REVIEW

Cobalt/Carbon Composites as Sulfur Hosts for High-Performance Lithium-Sulfur Batteries

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Abstract

Lithium-sulfur (Li-S) battery is one of the promising energy storage devices because of its high energy density. However, the sulfur cathode suffers from sluggish electrochemical reaction kinetics, slow charge transfer, large volume expansion and severe shuttle effect of lithium polysulfides inevitably resulting in low reversible capacity, poor rate performance and short cycle life, limiting its practical applications. Herein, the recent progress of cobalt/carbon composites, including cobalt nanoparticles and cobalt single atoms, as the sulfur host materials in Li-S batteries is overviewed. In general, cobalt plays the role of electrocatalyst, which inhibits the shuttle effect of lithium polysulfides, accelerates the electrochemical reaction kinetics, facilitates ion/electron transfer and alleviates volume expansion. Meanwhile, the prospects for the development of cobalt/carbon composites as sulfur hosts in Li-S batteries are proposed. It is expected to offer a whole blueprint and constructive suggestions for the cobalt/carbon composites as sulfur hosts for Li-S batteries, and these strategies can also be effective for other metal-sulfur batteries.

Keywords: Lithium-sulfur batteries; Sulfur hosts; Cobalt/carbon composites; Electrocatalysts; Electrochemical performance

1. Introduction

Recently, lithium-ion batteries (LIBs) have been extensively applied in electric vehicles due to their low self-discharge, superior cycling stability, and environmentally friendly [1–5]. In general, commercial LIBs consist of an ion-insertion cathode ($LiCoO_2$, $LiFePO_4$, or $LiNi_xMn_yCo_zO_2$) and a graphite anode, and deliver a cell-level energy density of 150–250 $Wh\cdot kg^{-1}$, driving 300–600 km for electric vehicles [6]. Notably, the existing LIBs technologies fail to satisfy the ever-increasing requirement of the driver and then inevitably cause range anxiety. Therefore, a goal of the cell-level energy density of 500 $Wh\cdot kg^{-1}$ with a pack-level cost of $<$ US\$100 $(kWh)^{-1}$ for electric vehicles has been proposed by the Battery 500 Consortium [7]. However, the future lithium metal batteries of Li/lithium-transition metal oxide (LMO) full cells are challenging to achieve an energy density of 500 $Wh\cdot kg^{-1}$ due to the insufficient specific capacity ($\leq$220 $mAh\cdot g^{-1}$) of LMO. Hence, it is urgent to exploit alternative battery systems with relatively high energy density to alleviate the range anxiety of the driver.

Among the discovered battery systems, lithium-sulfur (Li-S) batteries are attracted extensive attention owing to their high theoretical energy density (2600 $Wh\cdot kg^{-1}$) and potentially low cost [8–10]. S cathode undergoes a multi-electron-

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transfer electrochemical reaction ($S_8 + 16\ Li^+ + 16\ e^- \rightarrow 8\ Li_2S$) and delivers a high theoretical specific capacity of 1675 $mAh \cdot g^{-1}$ with an average voltage of 2.20 V (*vs.* Li^+/Li) [11]. In addition, the Holy Grail electrode of Li metal was applied as an anode for Li-S batteries, which has a high theoretical capacity of 3860 $mAh \cdot g^{-1}$ and ultralow reduction potential (−3.04 V *vs.* Standard Hydrogen Electrode) [12]. Therefore, Li-S batteries are expected to achieve a full-cell-level energy density of >600 $Wh \cdot kg^{-1}$, and considered as a promising candidate for long-range electric vehicles. However, there still exist a few challenges that hinder the commercialization of Li-S batteries. First of all, the safety issues of Li-S batteries are more thorny than commercial LIBs due to the utilization of Li metal anode [13]. Then, the pulverization of the S cathode caused by the huge volume changes expansion during the charge/discharge process can result in the degradation of electrochemical performance [14]. Subsequently, the lithium polysulfide intermediates have a relatively high solubility in the conventional organic electrolyte, causing the loss of active materials, low Coulombic efficiency, inferior cycling stability, and severe self-discharge [15]. Finally, the poor intrinsic electronic conductivities of S cathode and Li_2S have a significantly negative effect on the electron transfer dynamics and S utilization [16].

Over the past decade, a variety of strategies have been performed to boost the electrochemical performance of Li-S batteries, including the optimizations of the cathode, separator, electrolyte, binder, and anode [17−23]. Among them, the design of advanced sulfur host materials is mainstream research. In 2009, Nazar's group first found that the shuttle effect of lithium polysulfides (LiPSs) can be inhibited to a certain extent by using mesoporous carbon as the sulfur host, resulting in the improved reversible capacity and cycling stability [24]. Subsequently, various carbon materials (*i.e.*, graphene, carbon nanotubes, hollow carbon spheres, and carbon nanofibers) were also applied to Li-S batteries [25−28]. In general, the high electronic conductivity, large specific surface area, and porous structure of carbon substrates are beneficial to improving the conductivity of S cathode/Li_2S, alleviating the volume expansion, and inhibiting the shuttling effect of LiPSs by physical adsorption. However, the weak physical interaction between the polar LiPSs and the nonpolar carbon materials inevitably causes the out diffusion of LiPSs during long-term cycling. In general, heteroatom doping not only can improve the conductivity of the carbon matrix, but also facilitate the chemical entrapment of LiPSs on carbon hosts [29]. Recently, incorporating catalysts into carbon materials has also proven to be an effective strategy to anchor LiPSs by accelerating the conversion of LiPSs [30,31]. It is advantageous to increase the utilization of S and decrease polarization during the cyclic process.

Nowadays, various catalysts (such as transition metals, metal sulfides, and metal nitrides) have been successfully introduced into carbon materials as sulfur hosts and the electrochemical performance of Li-S batteries is greatly enhanced [32,33]. Among them, transition metals have been considered as promising candidates for Li-S batteries because of their outstanding catalytic properties and potentially low cost [34]. In addition, transition metals can effectively adsorb LiPSs and accelerate electron transfer kinetics [35]. It is worth noting that the cobalt (Co) with 3d orbital electron configuration $t_{2g}^6 e_{2g}^1$ shows a relatively low intrinsic spin state. Benefiting from the delocalization of unpaired electrons, the charge can transfer from the Co center to the adjacent molecule, resulting in improved specific conversion redox [36]. In this review, we overview the recent progress on the sulfur host of Co/carbon composites that contain Co nanoparticles or Co single atoms. Besides, the advantages of Co/carbon composites as sulfur hosts are summarized. Finally, the future research directions of Co/carbon composites as sulfur hosts for Li-S batteries are proposed.

2. Cobalt nanoparticles/carbon composites as sulfur hosts

To date, various sulfur hosts containing Co nanoparticles have been discovered for Li-S batteries [37−41]. Porous carbon with a large specific surface area can effectively absorb polysulfides and avoid the aggregation of Co nanoparticles, which has attracted extensive attention as a support for Co nanoparticles in Li-S batteries [42−46]. For instance, Dong's group prepared a 3D nitrogen-doped graphitic carbon and Co nanoparticles (Co-N-GC) composite using metal-organic frameworks (ZIF-67) as the precursor (Fig. 1a) [47]. The uniform distributions of Co nanoparticles (22.09 nm) and the nitrogen-containing groups in the carbon matrix show a synergic catalytic effect on the S reduction and oxidation reactions during the charge/discharge process. Furthermore, the obtained Co-N-GC composite as a sulfur host not only provides an ideal electronic matrix but also efficiently inhibits polysulfide dissolution. Benefiting from the above advantages, the S@Co-N-GC cathode exhibits a superior rate performance (Fig. 1b) and large discharge capacity of

