysts due to their superior electronic conductivity and strong polarity[115]. MoP nanoparticles decorated on CNTs (CNT-MoP) were taken as a sulfur host[116], as shown in Figure 8F. MoP has a strong chemisorption effect on LiPS, which improves the cycling stability of CNT-MoP-S electrodes. In addition, experimental results showed that the CNT-MoP electrode exhibited higher redox current density and lower charge transfer resistance, indicating that MoP nanoparticles can accelerate the redox kinetics of LiPS conversion. Ye *et al*. prepared CoP nanoparticles embedded in hollow polyhedron/CNT (CoP@HPCN-MWCNT) as sulfur hosts with the following advantages: (1) The hollow polyhedron structure can alleviate the volume expansion of sulfur; (2) Uniformly dispersed CoP nanoparticles can effectively catalyze the LiPS conversion; and (3) Conductive polyhedral carbon shell can promote Li^+ and electron transport[117]. When the sulfur loading is 3.7 mg cm^{-2}, the CoP@HCPN-MWCNT/S electrode delivers a capacity of 729 mA h g^{-1} after 200 cycles. Huang *et al.* synthesized iron phosphide (FeP) nanocrystals as sulfur hosts[118]. It was found that FeP nanocrystals not only show chemisorption towards

LiPS but also can accelerate redox reaction and reduce nucleation barrier of Li_2S. The FeP/rGO/CNTs electrode shows higher redox charge transfer ability, indicating stronger catalytic activity. In brief, FeP nanocrystals as sulfur hosts have two advantages: (1) FeP nanocrystals have chemisorption for LiPS, effectively reducing the shuttle effect of LiPS; (2) FeP nanocrystals act as catalysts in sulfur redox reaction, promoting LiPS conversion. Therefore, the FeP/rGO/CNT-S electrode has good cyclic stability, and the capacity decay is 0.04% after 400 cycles at 1 C.

Other catalytic materials

(1) Single-atom transition metal catalysts

Single-atom (SA) transition metal catalysts have attracted great attention due to their unique quantum size and high-frequency element utilization[119]. In the sulfur cathode, the SA catalyst combines strong chemisorption for LiPS, rapid electron transfer, and improved electrolyte permeability, which promotes LiPS conversion and Li_2S deposition and improves sulfur utilization[120,121]. Du *et al.* studied the electrochemical performance of Co-SAs embedded in N-doped graphene skeleton (Co-N/G) as a sulfur host[122]. When the sulfur loading is 6.0 mg cm^{-2}, the initial specific discharge capacity of the Co-N/G-S electrode is 1,210 mA h g^{-1} at 0.2 C, and the capacity decay is 0.029% after 100 cycles. As Fermi level density increases, Co-N/G exhibits stronger metallic properties, resulting in higher electrical conductivity of 290 S cm^{-1}. In addition, for the rate-controlled step ($Li_2S_2 \rightarrow Li_2S$) in the discharge process, Gibbs free energy of Co-N/G is 0.71 eV, while that of N/G is 1.21 eV, indicating that S is thermodynamically more inclined to occur on the substrate embedded with Co-SAs[123,124].

(2) Heterostructures catalysts

The heterogeneous structure combines the advantages of various electrocatalysts to improve the efficiency of catalysts. TiO_2 has strong adsorption towards LiPS, while its low electron conductivity is not conducive to speeding up LiPS conversion. As a result, LiPS adsorbed on the TiO_2 surface requires a longer diffusion process to reach the conductive substrate and then be reduced, which may limit the overall reaction rate. TiN can promote nucleation and growth of Li_2S, while it shows weak adsorption capacity for LiPS. As shown in Figure 9A, TiN and TiO_2 were combined to form a heterogeneous structure, and LiPS adsorbed on the surface of TiO_2 can be diffused to the surface of TiN to be reduced, thus accelerating the kinetics of LiPS redox reaction[125]. The heterogeneous structure of the TiO_2-TiN electrocatalyst is shown in Figure 9B, which co-exists in the form of large particles. The interface between them not only serves as a highly active site to adsorb LiPS but also provides a fast electron transfer path for LiPS conversion.

As shown in Figure 9C, heterogeneous catalysts (CP-2TiN:8TiO_2 and CP-7TiN:3TiO_2) have a higher capacity of Li_2S deposition than single catalysts (TiN or TiO_2) when Li_2S deposition experiment is conducted. This suggests that electrocatalysts with heterogeneous structures can promote the conversion of LiPS to Li_2S. Similarly, VO_2 shows weak adsorption capacity for LiPS, which can be combined with VN to form a heterostructure (VO_2-VN) to optimize the performance of electrocatalysts[126]. To optimize the energy band of transition metal oxides, Wang *et al.* designed a microcatalytic reactor with Co_3O_4/ZnO heterojunction embedded in polyhedral carbon nanocages (CZO/HNC) to serve as a bi-functional host for S and Li electrodes[127]. The internal electric field between ZnO and Co_3O_4 can promote interfacial charge transfer and reaction kinetics, and CZO/HNC provides sufficient active sites for the adsorption towards LiPSs on the cathode and uniform nucleation of Li^+ on the anode. Therefore, the LSBs exhibit a long lifetime of more than 1,000 cycles, and the capacity decay is as low as 0.05%.

