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Metal Atom-Decorated Carbon Nanomaterials for Enhancing Li-S/Se Batteries Performances: A Mini Review

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Lithium-sulfur (Li-S) and lithium-selenium (Li-Se) batteries are both facing the cathode issues of low Coulombic efficiency and unstable cycling stability due to the severe shuttle effect of lithium polysulfides or lithium polyselenides. Simultaneously inhibiting polysulfides/polyselenides dissolution in organic electrolytes and propelling them to conversion via introducing polar, catalytic materials has been proven as an effective strategy to enhance the durability of Li-S and Li-Se batteries. In this mini review, we systematically introduce various metal atom-decorated carbon nanomaterials to determine how to enhance the electrochemical performances of Li-S and Li-Se batteries by inhibiting the polysulfides/polyselenides shuttle phenomenon as well as catalyzing them toward quick redox conversions. We also briefly include the drawbacks and bottlenecks of this kind of material when used in Li-S and Li-Se batteries

Keywords: metal atoms, decorated, carbon nanomaterials, Li-S batteries, Li-Se batteries

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INTRODUCTION

The expanding electric vehicle market and the popularization of smart grids has triggered the urgent demand for energy-storage devices with long-cycle life and high-energy density (Ma et al., 2020b; Sheng et al., 2020). Li-S and Li-Se batteries have been commonly regarded as appealing choices for high-energy storage technology as they demonstrate high theoretical energy density (2,600 Wh kg^{-1} and 2,800 Wh L^{-1} for Li-S battery; 1,160 Wh kg^{-1} and 2,600 Wh L^{-1} for Li-Se battery) as well as acceptable low costs (Gu and Lai, 2019; Jin et al., 2020).

However, there are still many technical challenges, from the electrolyte to the anode as well as the cathode, for Li-S/Se batteries that need to be tackled (Chen et al., 2019a; Yan et al., 2019; Liu et al., 2020b). In terms of the cathode, Nazar's group first employed the CMK-3 as the sulfur host to effectively inhibit polysulfide shuttling (Ji et al., 2009), since then scientists have spent a significant portion of time and energy on how to inhibit the serious shuttle phenomenon of Li polysulfide (LiPS) and Li polyselenide (LiPSe) intermediates during the charge/discharge process. From the very beginning the physical adsorption of porous carbon (Gu et al., 2015b), to the chemical adsorption of heteroatoms doped in a carbon framework (Gu et al., 2015a; Gu et al., 2016b; Gu et al., 2018; Gu et al., 2020b), until now the stronger chemical adsorption by employing various carbon/metal compounds (Gu et al., 2016a; Gu and Lai, 2017; Gu et al., 2020a), the LiPS and LiPSe shuttle phenomenon has been significantly alleviated. Without doubt, a carbon host was the most popular choice to address

the problems of Li-S and Li-Se cells during the past decades as it had high conductivity and good adsorption force with LiPS and LiPSe (Zeng et al., 2017; Zheng et al., 2019; Li et al., 2020b; Han et al., 2020).

However, recent research found that if the sluggish redox kinetics, with increased internal resistance cause low S/Se utilization and poor Coulombic efficiency (CE) did not address (Gu and Lai, 2019; He and Manthiram, 2019; Lim et al., 2019; Song et al., 2019; Ruan et al., 2020) the cathode problems of Li-S/Se batteries, these problems would be impossible to solve completely even if the immediate shuttle effect was effectively restrained using various carbon-based hosts. Therefore, researchers around the world are gradually focusing on how to improve redox kinetics and limit the shuttle effects of LiPS/LiPSe simultaneously (Zhang et al., 2019f; Hong et al., 2020).

Interestingly, nano-sized catalysts including single-atom catalysts recently demonstrated excellent catalytic properties compared to conventional catalysts (Liu, 2016; Cao et al., 2018; Cui et al., 2018; O'Connor et al., 2018; Zhang et al., 2019b). However, scientists also found that single-atom catalysts were not easily prepared. An effective strategy is to deposit the ultra-small metal nanoparticles on the carbon surface or dope the metal atoms in the carbon framework to produce a so-called single-atom-like catalyst (Gawande et al., 2020; Ren et al., 2020). As expected, the single metal atom-decorated (deposited/doped) carbon catalysts illustrated excellent catalytic performances on oxygen reduction reaction (Wang et al., 2020b; Ren et al., 2020), oxygen evolution reaction (Hou et al., 2019; Wang et al., 2020b), hydrogen evolution reaction (Zhang et al., 2019d; Ren et al., 2020), CO_2 reduction reaction (Wang et al., 2019a; Lu et al., 2019; Yang et al., 2019), and nitrogen electroreduction (Chen et al., 2018b), etc.

As the metal atom-decorated carbon materials not only have an excellent catalytic property that could effectively catalyze the polysulfides conversion during the charge/discharge process, but also provide strong chemical adsorption on polysulfides due to the polar metal atoms/heteroatoms. Therefore, an increasing number of investigations reported the simultaneous use of metal atom-decorated carbon materials as catalysts and shuttle inhibitors for LiPS and LiPSe. And this mini-review has summarized how the performances of Li-S and Li-Se batteries could be improved by these various kinds of metal atom-decorated carbon nanomaterials.

METAL ATOM-DECORATED CARBON NANOMATERIALS FOR ENHANCING LI-S BATTERIES PERFORMANCES

Reducing particles size to nanometers or even to an atomic scale has emerged as a promising route to extend the reactivity of materials. In this part, nano-metal atoms including single metal atom-decorated carbon materials for enhancing Li-S batteries will be introduced in detail.