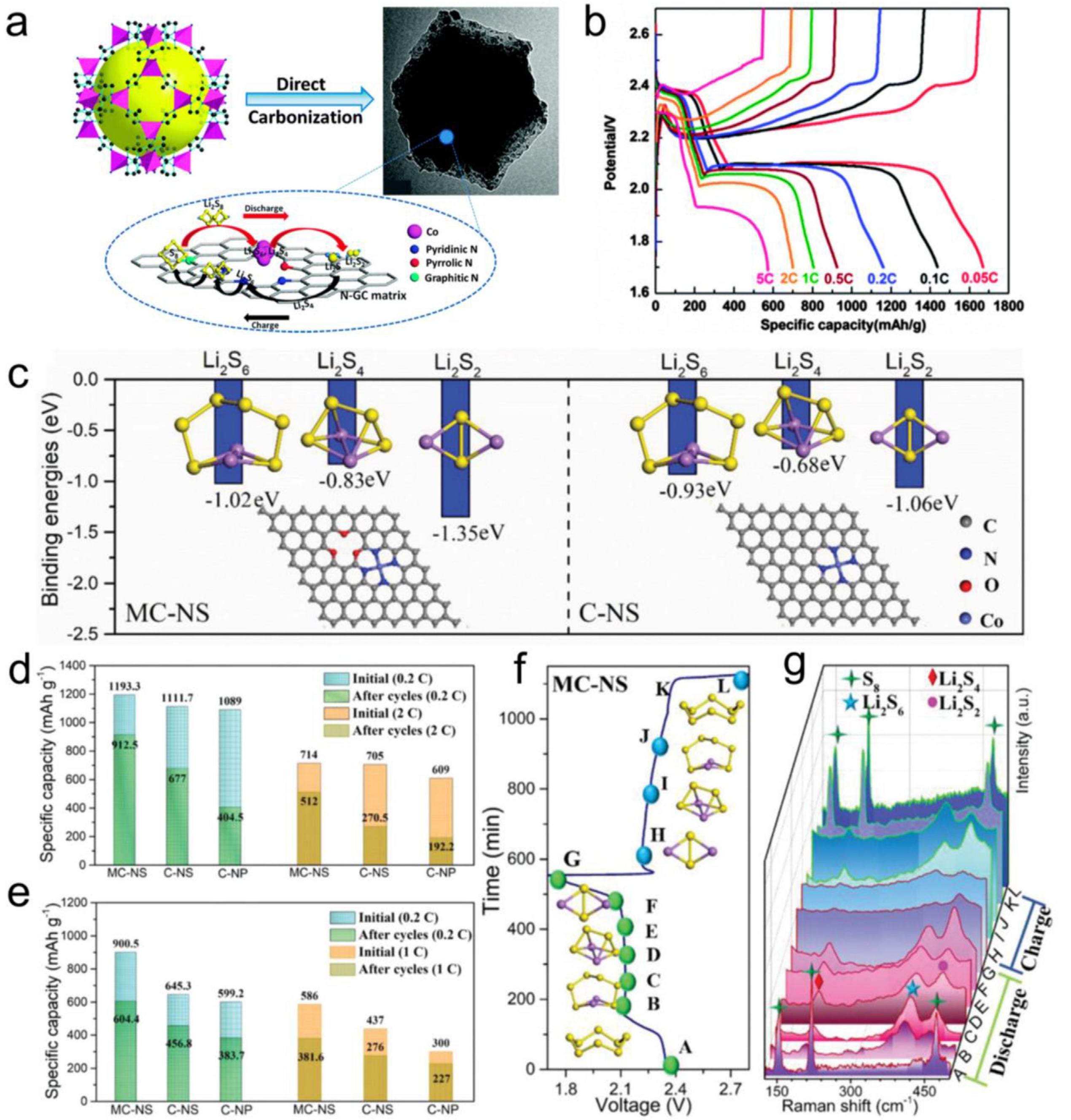

Fig. 1. (a) Schematic illustration of Co-N-GC composite preparation and the catalytic effect for LiPSs during the cycling. (b) The rate performance of S@Co-N-GC composite electrode. Reproduced with permission [47]. Copyright 2016, The Royal Society of Chemistry. (c) The binding energies of MC-NS (left) and C-NS (right) for LiPSs. The capacity retention plots of MC-NS/S, C-NS/S, and C-NP/S with sulfur loadings of (d) 1.5 mg·cm^{-2} and (e) 4.5 mg·cm^{-2} at various current densities. (f) The charge/discharge curve and (g) the corresponding selected Raman spectra of MC-NS/S cathode during the charge and discharge processes. Reproduced with permission [48]. Copyright 2019, WILEY-VCH.

1670 mAh·g^{-1} with a Coulombic efficiency of 98.9% even at a high sulfur content (70 wt%). Subsequently, Shao's group reported honeycomb-like mesoporous N-doped carbon nanosheets with uniform Co nanoparticles (ca. 10 nm, named MC-NS), which possess abundant Co-N-C catalytic sites and defects [48]. As shown in Fig. 1c, MC-NS shows higher adsorption energies for LiPSs (Li_2S_2, Li_2S_4, and Li_2S_6) than C-NS (carbon nanosheet). Meanwhile, the MC-NS electrode achieves a higher current density in the cyclic voltammetric test of symmetrical cells with Li_2S_6. These results indicate that the MC-NS can effectively inhibit the shuttle effect of polysulfides. Therefore, the MC-NS/S delivers excellent cycling stability (Fig. 1d and e). Besides, *in situ* Raman spectra demonstrated that the MC-NS is favorable for the reversible conversion of polysulfide during the charge/discharge process, leading to high utilization of sulfur, large reversible capacity, and good rate performance (Fig. 1f and g). To obtain a better catalytic effect, El-Kadri's group prepared ultrafine and well-dispersed Co nanoparticles by strong electrostatic adsorption [49]. These Co nanoparticles (ca. 3.5—4.5 nm) were evenly distributed on the N-doped porous carbon, which is used as a sulfur host and shows superior electrochemical performance.

Recently, Pan's group synthesized highly dispersed Co clusters in N-doped porous carbon (N-PC@uCo) by applying a glucose adsorbed metal-organic framework as the precursor [50]. Glucose plays an important role in avoiding the aggregation of Co. As shown in Fig. 2a, the N-PC@uCo as a sulfur host own various advantages (including high conductivity, high sulfur loading, effective stress relief, fast Li^+ kinetics, fast interface e^- transport, fast redox of Li_2S_n and strong absorption). Significantly, the importance of well-dispersed Co was also systematically investigated through experiments and DFT calculations. Compared with N-PC/S (nitrogen-doped porous carbon/sulfur) and N-PC@aCo/S (nitrogen-doped porous carbon with aggregated cobalt particles/sulfur), the N-PC@uCo/S electrode shows a higher Li^+ diffusion coefficient. Meanwhile, the symmetric cell with N-PC@uCo in 0.4 $mol \cdot L^{-1}$ Li_2S_6-DOL/DME electrolyte shows a higher current density and lower charge transfer resistance. The DFT calculations reveal that the Co cluster has the lowest energy barrier for Li^+ diffusion (Fig. 2b) and the highest binding energy for Li_2S_n (Fig. 2c and d). These results demonstrated that the highly dispersed Co cluster is in favor of the Li diffusion, simultaneously stimulating the redox reactions of LiPSs and preventing its shuttling effect. Therefore, the N-PC@uCo/S electrode displays superior cycling stability (a good capacity retention of 86% even after 500 cycles) and excellent rate performance (a high reversible capacity of 600 $mAh \cdot g^{-1}$ at 5 C).

The hollow structure has also attracted extensive attention for Li-S batteries because it can provide enough voids for sulfur storage and prevents the shuttling effect of polysulfides [51—54]. For example, Sun's group reported an entangled N-doped carbon nanotube array with encapsulated Co nanoparticles (Co-N-CNTA) [55]. The effective electrocatalysis and confinement of Co-N-CNTA for LiPSs were demonstrated by DFT calculations, *in situ* UV-vis spectroscopy, and electrochemical analysis. Meanwhile, the orderly hierarchical architecture enables a high content of sulfur. As a result, the Co-N-CNTA/S electrode shows a low overpotential and superior cycling stability (a capacity retention of 77.89% after 1000 cycles). Even at an elevated sulfur loading, the Co-N-CNTA/S electrodes also show high reversible capacities and good cycling performance (Fig. 3a). As shown in Fig. 3b, the pouch cell assembled by Co-N-CNTA/S (5.0 $mg \cdot cm^{-2}$) and Li metal shows a reversible capacity of 4.823 $mAh \cdot cm^{-2}$ even after 150 cycles, and successful lighted 80 light-emitting diodes. These results indicate that the Co-N-CNTA/S is a promising cathode candidate for Li-S batteries. Moreover, Huang and co-workers applied a hollow