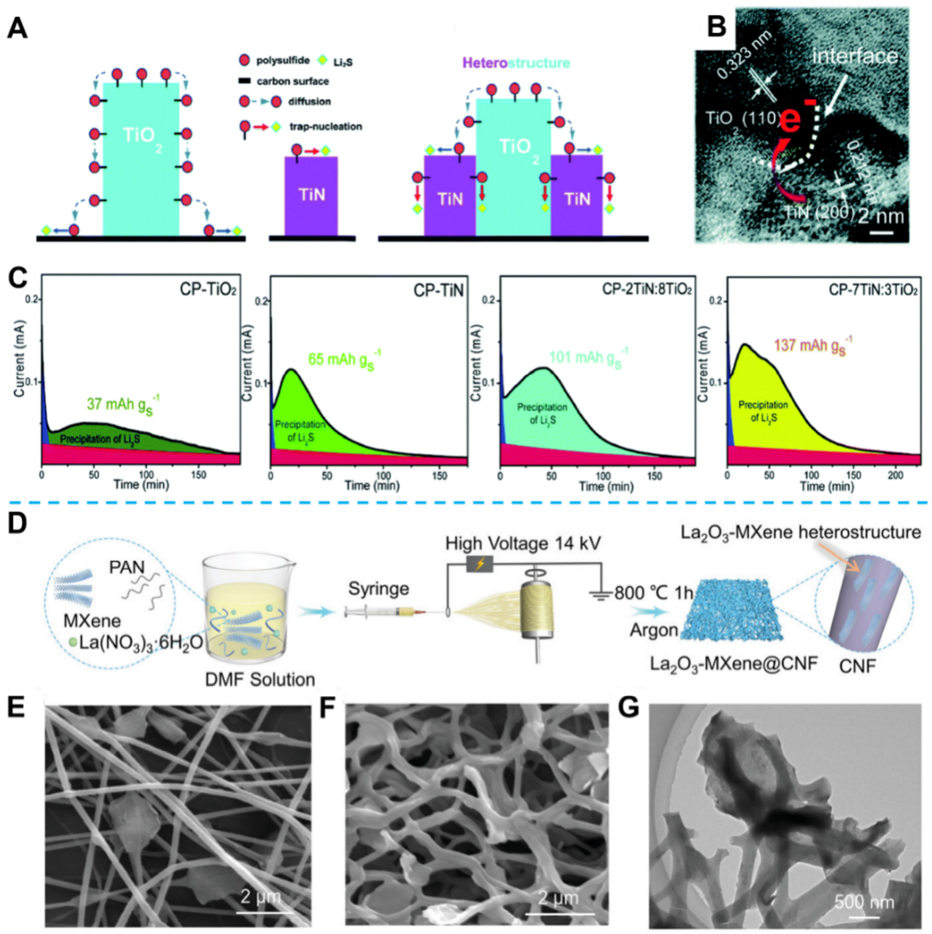

Figure 9. (A) Schematic of LiPS conversion processes, (B) TEM image of TiO_2-TiN structure, and (C) potentiostatic discharge curves at 2.05 V on different surfaces[125]. Copyright RSC Publishing 2017. (D) Schematic illustration for the preparation process, SEM images of the electrospun La_2O_3-MXene nanofibers after (E) spinning and (F) carbonization, and (G) TEM images of La_2O_3-MXene@CNF[128]. Copyright John Wiley and Sons 2023.

A high-efficiency catalytic material (La_2O_3-MXene@CNF) prepared by a simple electrospinning and carbonization process as a multifunctional sulfur host for LSBs was proposed [Figure 9D-G][128]. The multi-dimensional characterizations combined with theoretical calculation show that the unique La_2O_3@MXene heterostructure has many advantages in enhancing adsorption ability and accelerating sulfur redox kinetics. It is indicated that the strong adsorption capacity provided by the La_2O_3 structure can trap dissolved LiPSs for subsequent catalytic conversion, while the insoluble thiosulfate intermediates produced by the hydroxyl terminal group on the surface of MXene greatly promote the conversion of LiPSs to Li_2S. Therefore, La_2O_3-MXene@CNF/S electrodes exhibit excellent electrochemical performance in LSBs.

SUMMARY AND OUTLOOK

In view of the excellent electrical conductivity, stability and structural versatility, the review places emphasis on recent progress of carbon-based sulfur hosts for LSBs. Aimed at the problems such as poor conductivity, large volume change, shuttle effect, *etc*., it is an ideal choice to design carbon-based sulfur hosts with high conductivity, high chemical absorption and high catalytic effect, which needs optimization of the structure and chemical composition of sulfur hosts. The introduction of carbon materials not only improves the conductivity of sulfur hosts, thus improving the sulfur utilization, but also alleviates the LiPS dissolution in the electrolyte, significantly improving the electrochemical performance of LSBs. To prepare the ideal carbon-based sulfur hosts, attention should be paid to considering advantages of structural design and chemical modification. When designing a functional sulfur host, multiple functions, such as physical confinement, chemisorption, and catalytic conversion, should be taken into consideration comprehensively to promote the development of high-specific energy, high-power, and fast-charging LSBs. However, there are still some problems that need to be solved. As one of next-generation directions of power systems, LSBs have several issues worthy of further research, as follows.