Noble Metal Atom-Decorated Carbon Materials

The noble metals, such as Au (Babu et al., 2015; Zhang et al., 2020), Pt (Al Salem et al., 2015; Qu et al., 2018; Liu et al., 2019), and Pd (Ma et al., 2019), etc., when combined with the conductive carbon substrates, commonly demonstrate superior catalytic properties on LiPS redox reactions.

In 2015, Arava's group first proposed an electrocatalysis concept in non-aqueous polysulfides redox reactions (Babu et al., 2015). They found that coating Pt or Ni on Al foil as the electrocatalytic current collectors could enhance both cycle life and reaction kinetics of the Li-S battery. Before long they reported that dispersed Pt nanoparticles on graphene layers could enhance the specific capacity by 40% over pristine graphene due to the excellent catalytic property of Pt nanoparticles, and such a Pt/graphene can also contribute to sulfur cathode stability cycling over 100 cycles with a Coulombic efficiency of 99.3% at a current rate of 0.2 C (Al Salem et al., 2015). Interestingly, in this work, Arava et al. also found that the Pt/graphene host could improve more performances for Li-S batteries compared to the Ni/graphene as shown in **Figures 1B,C**. Zhang et al. reported a nanoscale polysulfide reactor achieved by a chemical Au–S interaction as shown in **Figure 1D** (Fan et al., 2015). The Au NPs with high conductivity can significantly control the deposition of the trapped LiPSs, contributing to the uniform distribution of sulfur species upon charging/discharging. Recently, Liang et al. reported a yolk–shell Au@microporous carbon nanosphere with the synergistic advantages of a hollow nanosphere and functional Au nanoparticles (Zhang et al., 2020), which also contributed to a high specific capacity, and good electrochemical activities and reaction kinetics of Li-S batteries. While Zuo's group skillfully imbedded palladium nanoparticles in hollow carbon spheres as the sulfur host. The Pd nanoparticles acted not only as electrocatalysts to accelerate the redox reaction kinetics of LiPS but also chemically trapped LiPS via the moderate Pd-S bonding.

The present investigations have proven the efficient catalytic function of LiPS by introducing noble metal atoms into the carbon, however, as shown in **Table 1**, the enhanced performances of Li-S batteries are not ideal, particularly on long cycling performances with higher sulfur loading.

Iron Series Metal Atom (Fe, Co, Ni)-Decorated Carbon Materials

Due to the high prices of noble metals, in recent decades, scientists have been devoted to developing noble-free catalysts, in which the iron series metal-carbon materials are regarded as one of the most promising catalysts. And there are large numbers of literature on this kind of catalyst application in different fields. Taking into account the good conductivity, good physical/chemical adsorption ability, and redox of LiPS, iron series metal atom-decorated carbon materials have begun to pique the interest of Li-S batteries researchers in the last three years (Li et al., 2016; Li et al., 2019f; Zhang et al., 2019g; Jin et al., 2019).