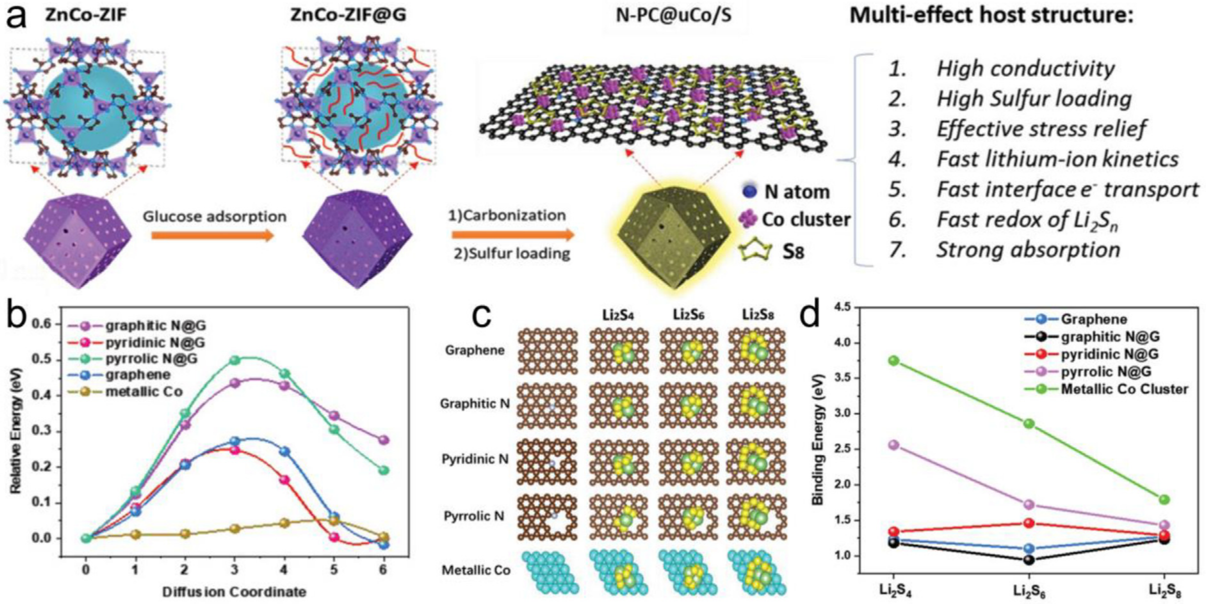

Fig. 2. (a) Schematic illustrations of the preparation process and the advantage of N-PC@uCo/S composites. (b) Li-ion diffusion energy barriers on different samples. (c) Atomic conformations and (d) binding energies for LiPSs adsorption on various samples. Reproduced with permission [50]. Copyright 2020, WILEY-VCH.

porous B,N-codoped graphitic carbon-Co composite (h-Co-BN-GC) as a sulfur host [56]. They demonstrated that the B,N-codoped in a carbon framework contained Co nanoparticles can increase the chemisorption and catalyst effect on LiPSs, and then effectively avoiding LiPSs diffusion and improving the electrochemical reaction kinetics of Li_2S_n. Subsequently, Deng et al. prepared a unique hollow Co-embedded and N-doped carbonaceous microflowers (H-Co-NCM) by *in situ* transformation of Co-Al layered double hydroxides [57]. The superior catalytic activity of H-Co-NCM for LiPSs was revealed by the Tafel polarization and Li_2S precipitation experiments (Fig. 3c—e). Compared with acetylene black, the H-Co-NCM shows a lower Tafel slope (53 *vs*. 934 $mV\cdot dec^{-1}$), higher exchange current density (0.225 *vs*. 0.019 $mA\cdot cm^{-2}$), and larger precipitation capacity (175.8 *vs*. 148.1 $mAh\cdot g^{-1}$). Recently, Zhang and co-workers reported a hollow graphitized carbon nanocage embedded with Co nanoparticles as a sulfur host for Li-S batteries [58]. In addition to the positive effect of Co nanoparticles, the unique hollow graphitized carbon nanocages provide a fast electron transport pathway and alleviate the volume changes during the charge/discharge process. Most recently, Wang and co-workers realized a high sulfur content of 90.5 wt% by using Co-embedded nitrogen-doped hollow carbon microspheres (Co@N-HCMSs) as host materials (Fig. 3f and g) [59]. Even at a high sulfur loading (5.1 $mg\cdot cm^{-2}$) and a low electrolyte/sulfur ratio (10 $\mu L\cdot mg^{-1}$), the S/Co@N-HCMSs still exhibit superior cycling stability (Fig. 3h).

Graphene with superior electronic conductivity was also applied as a support for Co nanoparticles [60,61]. For example, Bao's group used a facile solvothermal method to synthesize N-doped graphene anchored with Co (Co-NCG), which was applied as a sulfur host for Li-S batteries [62]. The crumpled structure of Co-NCG endows enough voids enabling a high sulfur loading. The nitrogen atom and Co can effectively inhibit the polysulfides shuttling effect and facilitate the redox reaction of S. Furthermore, Chen and co-workers applied Co/Co-N_x@NG (Co nanoparticles anchored on the Co-N_x centers grafted N-doped graphene) as a sulfur host for Li-S batteries [63]. The Co/Co-N_x@NG/S possesses high catalytic activity and electronic conductivity, suggesting the potential of superior electrochemical performance.

Hybrid carbons combined the advantages of different carbon materials were also applied in Co nanoparticles-based sulfur hosts. Yin and co-workers first proposed a reduced graphene oxide (RGO) wrapped Co embedded porous carbon polyhedrons (RGO/C-Co) as a sulfur host for Li-S batteries [64]. The shuttle effect of polysulfides was effectively inhibited by the synergetic effect of RGO nanosheets barrier layers, evenly dispersed Co nanoparticle (2—10 nm), and porous carbon matrix. Therefore, the RGO/C-Co-S presents superior cycling stability. Remarkably, Zhao et al. found that the Co nanoparticles derived from metal-organic frameworks also can *in situ* catalyze the growth of carbon nanotubes (CNTs) [65]. Hence, a hybrid composite of carbon nanotubes and Co nanoparticles (CNT@Co-N-C) was prepared, and the nanosized Co particles are uniformly dispersed into N-doped carbon. The CNTs with superior electronic conductivity ensure fast electron transport. Therefore, CNT@Co-N-C/S electrode delivers an excellent rate performance. Similarly, Peng et al. reported a sulfur host of Co nanoparticles decorated CNTs-grafted carbon nanocages (CNT-NC@GC) [66]. The CNTs are also *in situ* introduced into the inner/outer surface of the nanocages, which benefit for the penetration of electrolytes and the fast migration of electrons/ions. Recently, Wang and co-workers synthesized a 3D composite host materials (Co/CNS/CNT, consisting of Co nanocrystals, carbon nanosheets, and carbon nanotubes) by a facile "lotus blooming" strategy (Fig. 4a and b) [67]. The unique structure of Co/CNS/CNT supplies vertical and horizontal electrons/ions transfer channels, and facilitates the evenly sulfur loading and electrolyte infiltration. Most recently, Huang et al. designed a distinctive core-shell structure (Co-doped CNT assembled polyhedron core@graphitized porous carbon aerogel shell, Co-GC@GPCA) [68]. The Co-GC core is beneficial for the conversion of LiPSs, preventing the shuttle of polysulfides. Meanwhile, the GPCA shell enables fast electron/ion transport, and offers space for sulfur reservoir and Li_2S_2/Li_2S deposition. Therefore, the S/Co-GC@GPCA electrode shows a high areal capacity (3.35 $mAh\cdot cm^{-2}$ after 50 cycles) even at a low electrolyte/sulfur ratio of 8.3 $\mu L\cdot mg^{-1}$.