(1) The development of carbon materials with highly active catalysts possessing multitudinous advantages, e.g., porous structure, large surface area, self-standing, polarity, and catalytic activity, is relatively independent and complex currently. However, their integrated development is still lacking. Therefore, controlling the relationship between the above three functions of carbon and performance of LSBs is a major focus in the future development. Feasible strategies, such as N, S/O or Co/Fe-N co-doping, integrating heterointerface catalysts, and SA catalysts into porous carbon, can be taken into consideration.

(2) Although catalytic sulfur hosts have made a great breakthrough in facilitating the conversion between sulfur and Li_2S/Li_2S_2, the collaborative relationship between chemical break of the catalyst-induced S-S/Li-S bonds and sustainable active sites and barrier-free mass/electron transfer remains unclear. In addition, the relationship between the catalytic activity of catalysts and adsorption capacity, which is related to the sustainability of catalysis, is still not widely understood. These challenges require quantitative analysis and sound theoretical guidance based on *in-situ* characterization techniques, such as *in-situ* Raman, X-ray diffraction (XRD), TEM, X-ray near edge spectroscopy (XANES), *etc*., and detailed theoretical calculations. More in-depth characterization of the triple functions of carbon can provide insight into its active sites, mechanisms and processes so as to guide practical applications.

(3) Compared with CNTs, graphene, and their derivatives, CNFs exhibit higher mechanical flexibility and stability in electrodes. However, low specific surface area and inherent surface inertness of CNFs lead to their low use weight and high interface curvature in LSB electrodes. The synergistic structure of CNFs and carbon nanomaterials is an effective strategy to provide mechanical stability while improving the sulfur loading and inhibiting the shuttle effect. Therefore, developing carbon-based sulfur hosts with ultra-flexibility, high performance, and breathability, which can be applied in wearable devices, laid the groundwork for further development of flexible LSBs.

DECLARATIONS

Authors' contributions

Conceptualization, investigation, and writing-original draft: Yu XF
Editing: Shao DY
Writing-review & editing, supervision, and funding acquisition: Xu J, Cao J

Availability of data and materials

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Conflicts of interest

All authors declared that there are no conflicts of interest.

Ethical approval and consent to participate

Not applicable.

Consent for publication

Not applicable.

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REFERENCES

1. Winter M, Barnett B, Xu K. Before Li ion batteries. *Chem Rev* 2018;118:11433-56. DOI PubMed
2. Bhargav A, Manthiram A. Li-S batteries, what's next? *Next Energy* 2023;1:100012. DOI
3. Mizushima K, Jones PC, Wiseman PJ, Goodenough JB. Li_xCoO_2 ($0 < x < -1$): a new cathode material for batteries of high energy density. *Mater Res Bull* 1980;15:783-9. DOI
4. Yao YX, Yan C, Zhang Q. Emerging interfacial chemistry of graphite anodes in lithium-ion batteries. *Chem Commun* 2020;56:14570-84. DOI PubMed
5. Wang L, Liu G, Xu R, et al. Enabling an intrinsically safe and high-energy-density 4.5 V-class lithium-ion battery with synergistically incorporated fast ion conductors. *Adv Energy Mater* 2023;13:2203999. DOI