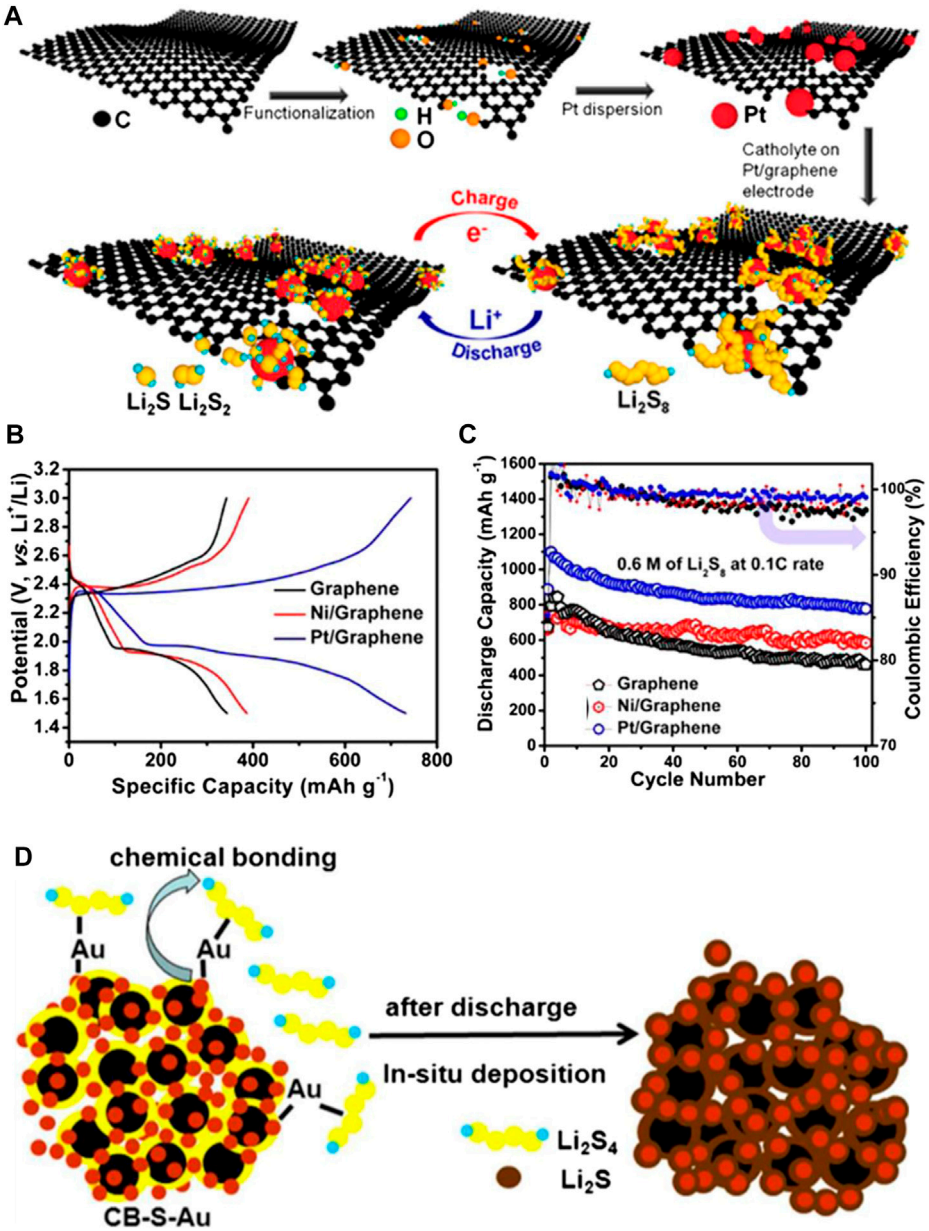

FIGURE 1 | (A) Schematic illustration of electrocatalyst-anchored graphene nanocomposite preparation and its interaction with PS during the charge/discharge process of the Li–S battery **(B)** voltage vs specific capacity profile and **(C)** galvanostatic charge/discharge behavior and Coulombic efficiency of pristine and electrocatalyst-anchored graphene electrodes vs Li^+/Li at 0.1 C rate in the potential range of 1.5–3.0 V. Reproduced with permission from Al Salem et al. (2015). Copyright © 2015 American Chemical Society **(D)** The function mechanism of the CB-S-Au cathode. Reproduced with permission from Fan et al. (2015). Copyright © 2015 American Chemical Society.

Cobalt-nitrogen doped carbon materials as the sulfur/Li_2S host are most frequently reported (He et al., 2016; Zhong et al., 2018; Hu et al., 2019; Li et al., 2019a; Li et al., 2019d; Wu et al., 2019; Yu et al., 2019; Liu et al., 2020a; Shao et al., 2020; Wang et al., 2020a; Wang et al., 2020c; Wang et al., 2020e; Yao et al., 2020). In 2017, Dong et al. reported a honeycomb-like Co@N–C composite that served as the sulfur host as shown in **Figure 2A** (Li et al., 2017). The cellular flake with a large surface area and honeycomb architecture could encapsulate much more sulfur, leading to high sulfur content (93.6 wt% and 7.5 mg cm^{-2} in an electrode) and the Co-N-C coordination center served as a bifunctional electrocatalyst to facilitate both the formation and the decomposition of Li_2S in the discharge and charge process as shown in **Figure 2B**. The S/cellular Co–N–C composites exhibited excellent rate performance up to 10 C (3.6 mg cm^{-2}) and great cycling stability as shown in **Figure 2C**. Huang's group implanted atomic cobalt within the skeleton of mesoporous carbon via a

TABLE 1 | Various noble metal atom-decorated carbon materials for enhancing the performances of Li-S batteries.

Composite name	Roles in Li-S batteries	Sulfur content (wt%) in the electrode	Sulfur loading in the electrode (mg cm^{-2})	Capacity performance (mAh g^{-1})	Cycle number	Test currents (C, 1C = 1,675 mA g^{-1})	References
Pt nanoparticles on graphene	Catalyst	–	1.21	789	100	0.2	(Al Salem et al., 2015)
Platinum and nitrogen dual-doped ordered mesoporous carbon	Sulfur host	67.5	2.0	505.5	100	0.2	(Qu et al., 2018)
C@PtNi	Sulfur host	60	1.2–1.5	600	300	1	(Liu et al., 2019)
Carbon black-Au	Sulfur host	50	1.3	641	160	0.5	(Fan et al., 2015)
Au@microporous carbon nanospheres	Sulfur host	50	0.5	664	40	0.1	Zhang et al., 2020)
Palladium nanocrystal-imbedded mesoporous hollow carbon spheres	Sulfur host	74.6	5.88	885	100	0.2	(Ma et al., 2019)

supramolecular self-templating strategy (Xie et al., 2019). The atomic cobalt sites with high polarity exhibited strong interactions with polysulfides and consequently enhanced the kinetics of the sulfur redox reactions (Xie et al., 2019). More importantly, they systematically evaluated the sulfur redox reaction via CV, EIS, Tafel slope, and a potentiostatic nucleation test, which provided a general evaluation criterion of the metal atom-decorated carbon materials for catalyzing the sulfur redox reaction. While Wu's group and Shen's group focused on the function of the Co-N-C bond in Li-S batteries (Du et al., 2019; Xiao et al., 2019). In Wu's work, they employed a combination of operando X-ray absorption spectroscopy and first-principles calculations to reveal that the Co–N–C coordination center served as a bifunctional electrocatalyst to facilitate both the formation and the decomposition of Li_2S in the discharge and charge processes, respectively (Du et al., 2019). The operando XANES experiment (**Figures 2D,E**) revealed the formation of Li_2S at the initial stage of discharge. This early formation of Li_2S, together with the relative electrochemical characterizations, demonstrated the improved electrochemical kinetics during the phase change between the soluble LiPSs and insoluble Li_2S_2/Li_2S on the Co-N/G support. And the DFT calculation in **Figures 2F–H** show that the formation of Li_2S from Li_2S_2 was the rate-limiting step in the whole discharge process as this step had the largest positive Gibbs free energy. The lower Gibbs free energy on Co–N/G (0.71 eV vs. 1.21 eV) for the reduction of Li_2S_2, indicated that the reduction of S was thermodynamically more favorable on Co–N/G than on the N/G substrate. In Shen's report (Xiao et al., 2019), they found during the annealing process that the cobalt atoms will coordinate with N atoms to form Co_4N. Because the electron transferred from Co to the doped N in the carbon matrix, this caused a larger polarization of Co in Co_4N. This synergistic effect between Co and doped N can contribute to increased binding energy between Co_4N and polysulfides (Xiao et al., 2019). Moreover, using the Co-decorated carbon materials as an interlayer or to modify the separator has also been widely reported (Chen et al., 2018a; Zhang et al., 2019c; Li et al., 2020d; Jiang et al., 2020; Song et al., 2020).