Generally, the free-standing sulfur host eliminated the inactive and low electronic conductivity binder, and thus improved the electrochemical performance of Li-S batteries [69]. Wu's group reported an inimitable free-standing sulfur host with an ultralight feature, and the ultrafine Co nanoparticles (ca. 5 nm) evenly disperses in N-doped porous carbon nanocages and supported by 3D graphene network (Co/N-PCN@rGO, Fig. 4c—e) [70]. The Co nanoparticles, N-doped porous carbon nanocages and 3D graphene network ensure fast reaction kinetics of LiPSs, high sulfur content and accelerated electron transport, respectively. Therefore, Co/N-PCN@rGO@S delivers a superior

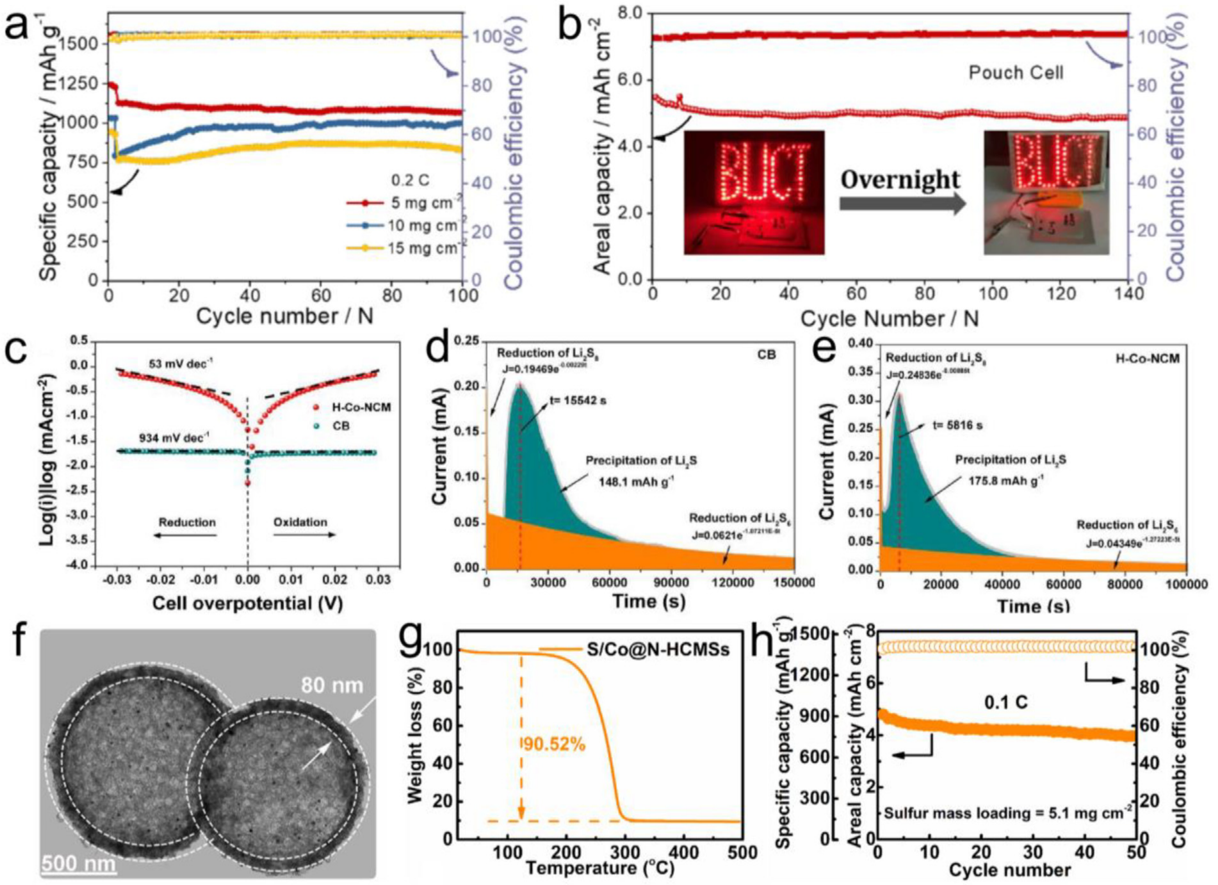

Fig. 3. (a) Cycling performance of Co-N-CNTA/S electrode with different sulfur loadings (5 mg·cm^{-2}, 10 mg·cm^{-2} and 15 mg·cm^{-2}). (b) Cycling performance of Li/Co-N-CNTA/S pouch cell (the insert: the optical photographs of light-emitting diodes lighted by the pouch cell). Reproduced with permission [55]. Copyright 2019, American Chemical Society. (c) Tafel plots of CB and H-Co-NCM. Fitting of current-time profile for a potentiostatic discharge at 2.05 V on (d) CB and (e) H-Co-NCM. Reproduced with permission [57]. Copyright 2020, Elsevier. (f) TEM image of Co@N-HCMSs. (g) TGA curve of S/Co@N-HCMSs. (h) Cycling performance of S/Co@N-HCMSs. Reproduced with permission [59]. Copyright 2021, Elsevier.

electrochemical performance. Similarly, Peng and co-workers prepared a freestanding Co/N-PCNF (3D interconnected, Co decorated and N-doped porous carbon nanofiber network) as a sulfur host by electrospinning [71].

3. Cobalt single atoms/carbon composites as sulfur hosts

It is well known that the selectivity and activity of an appointed electrocatalyst are strongly associated with the intrinsic activity and quantity of surface active sites. In general, the active sites can be significantly improved by reducing the size of catalyst particles to enhance their surface area [72−74]. Therefore, reducing the size of catalyst particles is an effective strategy to increase the electrocatalytic activity of the electrocatalyst. Single atom catalysts (SACs) are the ultimate small-size limit for electrocatalysts, which contain single atoms coordinated by various non-metal atoms and dispersed on different substrates [75−77]. SACs not only show a maximal utilization of the active sites but also exhibit the advantages of high catalytic activities and selectivity [78−80]. Hence, SACs have been considered as promising electrocatalysts for high-performance Li-S batteries.

In 2019, Ji's group reported a Co SAC (monodisperse Co atoms embedded in nitrogen-doped graphene (Co-N/G)) as the host material for Li-S batteries [81]. As shown in Fig. 5a, the Co atoms are well-dispersed on the graphene. The atomistic coordination configuration of Co single atoms was investigated by X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) techniques. The results revealed that the Co atoms in Co-N/G form Co-N-C coordination centers via coordination with N atoms. When using Co-N/G as the host material, the overpotential for phase evolution between the soluble LiPSs and insoluble Li_2S_2/Li_2S during the charge and discharge processes was significantly

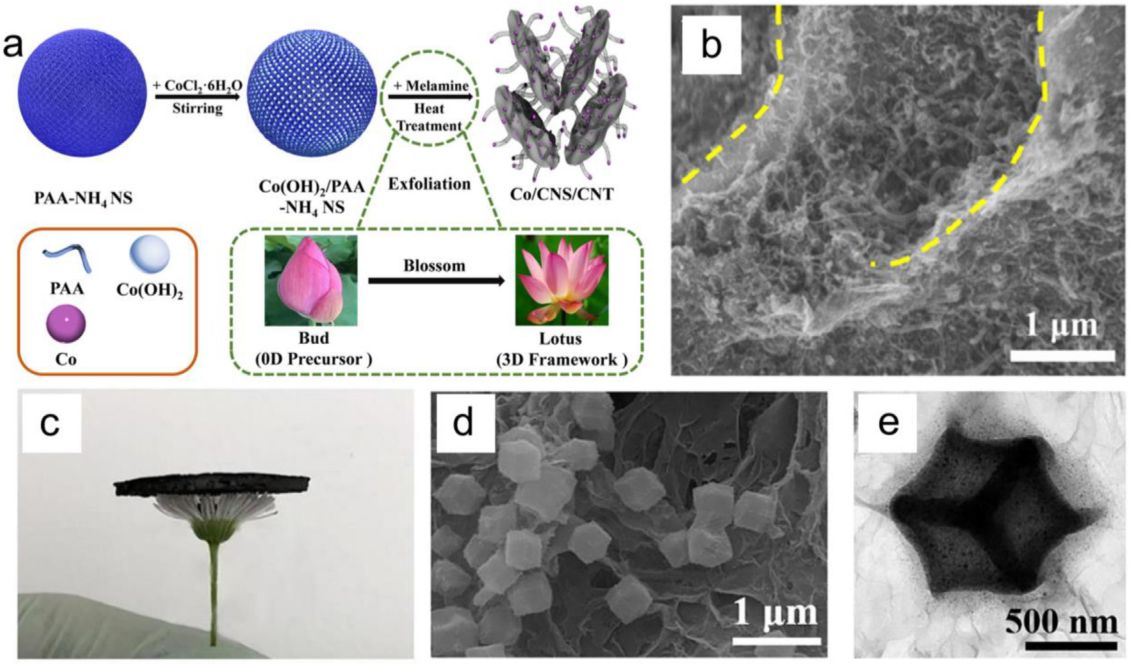

Fig. 4. (a) Schematic illustration of Co/CNS/CNT preparation. (b) SEM image of Co/CNS/CNT. Reproduced with permission [67], Copyright 2021, American Chemical Society. (c) Free-standing and ultralight feature of Co/N-PCN@rGO composites. (d) FESEM and (e) TEM images of Co/NPCN@rGO composites. Reproduced with permission [70], Copyright 2020, Elsevier.