6. Kundu D, Vajargah SH, Wan L, Adams B, Prendergast D, Nazar LF. Aqueous *vs.* nonaqueous Zn-ion batteries: consequences of the desolvation penalty at the interface. *Energy Environ Sci* 2018;11:881-92. DOI
7. Zhao LF, Hu Z, Lai WH, et al. Hard carbon anodes: fundamental understanding and commercial perspectives for Na-ion batteries beyond Li-ion and K-ion counterparts. *Adv Energy Mater* 2021;11:2002704. DOI
8. Bonnick P, Muldoon J. The Dr Jekyll and Mr Hyde of lithium sulfur batteries. *Energy Environ Sci* 2020;13:4808-33. DOI
9. Zhao Y, Ye Y, Wu F, Li Y, Li L, Chen R. Anode interface engineering and architecture design for high-performance lithium-sulfur batteries. *Adv Mater* 2019;31:e1806532. DOI
10. Ji H, Wang Z, Sun Y, et al. Weakening Li^+ De-solvation barrier for cryogenic Li-S pouch cells. *Adv Mater* 2023;35:e2208590. DOI
11. Manthiram A, Fu Y, Su YS. Challenges and prospects of lithium-sulfur batteries. *ACC Chem Res* 2013;46:1125-34. DOI PubMed
12. Bandyopadhyay S, Nandan B. A review on design of cathode, anode and solid electrolyte for true all-solid-state lithium sulfur batteries. *Mater Today Energy* 2023;31:101201. DOI
13. Zhao M, Li BQ, Zhang XQ, Huang JQ, Zhang Q. A perspective toward practical lithium-sulfur batteries. *ACS Cent Sci* 2020;6:1095-104. DOI PubMed PMC
14. Bi CX, Zhao M, Hou LP, et al. Anode material options toward 500 Wh kg^{-1} lithium-sulfur batteries. *Adv Sci* 2022;9:e2103910. DOI PubMed PMC
15. Gong Y, Li J, Yang K, et al. Towards practical application of Li-S battery with high sulfur loading and lean electrolyte: will carbon-based hosts win this race? *Nanomicro Lett* 2023;15:150. DOI PubMed PMC
16. Zhang T, Zhang L, Zhao L, Huang X, Hou Y. Catalytic effects in the cathode of Li-S batteries: accelerating polysulfides redox conversion. *EnergyChem* 2020;2:100036. DOI
17. Yang JL, Cai DQ, Hao XG, et al. Rich heterointerfaces enabling rapid polysulfides conversion and regulated Li_2S deposition for high-performance lithium-sulfur batteries. *ACS Nano* 2021;15:11491-500. DOI
18. Xiang Y, Lu L, Kottapalli AGP, Pei Y. Status and perspectives of hierarchical porous carbon materials in terms of high-performance lithium-sulfur batteries. *Carbon Energy* 2022;4:346-98. DOI
19. He Y, Zou P, Bak S, et al. Dual passivation of cathode and anode through electrode-electrolyte interface engineering enables long-lifespan Li metal-SPAN batteries. *ACS Energy Lett* 2022;7:2866-75. DOI
20. Xing C, Chen H, Qian S, et al. Regulating liquid and solid-state electrolytes for solid-phase conversion in Li-S batteries. *Chem* 2022;8:1201-30. DOI
21. Chen X, Hou T, Persson KA, Zhang Q. Combining theory and experiment in lithium-sulfur batteries: current progress and future perspectives. *Mater Today* 2019;22:142-58. DOI
22. Sun X, Qiu Y, Jiang B, et al. Isolated Fe-Co heteronuclear diatomic sites as efficient bifunctional catalysts for high-performance lithium-sulfur batteries. *Nat Commun* 2023;14:291. DOI PubMed PMC
23. Zhou S, Shi J, Liu S, et al. Visualizing interfacial collective reaction behaviour of Li-S batteries. *Nature* 2023;621:75-81. DOI
24. Zhou L, Danilov DL, Qiao F, et al. Sulfur reduction reaction in lithium-sulfur batteries: mechanisms, catalysts, and characterization. *Adv Energy Mater* 2022;12:2202094. DOI
25. Chen Y, Wang T, Tian H, Su D, Zhang Q, Wang G. Advances in lithium-sulfur batteries: from academic research to commercial