Compared to the cobalt-decorated carbon materials, there have been few reported iron and nickel-decorated carbon materials (Yao et al., 2018; Jiang et al., 2019; Li et al., 2019e; Ye et al., 2019; Zeng et al., 2019). Niu et al. prepared a kind of $Ni–N_4$ structure via doping single nickel atoms on nitrogen-doped graphene (Ni@NG) and then employed them to modify the separators of Li–S batteries (Zhang et al., 2019e). The oxidized Ni sites of the $Ni–N_4$ structure acted as LiPS traps, efficiently accommodating polysulfide ion electrons by forming strong S_x^{2-}···Ni–N bonding as well as catalyzing the LiPS redox conversion as shown in **Figure 3A**. As a result, the Li–S battery based on this Ni@NG modified separator illustrated excellent rate performance and stable cycling life with only 0.06% capacity. Hou et al. created a holey Fe, N co-doped graphene (HFeNG) to promote the cycle stability and rate capacity of Li–S batteries (Wang et al., 2019b). Via the X-ray absorption spectroscopy and density functional theory calculations, they first confirmed that the Fe atoms were anchored by 4 N atoms (Fe–N_4 moiety) or 2 N atoms (Fe–N_2 moiety) localized on the graphene sheets and edge of holes, respectively. The Fe–N_2 moiety at the edges could provide stronger adsorption forces on LiPS (**Figures 3B,C**) and the holey structure could promote the mass transportation of Li^+ as well as prohibit the transportation of LiPS (**Figure 3D**). Accordingly, the as-obtained S/HFeNG delivered a high rate capacity of 810 mAh g^{-1} at 5 C and a stable cycling performance with a capacity decay of 0.083% per cycle.

Except for one kind of metal atom-decorated carbon material, binary or ternary metal atom-decorated carbon materials have also been reported for enhancing the performances of Li-S batteries (Chen et al., 2019b; Jing et al., 2019; Li et al., 2019c; Ogoke et al., 2019; Zhang et al., 2019a). For instance, Chen's group reported a CoNi-carbon nanofiber@carbon fabric heterostructure (CoNi-CNF-CF, **Figure 3E**) as the interlayer for Li-S batteries. The weaving carbonaceous scaffold with vertically rooted CNF tentacles facilitated both short- and long-range electrical conduction as well as the efficient exposure of active sites, while the multiple adsorptive and catalytic sites enabled strong sulfur confinement and expedited sulfur conversion. And in this work, they confirmed that the CoNi-CNF@CF showed a stronger current response with a higher deposition capacity as well as a smaller onset potential at around −0.45 V and larger oxidation current compared to

TABLE 2 | Various Fe/Co/Ni-decorated carbon materials for enhancing the performances of Li-S batteries.