decreased (Fig. 5b and c). The electrochemical reaction processes of S@Co-N/G were further revealed by operando XANES spectra (Fig. 5d). It is worth noting that the Li_2S is observed at the incipient of discharge. The unique phenomenon and lowered overpotentials of S@Co-N/G disclosed that the Co-N/G is in favor of the formation and decomposition of Li_2S. Meanwhile, first-principles calculations also demonstrate that the Co-N-C centers in Co-N/G play a key role in facilitating the formation and decomposition of Li_2S during the (de)lithiation process (Fig. 5e). Therefore, S@Co-N/G composite with an ultrahigh sulfur content (90 wt%) exhibits a high initial discharge capacity of 1210 $mAh \cdot g^{-1}$ and good rate performance (618 $mAh \cdot g^{-1}$ at 4 C). When S loading increases to 6.0 $mg \cdot cm^{-2}$, the electrode still delivers an areal capacity of 5.1 $mAh \cdot cm^{-2}$ with superior cycling stability (a capacity retention of 97.1% after 100 cycles). This work indicated that the Co single atoms show huge potential for high-performance Li-S batteries.

Thereafter, more and more groups focus on developing high-performance Co single atom-based electrode materials for Li-S batteries. For example, Huang and co-workers prepared Co single atom-based host materials for Li-S batteries via applying an unusual binary Co-Zn zeolitic imidazolate frameworks (CoZn-BZIF) as precursors (Fig. 6a) [82]. The Zn and Co are uniformly distributed in CoZn-BZIF because of the same coordination of Zn^{2+} and Co^{2+} with 2-mehylimidzole. When Zn^{2+} is removed from CoZn-BZIF, the nitrogen occupies the open sites and coordinates with Co^{2+}, which effectively inhibits the particle coalescing. Therefore, the Co single atoms evenly distribute on the polyhedron-shaped nitrogen-doped carbon matrix (Co-SAs@NC). As shown in Fig. 6b−d, Co-SAs@NC as host materials exhibit the best rate performance and cycling stability. The reason for the superior electrochemical performance of S@Co-SAs@NC was investigated by experimental and theoretical calculations. The results disclosed that the distinctive component of Co-N_4 in Co-SAs@NC can effectively trap LiPSs, as well as can electrochemically catalyze the reversible conversion of both high-order and low-order LiPSs, mitigating the polysulfide shuttling effect. Subsequently, a conjugated microporous polymer (CMP) with unique structures and tunable functionality is also used as a support for Co single atom catalyst and applied in Li-S batteries [83]. The Co-CMP (Co single atoms uniform dispersed in CMP) was prepared by standard Sonogashira coupling methodology. Both the XANES spectroscopic study and DFT simulations revealed that the Co-CMP can effectively facilitate the conversion between the polysulfides and Li_2S. Therefore, the Co-CMP electrode exhibits higher Li-ion diffusion coefficients (1.3×10^{-9} and 2.77×10^{-9} $cm^2 \cdot s^{-1}$) and lower charge transfer resistance (47.90 Ω). The S@Co-CMP delivers good cycling stability and rate performance.

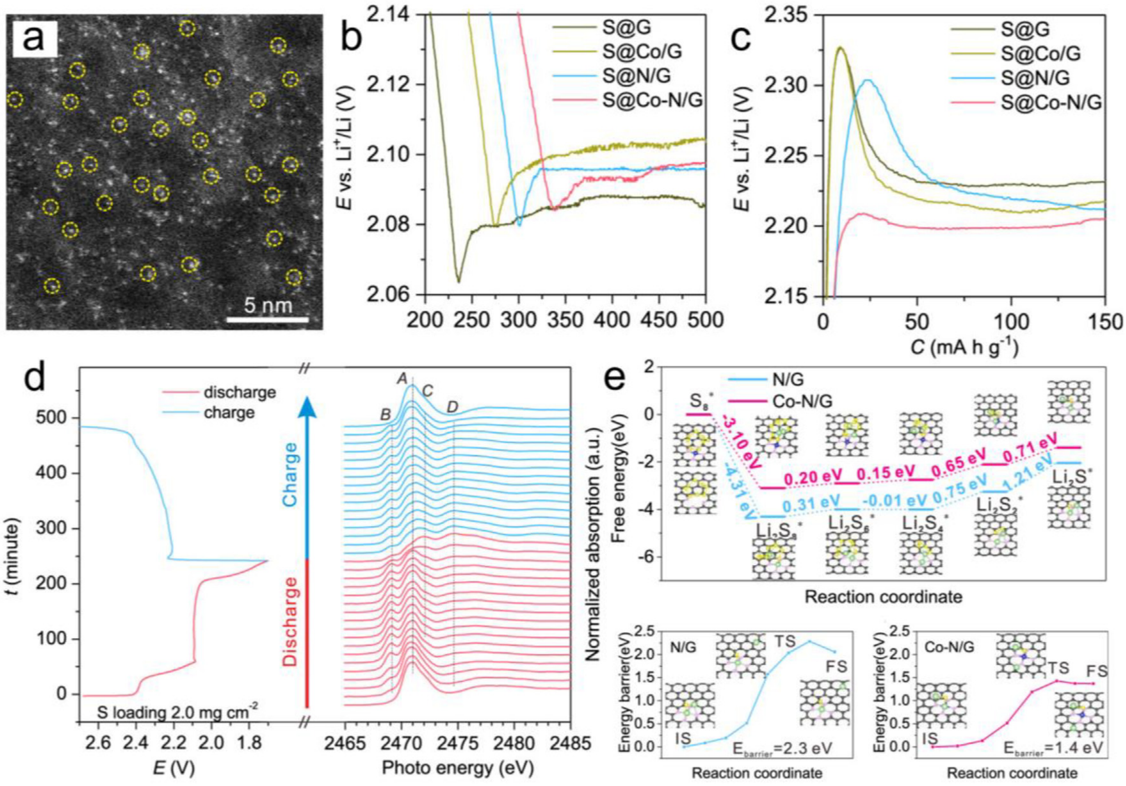

Fig. 5. (a) HAADF-STEM image of Co-N/G composite. (b) Discharge and (c) charge curves showing the overpotentials for phase evolution between the LiPSs and Li_2S_2/Li_2S. (d) Evolution of S K-edge XANS during the charge/discharge process. (e) Energy profiles of the reduction of LiPSs (top) and the decomposition of Li_2S (bottom) on different substrates. Reproduced with permission [81], Copyright 2019, American Chemical Society.

Recently, hollow carbon spheres are also applied as a support for Co single atoms because of their high electrical conductivity and huge voids. Liu's group proposed incorporating Co single atoms into the nitrogen-doped hollow carbon sphere (ACo@HCS) [84]. The ACo@HCS was obtained by applying SiO_2 nanosphere as a hard template with polymerization and controlled pyrolysis (Fig. 7a and b). The Co single atom not only can effectively absorb LiPSs, but also accelerate the electrochemical reaction kinetics of LiPSs, thus avoiding the polysulfide shuttling effect. The ACo@HCS-S electrode delivers excellent cycling stability, a high capacity of 1003 $mAh \cdot g^{-1}$ after 500 cycles at 1.0 C with a capacity decay of 0.002% per cycle (Fig. 7c). Most recently, Wang et al. prepared an ultrathin porous 3D nitrogen-doped carbon-supported Co single atom catalyst (SACo/NDC) via applied NaCl as the soluble template with a facile freeze-drying-sintering method and applied it as a sulfur host for Li-S batteries [36]. The NaCl not only is in favor of the uniform dispersion of Co single atoms, but also promotes the formation of the connected 3D porous framework. The Co single atoms accelerate the conversion of LiPSs during cycling, resulting in high utilization of S and low polarization. Meanwhile, the ultrathin 3D carbon framework provides suitable space for uniform S loading, enables fast transfers of ions and electrons, alleviates volume change and inhibits polysulfide shuttling. Therefore, the SACo/NDC@S cathodes deliver superior cycling stability and good rate performance.