viability. *Adv Mater* 2021;33:e2003666. DOI

26. Song Y, Cai W, Kong L, Cai J, Zhang Q, Sun J. Rationalizing electrocatalysis of Li-S chemistry by mediator design: progress and prospects. *Adv Energy Mater* 2020;10:1901075. DOI
27. Li C, Xi Z, Guo D, Chen X, Yin L. Chemical immobilization effect on lithium polysulfides for lithium-sulfur batteries. *Small* 2018;14:1701986. DOI
28. Tang T, Hou Y. Multifunctionality of carbon-based frameworks in lithium sulfur batteries. *Electrochem Energy Rev* 2018;1:403-32. DOI
29. Li Z, Zhou Y, Wang Y, Lu Y. Solvent-mediated Li_2S electrodeposition: a critical manipulator in lithium-sulfur batteries. *Adv Energy Mater* 2019;9:1802207. DOI
30. Yuan H, Peng H, Li B, et al. Conductive and catalytic triple-phase interfaces enabling uniform nucleation in high-rate lithium-sulfur batteries. *Adv Energy Mater* 2019;9:1802768. DOI
31. Hou R, Zhang S, Zhang Y, et al. A “three-region” configuration for enhanced electrochemical kinetics and high-areal capacity lithium-sulfur batteries. *Adv Funct Mater* 2022;32:2200302. DOI
32. Zhang X, He B, Li W, Lu A. Hollow carbon nanofibers with dynamic adjustable pore sizes and closed ends as hosts for high-rate lithium-sulfur battery cathodes. *Nano Res* 2018;11:1238-46. DOI
33. Ma F, Srinivas K, Zhang X, et al. Mo_2N quantum dots decorated N-doped graphene nanosheets as dual-functional interlayer for dendrite-free and shuttle-free lithium-sulfur batteries. *Adv Funct Mater* 2022;32:2206113. DOI
34. He B, Liu D, Cheng Z, et al. Enabling selenium-rich Se_xS_y cathodes to work in carbonate-based electrolytes. *Adv Energy Mater* 2022;12:2102832. DOI
35. Deng W, Phung J, Li G, Wang X. Realizing high-performance lithium-sulfur batteries via rational design and engineering strategies. *Nano Energy* 2021;82:105761. DOI
36. Yu Z, Liu M, Guo D, et al. Radially inwardly aligned hierarchical porous carbon for ultra-long-life lithium-sulfur batteries. *Angew Chem Int Ed* 2020;59:6406-11. DOI
37. Djuandhi L, Mittal U, Sharma N, Andersen HL. The role of carbon-based cathode components in Li-S batteries. *J Electrochem Soc* 2023;170:010522. DOI
38. Wang R, Yang J, Chen X, et al. Highly dispersed cobalt clusters in nitrogen-doped porous carbon enable multiple effects for high-performance Li-S battery. *Adv Energy Mater* 2020;10:1903550. DOI
39. Peng H, Zhang Y, Chen Y, et al. Reducing polarization of lithium-sulfur batteries via ZnS/reduced graphene oxide accelerated lithium polysulfide conversion. *Mater Today Energy* 2020;18:100519. DOI
40. Li G, Qiu W, Gao W, et al. Finely-dispersed Ni_2Co nanoalloys on flower-like graphene microassembly empowering a Bi-service matrix for superior lithium-sulfur electrochemistry. *Adv Funct Mater* 2022;32:2202853. DOI
41. Zhang W, Xu B, Zhang L, et al. Co_4N-decorated 3D wood-derived carbon host enables enhanced cathodic electrocatalysis and homogeneous lithium deposition for lithium-sulfur full cells. *Small* 2022;18:e2105664. DOI
42. Xu Z, Kim J, Kang K. Carbon nanomaterials for advanced lithium sulfur batteries. *Nano Today* 2018;19:84-107. DOI
43. Zhang LL, Zhao XS. Carbon-based materials as supercapacitor electrodes. *Chem Soc Rev* 2009;38:2520-31. DOI PubMed
44. Ji X, Lee KT, Nazar LF. A highly ordered nanostructured carbon-sulphur cathode for lithium-sulphur batteries. *Nat Mater* 2009;8:500-6. DOI PubMed
45. Yu X, Li W, Hu Y, Ye C, Lu A. Sculpturing solid polymer spheres into internal gridded hollow carbon spheres under controlled pyrolysis micro-environment. *Nano Res* 2021;14:1565-73. DOI
46. Zhang Y, Li W, He B, Yu X, Hou L, Lu A. Utilizing the alterable solubility of chitosan in aqueous solution to synthesize nanosized sulfur for high performance Li-S batteries. *Chin J Chem* 2019;37:775-80. DOI
47. Zhang L, He B, Li W, Lu A. Surface free energy-induced assembly to the synthesis of grid-like multicavity carbon spheres with high level in-cavity encapsulation for lithium-sulfur cathode. *Adv Energy Mater* 2017;7:1701518. DOI
48. Liu Y, Ma Z, Yang G, et al. Multifunctional $ZnCo_2O_4$ quantum dots encapsulated in carbon carrier for anchoring/catalyzing polysulfides and self-repairing lithium metal anode in lithium-sulfur batteries. *Adv Funct Mater* 2022;32:2109462. DOI
49. Xiang J, Shen W, Guo Z, et al. A supramolecular complex of C_{60}-S with high-density active sites as a cathode for lithium-sulfur batteries. *Angew Chem Int Ed* 2021;60:14313-8. DOI
50. Fu C, Oviedo MB, Zhu Y, et al. Confined lithium-sulfur reactions in narrow-diameter carbon nanotubes reveal enhanced electrochemical reactivity. *ACS Nano* 2018;12:9775-84. DOI
51. Lin J, Mo Y, Li S, Yu J. Nitrogen-doped porous carbon fiber/vertical graphene as an efficient polysulfide conversion catalyst for high-performance lithium-sulfur batteries. *J Mater Chem A* 2022;10:690-8. DOI
52. Peng L, Wei Z, Wan C, et al. A fundamental look at electrocatalytic sulfur reduction reaction. *Nat Catal* 2020;3:762-70. DOI
53. Zhou G, Li L, Wang DW, et al. A flexible sulfur-graphene-polypropylene separator integrated electrode for advanced Li-S batteries. *Adv Mater* 2015;27:641-7. DOI
54. Han Z, Zhao S, Xiao J, et al. Engineering d-p orbital hybridization in single-atom metal-embedded three-dimensional electrodes for Li-S batteries. *Adv Mater* 2021;33:e2105947. DOI
55. Qi C, Li Z, Wang G, et al. Microregion welding strategy prevents the formation of inactive sulfur species for high-performance Li-S battery. *Adv Energy Mater* 2021;11:2102024. DOI
56. Lu R, Cheng M, Mao L, et al. Nitrogen-doped nanoarray-modified 3D hierarchical graphene as a cofunction host for high-