Composite name	Roles in Li-S batteries	Sulfur content (wt%) in the electrode	Sulfur loading in the electrode (mg cm^{-2})	Capacity performance (mAh g^{-1})	Cycle number	Test currents (C, 1C = 1,675 mA g^{-1})	References
Co-MOF-derived carbon superstructure	Sulfur host	48.0	1.4	400.86	610	0.5	(Jin et al., 2019)
Reduced graphene oxide/C–Co	Sulfur host	43.4	1	949	300	0.18	(Li et al., 2016)
B,N co-doped carbon nanotubes loaded with Co nanoparticles	Sulfur host	56.9	1.8	1,008	400	1	(Wang et al., 2020e)
Cobalt clusters in nitrogen-doped porous carbon	Sulfur host	52.8	1.8	780	500	1	(Wang et al., 2020c)
Cobalt-embedded N-doped CNTs	Sulfur host	53.2	1.3	428	500	0.6	(Shao et al., 2020)
Carbon nanotube-intercalated Co-N-C	Sulfur host	55.8	0.62	428.3	500	1	(Liu et al., 2020a)
Co embedded N-doped graphitic carbon	Sulfur host		2	556.9	500	2	(Yu et al., 2019)
Cobalt-B, N co-doped-graphitic carbon polyhedrons	Sulfur host	-	1.3	877	500	0.5	(Li et al., 2019d)
Cobalt-coordinated framework porphyrin on graphene	Sulfur host	63.0	2.8	850	300	1	(Li et al., 2019a)
Cobalt–nitrogen–carbon nanotube array	Sulfur host	40.0	2.0	814.0	1,000	1	(Hu et al., 2019)
Co/N-doped carbon nanosheet	Sulfur host	51.2	1.3	694	600	1	(Zhong et al., 2018)
Honeycomb-like Co@N–C	Sulfur host	84.2	3.6	514	850	2	(Li et al., 2017)
Atomic cobalt within mesoporous carbon	Sulfur host		1.2	837.3	300	0.5	(Xie et al., 2019)
Cobalt atoms embedded in nitrogen-doped graphene	Sulfur host	67.5	2.0	681	500	1	(Du et al., 2019)
Co/nitrogen-doped carbon nanosheets/CNT	Sulfur host	64.0	5	522.1	500	1	(Song et al., 2020)
Co/N-doped carbon	Sulfur host and separator modification	64.7	1.5	711.2	1,000	1.0	(Jiang et al., 2020)
Co-N-C/reduced graphene oxide	Separator modification	77.8	1–1.2	615.9	500	0.5	(Chen et al., 2018a)
Cobalt-embedded carbon nanofiber	Current collector	-	4.6	730	300	0.5	(Li et al., 2019f)
Cobalt decorated nitrogen-doped carbon nanofibers	Current collector	-	4.74	938.0	300	0.2	(Yao et al., 2020)
Co_4N nanoparticle/N-doped carbon	Current collector	-	1	745.0	400	1	(Xiao et al., 2019)
Cobalt-anchored nitrogen-doped carbon nanosheets	Interlayer	44.8	1.0	787	100	0.5	(Li et al., 2020d)
Fe-nitrogen-doped graphene	Separator modification		4.5	891.6	750	0.5	(Zhang et al., 2019c)
Fe–N co-doped carbon	Sulfur host	70.0	1.5	565	1,000	2	(Ye et al., 2019)
Hierarchical porous Fe/N-doped carbon nanofibers	Sulfur host	60.0	3.5	1,092	500	0.5	(Jiang et al., 2019)
Holey Fe, N co-doped graphene	Sulfur host	-	2	866.7	300	0.5	(Wang et al., 2019b)
Porous carbon nanofibers assembled with nickel	Sulfur host	72	1.5	910	500	0.2	(Li et al., 2019e)
Ni/G composites	Sulfur host	48.3	1–1.5	830	500	0.2	(Yao et al., 2018)
Single nickel atoms on nitrogen-doped graphene	Separator modification	-	-	965.8	200	1.0	(Zhang et al., 2019e)
CoNi-Embedded nitrogen-enriched porous carbon	Sulfur host	52.5	2	≈550	200	0.2	(Li et al., 2019c)

(Continued on following page)

TABLE 2 | (*Continued*) Various Fe/Co/Ni-decorated carbon materials for enhancing the performances of Li-S batteries.

Composite name	Roles in Li-S batteries	Sulfur content (wt%) in the electrode	Sulfur loading in the electrode (mg cm^{-2})	Capacity performance (mAh g^{-1})	Cycle number	Test currents (C, 1C = 1,675 mA g^{-1})	References
CoFe-Prussian blue analogues derived carbon	Sulfur host	18	-	447.4	500	1	(Jing et al., 2019)
Ni–Fe–P/N-doped Carbon nanobox	Sulfur host	57.6	1.2–1.5	454.6	300	1.0	(Chen et al., 2019b)
FeCoNi-Graphene nanotube	Sulfur host	48	1.0	554.4	500	1	(Ogoke et al., 2019)
NiCo-CNF@CF	Interlayer	56.8	2.1	≈810	1,000	1	(Zhang et al., 2019a)
Nitrogen-doped graphene nanoribbons@Co/CoOOH	Sulfur host	51.7	3.9	516.7	1,000	0.5	(Tan et al., 2020)
Co/CoP@nitrogen-doped carbon	Sulfur host	53.1	2.5	567	1,000	2	(Li et al., 2020c)
Co–TiO_2 nanoparticles anchored in porous carbon	Sulfur host	58.9	1.0	698	200	0.2	(Li et al., 2020a)
Cobalt-doped porous carbon polyhedrons@TiO_2 nanostructure	Sulfur host	-	-	≈530	200	0.5	(Li et al., 2019b)

TABLE 3 | Other transition metal atom-decorated carbon materials for enhancing the performances of Li-S batteries.

Composite name	Roles in Li-S batteries	Sulfur content (wt%) in the electrode	Sulfur loading in the electrode (mg cm^{-2})	Capacity performance (mAh g^{-1})	Cycle number	Test currents (C, 1C = 1,675 mA g^{-1})	References
Samarium-doped carbon aerogel	Sulfur host	61.3	2.3	866	300	0.2	(Sheng et al., 2019)
Cadmium-doped carbon aerogels	Sulfur host	80.2	2.4–2.6	871	300	0.5	(Ma et al., 2020)
Te-decorated ketjen black	Sulfur host	64.45	1–1.2	656	1,000	3	(Xu et al., 2018)
Porous vanadium–nitrogen–carbon	Sulfur host	70	1.0	392.6	500	1	(Fan et al., 2020)
Vanadium single atoms on nitrogen-doped graphene	Sulfur host	80	2.0	485	200	0.5	(Zhou et al., 2019)

Co-CNF@CF. However, why CoNi-CNF@CF could exhibit such superior performances was not clear. While Wu and his co-workers reported a ternary metal atom (Fe, Co, Ni)-decorated graphene nanotube (GNT) material as the sulfur host for Li-S batteries (Ogoke et al., 2019). Compared to Co and CoNi, ternary FeCoNi yielded the largest diameters and the thickest wall of tubes, which increased surface areas and pore volumes with dominant mesopores that benefited from the incorporation of S into the GNT hosts. Moreover, the addition of Fe likely further improved the capacity retention of S@M-GNT cathodes (**Figure 3F**) through providing more favorable graphitic N and active atomic FeN_4 sites, therefore enhancing electrochemical reaction kinetics and chemically/physically encapsulating the sulfur active material.