In general, the electrocatalyst performance is closely related to the content of single metal atoms. However, the reported Co single atom-based S host usually shows a low Co loading. Therefore, increasing the content of Co single atom is an effective way to further improve the electrochemical performance of Li-S batteries. For example, Sun's group synthesized monodispersed Co single atoms embedded in nitrogen-doped carbon nanosheets with a high Co content of 15.3 wt% (CoSA-N-C) via a facile salt-template method (Fig. 7d) [85] During the pyrolysis process, the existence of KCl template effectively mitigates the shrinking of the ZIF-67 layer, making the carbon supports possess densely distribute Co single atoms and Co-N moiety. The obtained CoSA-N-C as host materials owns various merits: (i) The deposition of Li_2S was regulated by the CoSA-N-C, which facilitates the high sulfur utilization and high conductivity during the electrochemical process. (ii) The electrochemical reaction

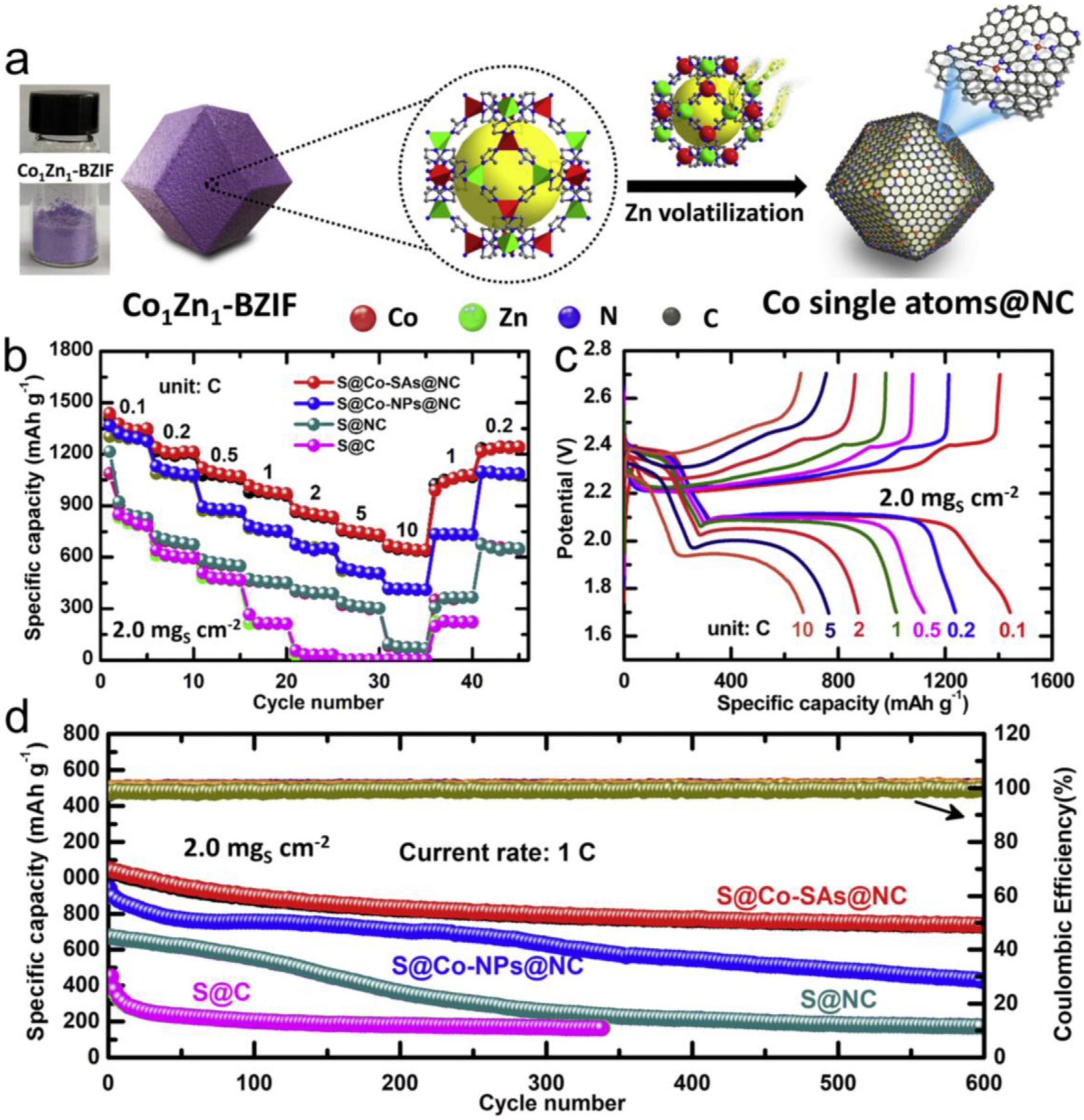

Fig. 6. (a) Schematic illustration of Co-SAs@NC preparation. (b) Rate performance of different samples. (c) The discharge/charge curves of S@Co-SAs@NC at various current densities. (d) Cycling performance of different samples. Reproduced with permission [82], Copyright 2020, Elsevier.

kinetics was significantly improved because the atomic Co-N_4 structure can promote the conversion of polysulfide and decrease the kinetic barrier of Li_2S decomposition. (iii) A high content of Co single atoms provides abundance sites to trap polysulfide and the N dopants bind the LiPSs molecules, both of them can effectively alleviate the polysulfide shuttling effect. (iv) The large surface area of CoSA-N-C ensures a high sulfur content (74.2 wt%) and high conductivity enables fast ion/mass transfer during the charge/discharge process. Benefiting from the above merits, the CoSA-N-C@S electrode delivers a high specific capacity (1574 $mAh\cdot g^{-1}$), good rate performance (624 $mAh\cdot g^{-1}$ at 5 C) and outstanding cycling stability (an ultrahigh capacity of 91.8% even after 120 cycles).

The practical application of Co single atom-based sulfur host for Li-S batteries was investigated by Zhao's group [86]. They proposed host materials design concept to realize an excellent electrochemical performance of Li-S pouch cell (Fig. 8a). The Co-N-C SAC and polar ZnS nanoparticles were applied as double-end binding (DEB) sites and even embedded into a highly oriented macroporous conductive framework (3d-omsh/ZnS,Co-N-C). The highly oriented macroporous conductive framework ensures a high sulfur content (ca. 78.2 wt%) and accelerates the transfer of ion/electron, which is responsible for the triple-phase (conductive support, catalyst, and electrolyte) boundary formation and high sulfur utilization. The DEB sites display a strong