performance flexible Li-S battery. *EcoMat* 2020;2:e12010. DOI

57. He B, Li W, Chen Z, et al. Multilevel structured carbon film as cathode host for Li-S batteries with superhigh-areal-capacity. *Nano Res* 2021;14:1273-9. DOI
58. Wang N, Zhang X, Ju Z, et al. Thickness-independent scalable high-performance Li-S batteries with high areal sulfur loading via electron-enriched carbon framework. *Nat Commun* 2021;12:4519. DOI PubMed PMC
59. Qin J, Wang R, Xiao P, Wang D. Engineering cooperative catalysis in Li-S batteries. *Adv Energy Mater* 2023;13:2300611. DOI
60. Yu X, Li W, He B, et al. Porous carbon/borocarbonitride hybrid with enhanced tap density as a polar host for ultralong life lithium-sulfur batteries. *Chem Eng J* 2022;430:132987. DOI
61. Wang J, Han W. A review of heteroatom doped materials for advanced lithium-sulfur batteries. *Adv Funct Mater* 2022;32:2107166. DOI
62. Pan J, Sun Y, Wu Y, et al. Yolk-double shells hierarchical N-doped carbon nanosphere as an electrochemical nanoreactor for high performance lithium-sulfur batteries. *Carbon* 2022;198:80-90. DOI
63. Ji L, Rao M, Zheng H, et al. Graphene oxide as a sulfur immobilizer in high performance lithium/sulfur cells. *J Am Chem Soc* 2011;133:18522-5. DOI
64. Zheng Y, Jiao Y, Ge L, Jaroniec M, Qiao SZ. Two-step boron and nitrogen doping in graphene for enhanced synergistic catalysis. *Angew Chem Int Ed* 2013;52:3110-6. DOI PubMed
65. Fang R, Zhao S, Pei S, et al. Toward more reliable lithium-sulfur batteries: an all-graphene cathode structure. *ACS Nano* 2016;10:8676-82. DOI
66. Song J, Yu Z, Gordin ML, Wang D. Advanced sulfur cathode enabled by highly crumpled nitrogen-doped graphene sheets for high-energy-density lithium-sulfur batteries. *Nano Lett* 2016;16:864-70. DOI
67. Hu C, Kirk C, Cai Q, et al. A high-volumetric-capacity cathode based on interconnected close-packed N-doped porous carbon nanospheres for long-life lithium-sulfur batteries. *Adv Energy Mater* 2017;7:1701082. DOI
68. Hou TZ, Xu WT, Chen X, Peng HJ, Huang JQ, Zhang Q. Lithium bond chemistry in lithium-sulfur batteries. *Angew Chem Int Ed* 2017;56:8178-82. DOI
69. Xu J, Su D, Zhang W, Bao W, Wang G. A nitrogen-sulfur co-doped porous graphene matrix as a sulfur immobilizer for high performance lithium-sulfur batteries. *J Mater Chem A* 2016;4:17381-93. DOI
70. Hao GP, Tang C, Zhang E, et al. Thermal exfoliation of layered metal-organic frameworks into ultrahydrophilic graphene stacks and their applications in Li-S batteries. *Adv Mater* 2017;29:1702829. DOI
71. Li L, Tu H, Wang J, et al. Electrocatalytic MOF-carbon bridged network accelerates Li^+-solvents desolvation for high Li^+ diffusion toward rapid sulfur redox kinetics. *Adv Funct Mater* 2023;33:2212499. DOI
72. Seh ZW, Zhang Q, Li W, Zheng G, Yao H, Cui Y. Stable cycling of lithium sulfide cathodes through strong affinity with a bifunctional binder. *Chem Sci* 2013;4:3673-7. DOI
73. Zhou W, Xiao X, Cai M, Yang L. Polydopamine-coated, nitrogen-doped, hollow carbon-sulfur double-layered core-shell structure for improving lithium-sulfur batteries. *Nano Lett* 2014;14:5250-6. DOI
74. Qiao X, Wang C, Zang J, et al. Conductive inks composed of multicomponent carbon nanomaterials and hydrophilic polymer binders for high-energy-density lithium-sulfur batteries. *Energy Stor Mater* 2022;49:236-45. DOI
75. Kong W, Sun L, Wu Y, et al. Binder-free polymer encapsulated sulfur-carbon nanotube composite cathodes for high performance lithium batteries. *Carbon* 2016;96:1053-9. DOI
76. Gu PY, Zhao Y, Xie J, et al. Improving the performance of lithium-sulfur batteries by employing polyimide particles as hosting matrixes. *ACS Appl Mater Interfaces* 2016;8:7464-70. DOI
77. Su D, Cortie M, Fan H, Wang G. Prussian blue nanocubes with an open framework structure coated with PEDOT as high-capacity cathodes for lithium-sulfur batteries. *Adv Mater* 2017;29:1700587. DOI PubMed
78. Ding Z, Zhao D, Yao R, Li C, Cheng X, Hu T. Polyaniline@spherical ordered mesoporous carbon/sulfur nanocomposites for high-performance lithium-sulfur batteries. *Int J Hydrogen Energy* 2018;43:10502-10. DOI
79. Zhang K, Li X, Yang Y, et al. High loading sulfur cathodes by reactive-type polymer tubes for high-performance lithium-sulfur batteries. *Adv Funct Mater* 2023;33:2212759. DOI
80. Hu H, Cheng H, Liu Z, Li G, Zhu Q, Yu Y. In situ polymerized PAN-assisted S/C nanosphere with enhanced high-power performance as cathode for lithium/sulfur batteries. *Nano Lett* 2015;15:5116-23. DOI
81. Chen CY, Peng HJ, Hou TZ, et al. A quinonoid-imine-enriched nanostructured polymer mediator for lithium-sulfur batteries. *Adv Mater* 2017;29:1606802. DOI
82. Dong F, Peng C, Xu H, et al. Lithiated sulfur-incorporated, polymeric cathode for durable lithium-sulfur batteries with promoted redox kinetics. *ACS Nano* 2021;15:20287-99. DOI
83. Zhao CX, Li XY, Zhao M, et al. Semi-immobilized molecular electrocatalysts for high-performance lithium-sulfur batteries. *J Am Chem Soc* 2021;143:19865-72. DOI
84. He B, Li W, Zhang Y, et al. Paragenesis BN/CNTs hybrid as a monoclinic sulfur host for high rate and ultra-long life lithium-sulfur battery. *J Mater Chem A* 2018;6:24194-200. DOI
85. Zhou S, Pei W, Zhao Y, Yang X, Liu N, Zhao J. Low-dimensional non-metal catalysts: principles for regulating p-orbital-dominated reactivity. *NPJ Comput Mater* 2021;7:186. DOI
86. Lee BJ, Zhao C, Yu JH, et al. Development of high-energy non-aqueous lithium-sulfur batteries via redox-active interlayer strategy.