In addition, a combination of metal atoms and metal compounds to modify the carbon materials is another strategy to construct an effective catalyst and anchor substrate for LiPS (Li et al., 2019b; Li et al., 2020a; Li et al., 2020c; Tan et al., 2020). For example, Yuan et al. reported nitrogen-doped graphene nanoribbons@Co/CoOOH as an integrated sulfur host as shown in **Figure 3G** (Tan et al., 2020). Due to the exceptional electronic conductivity of nitrogen-doped graphene, the strong chemical adsorption and high catalytic activity of Co/CoOOH, the resulted S/nitrogen-doped graphene@Co/CoOOH cathode illustrated an excellent long-duration cyclic performance even with high areal S loading (~3.9 mg cm^{-2}).

Finally, our conclusions about these various Fe/Co/Ni-decorated carbon material applications in Li-S batteries are listed in **Table 2**. As can be seen, these iron series metal atom-doped carbon materials indeed enhance the electrochemical performances of the batteries via strong chemical trapping and excellent catalyzing even at a very high sulfur loading amount.

Other Transition Metal Atom-Decorated Carbon Materials

In addition to the above two categories of metal atom-decorated carbon materials, in recent years, some other transition metal atom-decorated carbon materials as the sulfur host have been

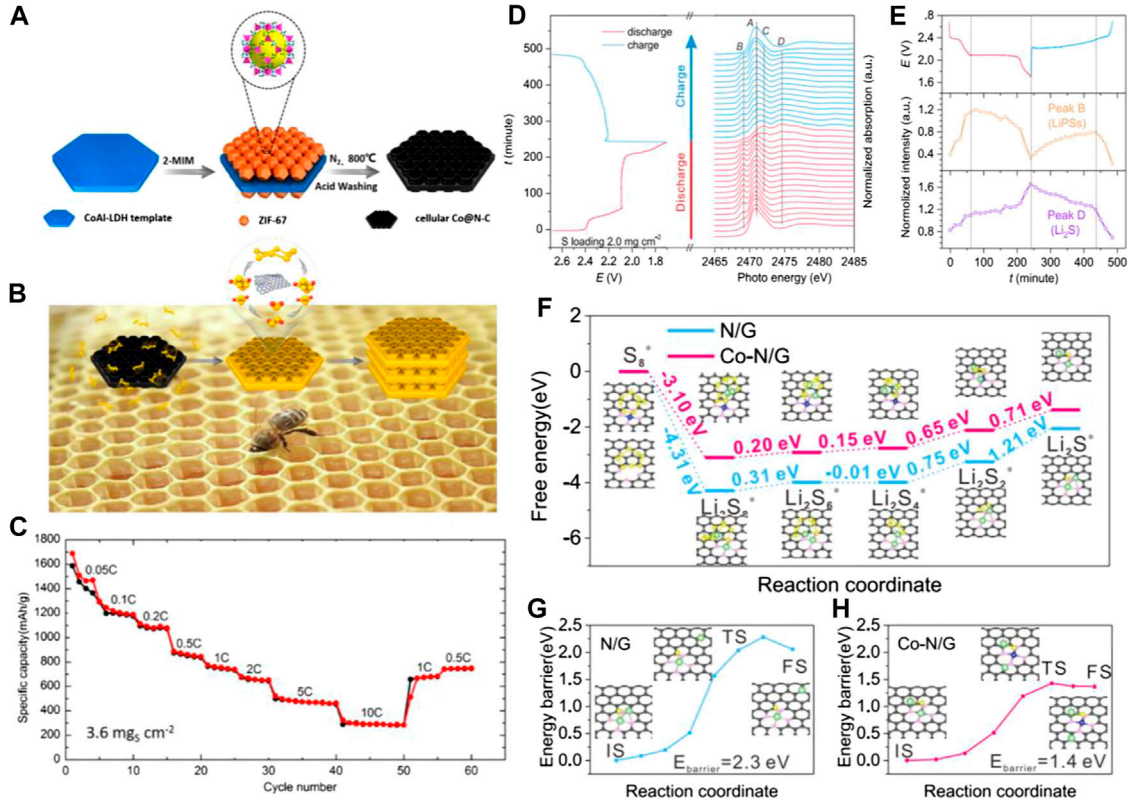

FIGURE 2 | (A) Schematic illustration of the step-by-step synthesis strategy for the cellular Co@N–C composite **(B)** the schematic illustration of the cellular Co@N–C composite which catalyzed the formation and the decomposition of Li_2S in the discharge and charge process **(C)** Rate performances of the 90 S/cellular Co@N–C at different current rates. Reproduced with permission from Li et al. (2017). Copyright © 2017 American Chemical Society **(D)** Evolution of S K-edge XANS during electrochemical cycling **(E)** evolution of the intensities of peak B (2,469.0 eV, representing concentration of LiPSs) and peak D (2,474.7 eV, representing Li_2S concentration) during electrochemical cycling **(F)** Energy profiles for the reduction of LiPSs on N/G and Co-N/G substrates, energy profiles of the decomposition of the Li_2S cluster on N/G **(G)** and Co-N/G **(H)**. The black, yellow, green, pink, and dark blue balls represent C, S, Li, N, and Co atoms, respectively. Reproduced with permission from Du et al. (2019). Copyright © 2019 American Chemical Society.

used to simultaneously accelerate the LiPS redox reaction and chemically trap the LiPS adsorption (Sheng et al., 2019; Fan et al., 2020; Ma et al., 2020).