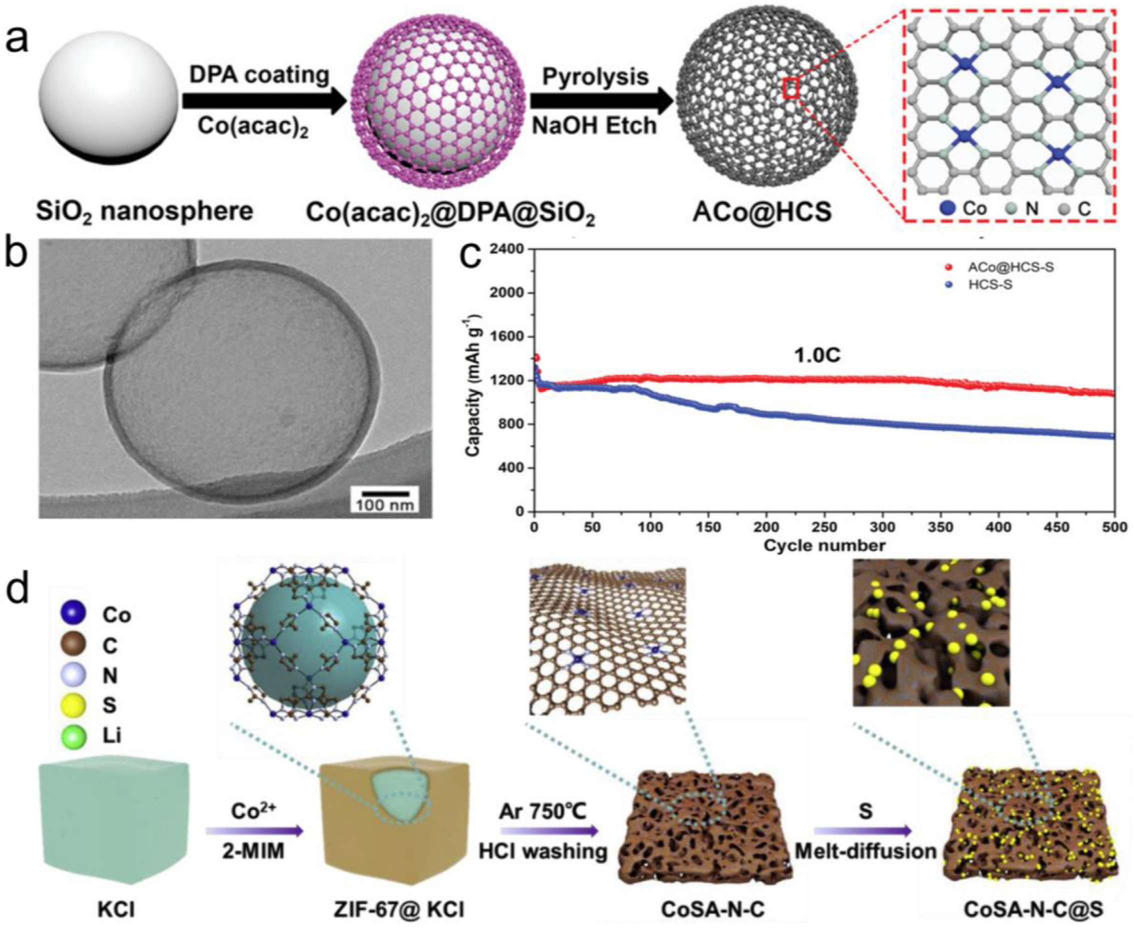

Fig. 7. (a) Schematic illustration for the synthesis process of ACo@HCS; (b) High-magnification TEM image of ACo@HCS; (c) Cycling performance of ACo@HCS-S and HCS-S. Reproduced with permission [84], Copyright 2022, Wiley-VCH; (d) Schematic illustration showing fabrication procedure of CoSA-N-C@S. Reproduced with permission [85], Copyright 2020, Elsevier.

confinement effect and high catalytic effect for LiPSs, resulting in improved electrochemical redox kinetics and effectively eliminating the polysulfide shuttling effect. The polysulfide shutting effect of 3d-omsh/ZnS,Co-N-C/S cathode was investigated by the time-of-flight secondary ion mass spectrometry (ToF-SIMS). The ToF-SIMS depth profiles and 3D rendering of S^- secondary ion in different cathodes are shown in Fig. 8b—d, and the 3d-omsh/Co-N-C/S shows the weakest intensities of the S^- peaks and the thinnest S migration layer. In addition, the Li metal anode combined with 3d-omsh/ZnS,Co-N-C/S cathode exhibits the weakest S signal. The results demonstrated that the polysulfide shuttling effect was eliminated by applying 3d-omsh/Co-N-C as a sulfur host. As a result, the 3d-omsh/ZnS,Co-N-C/S electrode shows the best cycling stability (93.86% capacity retention after 100 cycles) and rate performance. Even at high sulfur loadings of 6 $mg\cdot cm^{-2}$ and 9 $mg\cdot cm^{-2}$, 3d-omsh/Co-N-C/S electrodes still exhibit high capacity retention values of 92.3% and 86.7% after 100 cycles, respectively. To evaluate the potential of 3d-omsh/ZnS,Co-N-C/S cathode for practical application, an Ah-level Li-S pouch cell with high sulfur loading (1.2 g), thin Li anode (only 100% excess, corresponding to an anode/cathode capacity ratio of ca. 2.6) and low E/S ratio (4 $\mu L\cdot mg^{-1}$) was assembled. The Ah-level pouch cell delivers a practical specific energy of 317 $Wh\cdot kg^{-1}$ with good cycling performance (a capacity retention of ca. 74% after 80 cycles) and high Coulombic efficiency (>95%). The superior electrochemical performance of Ah-level Li-3d-omsh/ZnS,Co-N-C/S pouch cell indicated that the 3d-omsh/ZnS,Co-N-C/S cathode shows a huge potential for practical application.

4. Conclusions and perspectives

Li-S batteries are considered as the most promising candidate for alleviating the range anxiety of drivers due to their high theoretical energy density (2600 $Wh\cdot kg^{-1}$) and potentially low cost. However, the S cathode still suffers from slow charge

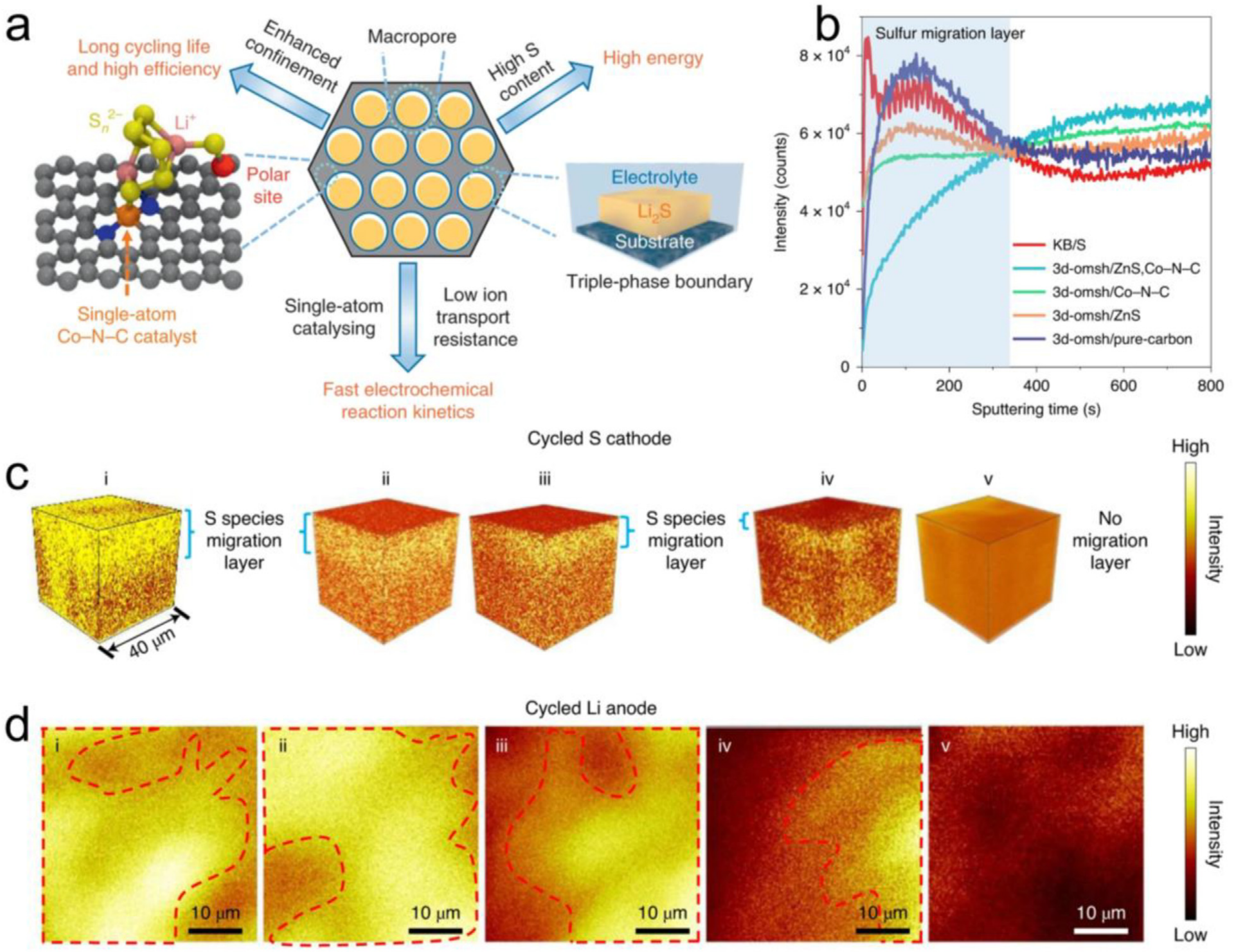

Fig. 8. (a) Schematic illustration of design strategy for the macroporous host with DEB sites. (b) ToF-SIMS depth profiles and (c) 3D rendering of S^- secondary ion distribution of various cycled cathodes and (d) ToF-SIMS S^- element mappings on the surface of cycled Li metal anode in various cells (i: Li-KB/S, ii: Li-3d-omsh/pure carbon/S, iii: Li-3d-omsh/ZnS/S, iv: Li-3d-omsh/Co-N-C/S, v: Li-3d-omsh/ZnS,Co-N-C/S) after 100 cycles at 1.0C. Reproduced with permission [86], Copyright 2021, Springer Nature.