Nat Commun 2022;13:4629. DOI PubMed PMC

87. Li L, Yu Y, Ye GJ, et al. Black phosphorus field-effect transistors. *Nat Nanotechnol* 2014;9:372-7. DOI
88. Li L, Chen L, Mukherjee S, et al. Phosphorene as a polysulfide immobilizer and catalyst in high-performance lithium-sulfur batteries. *Adv Mater* 2017;29:1602734. DOI
89. Liang J, Yin L, Tang X, et al. Kinetically enhanced electrochemical redox of polysulfides on polymeric carbon nitrides for improved lithium-sulfur batteries. *ACS Appl Mater Interfaces* 2016;8:25193-201. DOI
90. Wen Y, Shen Z, Hui J, Zhang H, Zhu Q. Co/CoSe junctions enable efficient and durable electrocatalytic conversion of polysulfides for high-performance Li-S batteries. *Adv Energy Mater* 2023;13:2204345. DOI
91. Li J, Shi K, Pan J, et al. Designing electrochemical nanoreactors to accelerate $Li_2S_{1/2}$ three-dimensional growth process and generating more Li_2S for advanced Li-S batteries. *Renewables* 2023;1:341-52. DOI
92. Xie Y, Ao J, Zhang L, et al. Multi-functional bilayer carbon structures with micrometer-level physical encapsulation as a flexible cathode host for high-performance lithium-sulfur batteries. *Chem Eng J* 2023;451:139017. DOI
93. Liu Q, Wu Y, Li D, et al. Dilute alloying to implant activation centers in nitride electrocatalysts for lithium-sulfur batteries. *Adv Mater* 2023;35:e2209233. DOI
94. Lu Y, Qin J, Shen T, et al. Hypercrosslinked polymerization enabled N-doped carbon confined Fe_2O_3 facilitating Li polysulfides interface conversion for Li-S batteries. *Adv Energy Mater* 2021;11:2101780. DOI
95. Yu X, Chen W, Cai J, Lu X, Sun Z. Oxygen vacancy-rich MnO nanoflakes/N-doped carbon nanotubes modified separator enabling chemisorption and catalytic conversion of polysulfides for Li-S batteries. *J Colloid Interface Sci* 2022;610:407-17. DOI
96. Wei Seh Z, Li W, Cha JJ, et al. Sulphur-TiO_2 yolk-shell nanoarchitecture with internal void space for long-cycle lithium-sulphur batteries. *Nat Commun* 2013;4:1331. DOI
97. Yu M, Ma J, Song H, et al. Atomic layer deposited TiO_2 on a nitrogen-doped graphene/sulfur electrode for high performance lithium-sulfur batteries. *Energy Environ Sci* 2016;9:1495-503. DOI
98. Fang M, Chen Z, Liu Y, et al. Design and synthesis of novel sandwich-type C@TiO_2@C hollow microspheres as efficient sulfur hosts for advanced lithium-sulfur batteries. *J Mater Chem A* 2018;6:1630-8. DOI
99. Rehman S, Tang T, Ali Z, Huang X, Hou Y. Integrated design of MnO_2@Carbon hollow nanoboxes to synergistically encapsulate polysulfides for empowering lithium sulfur batteries. *Small* 2017;13:1700087. DOI
100. Xu J, Zhang W, Chen Y, Fan H, Su D, Wang G. MOF-derived porous N-Co_3O_4@N-C nanododecahedra wrapped with reduced graphene oxide as a high capacity cathode for lithium-sulfur batteries. *J Mater Chem A* 2018;6:2797-807. DOI
101. Zhou L, Li H, Wu X, et al. Double-shelled Co_3O_4/C nanocages enabling polysulfides adsorption for high-performance lithium-sulfur batteries. *ACS Appl Energy Mater* 2019;2:8153-62. DOI
102. Chu R, Nguyen TT, Bai Y, Kim NH, Lee JH. Uniformly controlled treble boundary using enriched adsorption sites and accelerated catalyst cathode for robust lithium-sulfur batteries. *Adv Energy Mater* 2022;12:2102805. DOI
103. Hua W, Shang T, Li H, et al. Optimizing the p charge of S in p-block metal sulfides for sulfur reduction electrocatalysis. *Nat Catal* 2023;6:174-84. DOI
104. Dai X, Lv G, Wu Z, et al. Flexible hierarchical Co-doped NiS_2@CNF-CNT electron deficient interlayer with grass-roots structure for Li-S batteries. *Adv Energy Mater* 2023;13:2300452. DOI
105. Zhou G, Tian H, Jin Y, et al. Catalytic oxidation of Li_2S on the surface of metal sulfides for Li-S batteries. *Proc Natl Acad Sci USA* 2017;114:840-5. DOI PubMed PMC
106. He J, Bhargav A, Manthiram A. High-performance anode-free Li-S batteries with an integrated Li_2S-electrocatalyst cathode. *ACS Energy Lett* 2022;7:583-90. DOI
107. Xie Y, Cao J, Wang X, et al. MOF-derived bifunctional $Co_{0.85}Se$ nanoparticles embedded in N-doped carbon nanosheet arrays as efficient sulfur hosts for lithium-sulfur batteries. *Nano Lett* 2021;21:8579-86. DOI
108. Chen T, Ma L, Cheng B, et al. Metallic and polar Co_9S_8 inlaid carbon hollow nanopolyhedra as efficient polysulfide mediator for lithium-sulfur batteries. *Nano Energy* 2017;38:239-48. DOI
109. Shi M, Liu Z, Zhang S, et al. A mott-schottky heterogeneous layer for Li-S batteries: enabling both high stability and commercial-sulfur utilization. *Adv Energy Mater* 2022;12:2103657. DOI
110. Lin H, Yang L, Jiang X, et al. Electrocatalysis of polysulfide conversion by sulfur-deficient MoS_2 nanoflakes for lithium-sulfur batteries. *Energy Environ Sci* 2017;10:1476-86. DOI
111. You Y, Ye Y, Wei M, et al. Three-dimensional MoS_2/rGO foams as efficient sulfur hosts for high-performance lithium-sulfur batteries. *Chem Eng J* 2019;355:671-8. DOI
112. Hu L, Dai C, Lim JM, et al. A highly efficient double-hierarchical sulfur host for advanced lithium-sulfur batteries. *Chem Sci* 2018;9:666-75. DOI PubMed PMC
113. Feng Y, Zu L, Yang S, et al. Ultrahigh-content Co-P cluster as a dual-atom-site electrocatalyst for accelerating polysulfides conversion in Li-S batteries. *Adv Funct Mater* 2022;32:2207579. DOI
114. Hu Z, Geng C, Wang L, Lv W, Yang Q. Revisiting the roles of carbon in the catalysis of lithium-sulfur batteries. *Adv Energy Sustain Res* 2024;5:2300148. DOI
115. Yu X, Tian D, Li W, et al. One-pot synthesis of highly conductive nickel-rich phosphide/CNTs hybrid as a polar sulfur host for high-rate and long-cycle Li-S battery. *Nano Res* 2019;12:1193-7. DOI
116. Mi Y, Liu W, Li X, Zhuang J, Zhou H, Wang H. High-performance Li-S battery cathode with catalyst-like carbon nanotube-MoP