For example, Cui's group first used the DFT calculation to calculate the decomposition barrier of various metal atoms (Fe, Mn, Ru, Zn, Co, Cu, V, and Ag) on N-doped graphene materials and discovered that vanadium single atoms on N-doped graphene (SAV@NG) showed the smallest decomposition barrier (1.10 eV) as shown in **Figure 4A** (Zhou et al., 2019). Reducing the decomposition barrier of Li_2S can greatly increase the utilization of active materials, decrease the formation of dead Li_2S, and achieve a long cycling life. Additionally, they also calculated the binding energy of Li_2S_6 on a different substrate. It showed that the SAV@NG also had the strongest binding energy as shown in **Figure 4B**, indicating the strongest chemical interaction between the SAV@NG and polysulfides, which means the shuttle effect can be effectively inhibited. Based on this guideline, they synthesized large-scale single atom vanadium catalysts deposited on graphene to load as high as 80 wt% sulfur content and the resulted SAV@NG achieved fast kinetics, i.e., a capacity of 645 mAh g^{-1} at 3 C rate.

Shen et al. reported a samarium-doped carbon aerogel as a polysulfide anchor for high-performance Li-S batteries (Sheng et al., 2019). Both the anchoring of polysulfides to uniformly doped Sm and the influence of the carbon aerogel structure could effectively prevent polysulfides escaping from the cathode, while also suppressing the shuttle effect and enhancing the utilization of sulfur. As a result, a CA/S/Sm electrode delivered an initial discharge capacity of 1,212 mAh g^{-1} at 0.5 C and a reversible capacity of 866 mAh g^{-1} after 300 cycles. Recently, Ding et al. also reported a cadmium-doping carbon aerogel for high-performance Li–S batteries (Ma et al., 2020). And the relative DFT calculation and experiment results have proved that Cd doping played a vital role in effectively entrapping the polysulfides.

Apart from iron series metal atom-decorated carbon materials, other transition metal atom-decorated carbon materials are also good candidates to enhance the long-cycling performances of Li-S batteries with high rate and high sulfur loading as shown in **Table 3**. They show more promising applications compared to the noble metal atom-decorated carbon materials.