transfer, sluggish electrochemical reaction kinetics, shuttle effect of LiPSs, and huge volume expansion/shrinking during the charge/discharge process, which inevitably hinder their practical application. Herein, we have summarized the recent progress on Co/carbon composites as sulfur hosts for Li-S batteries. In general, Co/carbon composites as sulfur hosts own various advantages (facilitated ion/electron transfer, accelerated reversible conversion of Li_2S_n, strong absorption of LiPSs, effective stress relief, Fig. 9), resulting in high reversible capacity, excellent rate performance, and outstanding cycling stability. To better understand the potential of discovering the Co/carbon composites as sulfur hosts for Li-S batteries, the electrochemical performances (reversible capacity, rate performance, and cycling stability) of some representative Co/carbon composites as sulfur hosts are shown in Table 1.

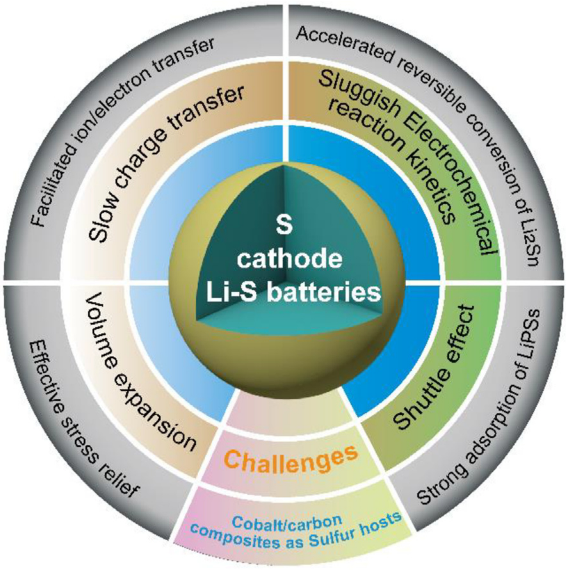

Fig. 9. Summary on the key challenges of S cathode for Li-S batteries and the advantages of Co/carbon composites as sulfur hosts.

Table 1. Comparison of the representative Co/carbon composites as sulfur hosts for Li-S batteries.

Cathode	Co content (wt%)	S content (wt%)	S loading ($mg \cdot cm^{-2}$)	Initial discharge capacity ($mAh \cdot g^{-1}$) /current density (C, 1.0 C = 1675 $mA \cdot g^{-1}$)	Rate performance (reversible capacity [$mAh \cdot g^{-1}$]/current density [C, 1.0 C = 1675 $mA \cdot g^{-1}$])	Cycle performance (capacity retention [%]/ current density [C, 1.0 C = 1675 $mA \cdot g^{-1}$]/ cycle number)	Ref.
S@Co-N-GC	38.6	70	2–2.5	1670/0.05	565/5	54.3/1/500	[47]
MC-NS/S	–	86	1.5	1618/0.1	529/5	77.4/0.2/100	[48]
S@Co-BIDC	0.94	71	1.2	1219/0.1	364/2	79/1/300	[49]
N-PC@uCo/S	6.09	76	1.8	1370/0.1	600/5	86/1/500	[50]
Co-N-CNTA/S	–	~40	2	1045/1	–	77.89/1/1000	[55]
80S/h-Co-BN-GC	10.9	79.6	1.3–1.4	1205/0.2	705/2	80.5/0.5/500	[56]
S@H-Co-NCM	–	82	2	1374/0.1	611/2	65.5/0.5/500	[57]
S@Co-NHGC	–	65	1–1.5	1600/0.1	600/3	50/3/400	[58]
S/Co@N-HCMSs	26.5	75.13	1	1203/0.1	692/4	60/1/500	[59]
Co-NCG/S	0.7	50	1–1.2	1355.3/0.1	578.9/5	80/1/200	[62]
Co/Co-N_x@NG/S	–	74	1.02	1300.3/0.1	884.2/2	51.4/2/705	[63]
RGO/C-Co-S	44.1	59	1.0	1218/ca. 0.18	479/ca. 3	78.1/0.18/300	[64]
S/N-Co-C@G-CNTs	–	79.6	1.87	1227.5/0.2	632.5/5	88.9/2/1000	[65]
CNT-NC@GC/S	2.5	79.2	1.3–1.4	1498/0.1		87.2/0.1/100	[66]
Co/CNS/CNT-S	–	69.7	4.0	1040/0.1	ca. 799/1	79.3/0.5/200	[67]
S/Co-GC@GPCA	3	63.33	2.04	939.9/0.1	439.1/2	56.2/1/504	[68]
Co/N-PCN@rGO@S	7.5	74	2.0	1290/0.2	880/2	67/1/500	[70]
Co/N-PCNF@S	–	62.2	2.0–3.0	1048/0.2	672/3	83/1/200	[71]
S@Co-N/G	–	90	2.0	1210/0.2	618/4	73.5/1/500	[81]
S@Co-SAs@NC	0.66	76	2.0	1438/0.1	670/10	ca. 70/1/600	[82]
S@Co-CMP	2.32	16	1.1	1336/0.1	766/2	55/0.5/1000	[83]
ACo@HCS-S	–	76.9	2.0	1322/0.1	794/2	99/1/500	[84]
SACo/NDC@S	3.15	65	1.5	1075.3/0.1	517.5/3	76/0.5/300	[36]
CoSA-NC@S	15.3	74.2	1.2	1574/0.05	624/5	65/1/1000	[85]

To meet the requirements for high-performance Li-S batteries, we strongly suggested that further researches on Co/carbon composites as sulfur hosts focus on the following aspects. (i) Despite various characterization techniques have been applied to disclose the action mechanisms of Co/carbon composites in Li-S batteries, insights into the action mechanism at the atomic scale are still scarce. Thus, the development of advanced *in situ* characterization techniques and DFT calculations are very meaningful. (ii) Although Co/carbon composites as sulfur hosts for Li-S batteries show superior electrochemical performance, the preparation process of Co/carbon composites is still complex to some extent. Therefore, it is urgent to develop facile, low-cost, and scalable strategies to achieve the large-scale preparation of high-performance Co/carbon composites as sulfur hosts. (iii) Until now, the electrochemical performance of Co/carbon composites as sulfur hosts is generally evaluated by coin-type cells with relatively low S loading, high electrolyte/S ratio, and an excess of lithium. In this regard, it is very significant to evaluate the potential of practical application by assembling Ah-level Li-S pouch cells with a high S loading, low electrolyte/S ratios, and limited cathode/anode ratios.

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高性能锂硫电池用钴/碳复合材料硫宿主

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摘要

锂硫电池由于具有较高的能量密度而被认为是极具发展前景的储能设备之一。然而，硫正极遭遇迟缓的反应动力学、缓慢的电荷转移、大的体积膨胀、严重的多硫化锂穿梭效应，这些问题不可避免地导致锂硫电池表现出低的可逆容量、差的倍率性能、短的循环寿命，限制了锂硫电池的实际应用。本文总结了钴/碳复合材料（包括钴纳米颗粒和钴单原子）作为硫宿主的研究进展。总的来说，钴扮演着电催化剂的角色，能够抑制多硫化锂的穿梭效应，加快电化学反应动力学，促进离子/电子转移以及缓解体积膨胀。同时，我们展望了钴/碳复合材料作为锂硫电池硫宿主的发展前景。本工作可为钴/碳复合材料作为锂硫电池硫宿主提供完整的蓝图和建设性的建议，同时这些策略也可用于其他金属-硫电池。

关键词：锂硫电池；硫宿主；钴/碳复合材料；电催化剂；电化学性能