promoting polysulfide redox. *Nano Res* 2017;10:3698-705. DOI

117. Ye Z, Jiang Y, Qian J, et al. Exceptional adsorption and catalysis effects of hollow polyhedra/carbon nanotube confined CoP nanoparticles superstructures for enhanced lithium-sulfur batteries. *Nano Energy* 2019;64:103965. DOI
118. Huang S, Lim YV, Zhang X, et al. Regulating the polysulfide redox conversion by iron phosphide nanocrystals for high-rate and ultrastable lithium-sulfur battery. *Nano Energy* 2018;51:340-8. DOI
119. Li S, Lin J, Chang B, et al. Implanting single-atom N_2-Fe-B_2 catalytic sites in carbon hosts to stabilize high-loading and lean-electrolyte lithium-sulfur batteries. *Energy Storage Mater* 2023;55:94-104. DOI
120. Li Z, Li B, Yu C, Wang H, Li Q. Recent progress of hollow carbon nanocages: general design fundamentals and diversified electrochemical applications. *Adv Sci* 2023;10:e2206605. DOI PubMed PMC
121. Zhou J, Tang W, Shu C, et al. Well-defined metal-N_4 sites coordinated defective carbon as efficient electrocatalysts for high performance lithium-sulfur batteries. *Mater Today Energy* 2022;30:101151. DOI
122. Du Z, Chen X, Hu W, et al. Cobalt in nitrogen-doped graphene as single-atom catalyst for high-sulfur content lithium-sulfur batteries. *J Am Chem Soc* 2019;141:3977-85. DOI
123. Yang JL, Yang P, Cai DQ, Wang Z, Fan HJ. Atomically dispersed Fe-N_4 and Ni-N_4 independent sites enable bidirectional sulfur redox electrocatalysis. *Nano Lett* 2023;23:4000-7. DOI
124. Yu X, He B, Li W, Wu T, Chen X, Lu A. Multi-cavity carbon nanofiber film decorated with Co-N_x doped CNTs for lithium-sulfur batteries with high-areal-capacity. *J Mater Chem A* 2022;10:12168-76. DOI
125. Zhou T, Lv W, Li J, et al. Twinborn TiO_2 -TiN heterostructures enabling smooth trapping-diffusion-conversion of polysulfides towards ultralong life lithium-sulfur batteries. *Energy Environ Sci* 2017;10:1694-703. DOI
126. Song Y, Zhao W, Kong L, et al. Synchronous immobilization and conversion of polysulfides on a VO_2-VN binary host targeting high sulfur load Li-S batteries. *Energy Environ Sci* 2018;11:2620-30. DOI
127. Wang B, Ren Y, Zhu Y, et al. Construction of Co_3O_4/ZnO heterojunctions in hollow N-doped carbon nanocages as microreactors for lithium-sulfur full batteries. *Adv Sci* 2023;10:e2300860. DOI PubMed PMC
128. Huang Z, Zhu Y, Kong Y, et al. Efficient synergism of chemisorption and wackenroder reaction via heterostructured La_2O_3-$Ti_3C_2T_x$-embedded carbon nanofiber for high-energy lithium-sulfur pouch cells. *Adv Funct Mater* 2023;33:2303422. DOI