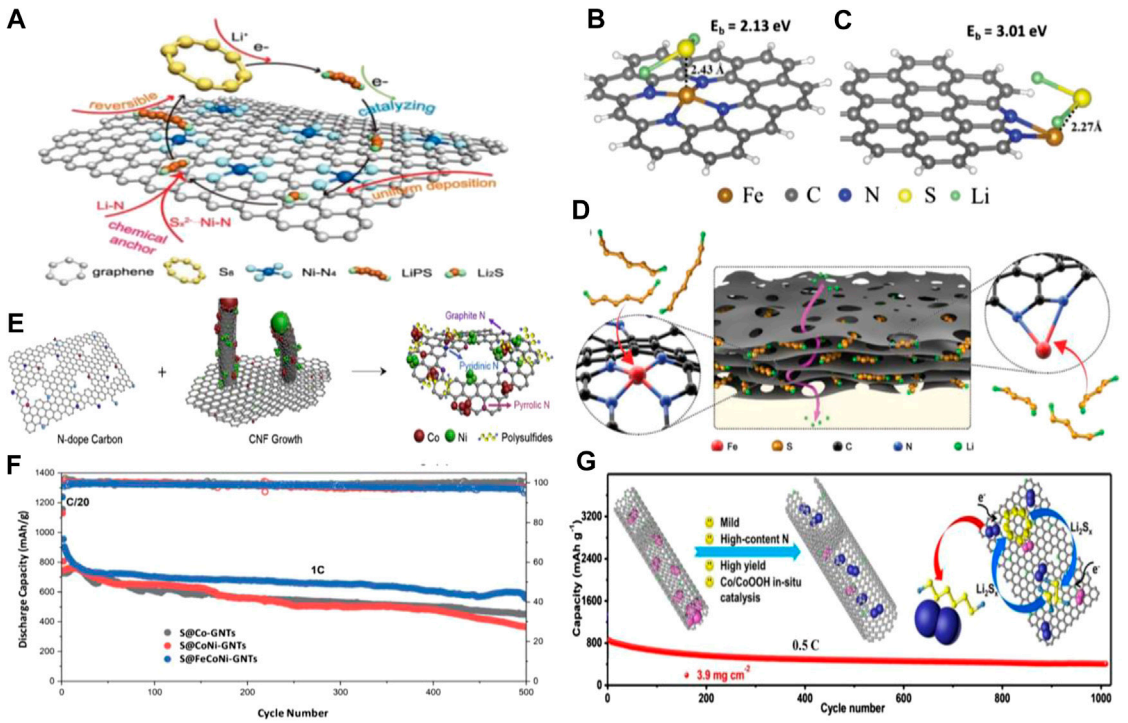

FIGURE 3 | (A) The catalytic and chemically trapping mechanism of the LiPS on the surface of Ni@NG in the electrochemical process. Reproduced with permission from Zhang et al. (2019e). Copyright © 2019 WILEY-VCH Verlag GmbH and Co. KGaA, Weinheim. Optimized configurations for the binding of Li_2S to **(B)** Fe–N_4 and **(C)** Fe–N_2 moieties on graphene (Li_2S binding energies and selected bond distances are indicated in images) **(D)** Schematic illustration of the confinement of sulfur and polysulfides in the layer structure and the additional ionic diffusion pathways (purple arrow line) through the holey structure (the black sheets). Reproduced with permission from Wang et al. (2019b). Copyright © 2018 WILEY-VCH Verlag GmbH and Co. KGaA, Weinheim **(E)** Designing strategy of NiCo-CNF@CF interlayer for Li-S batteries. Reproduced with permission from Zhang et al. (2019a) Copyright © 2019 Elsevier Ltd **(F)** Capacity retention between S@Co-GNTs, S@CoNi-GNTs, and S@FeCoNi-GNTs at 1 **C**. Reproduced with permission from Ogoke et al. (2019). Copyright © 2019 The Royal Society of Chemistry **(G)** The schematic of 1D high-content N-doped graphene nanoribbons@Co/CoOOH high-yield and *in-situ* fabricated as an integrated host for Li-S batteries and the long cycling performance. Reproduced with permission from Tan et al. (2020) Copyright © 2020 The Royal Society of Chemistry.

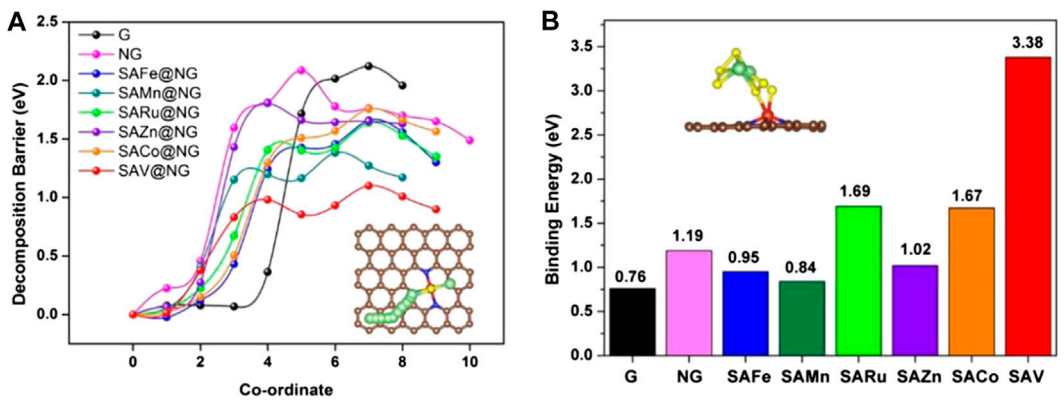

FIGURE 4 | (A) Decomposition barriers of Li_2S **(B)** binding energy of Li_2S_6 on the graphene, NG, SACo@NG, SAV@NG, SAFe@NG, SAMn@NG, SARu@NG, and SAZn@NG, respectively. Reproduced with permission from Zhou et al. (2019). Copyright © 2019 American Chemical Society.

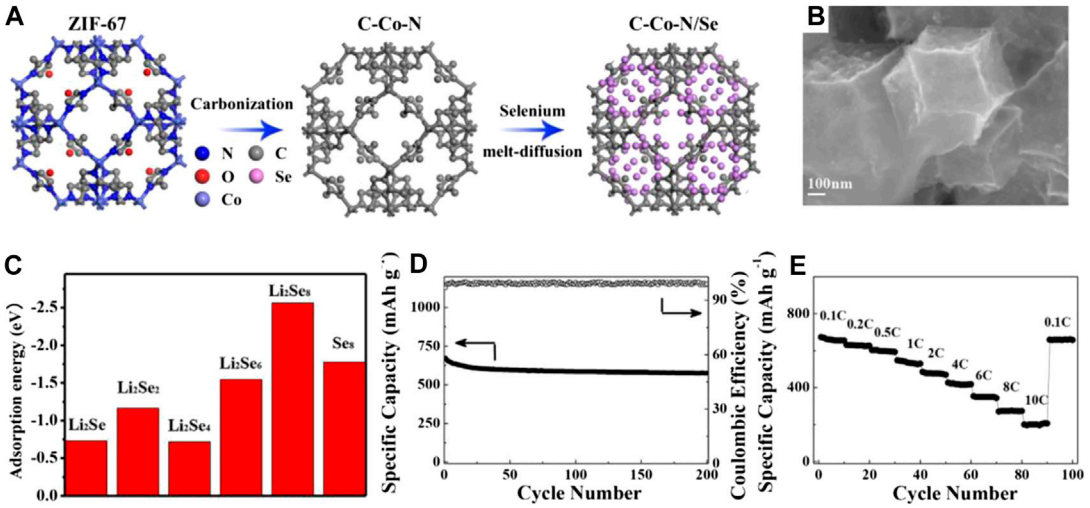

FIGURE 5 | (A) Schematic illustration of the synthetic process for C-Co-N/Se **(B)** SEM images of C-Co-N/Se composites **(C)** The calculated absorption energy values of lithium polyselenides species in C-Co-N **(D)** cycling stability of the C-Co-N/Se cathodes at 0.1°C for 200 cycles **(E)** rate performances at various C-rates of the C-Co-N/Se cathodes. Reproduced with permissions from the ref (He et al., 2017). Copyright © 2017 Elsevier Ltd.

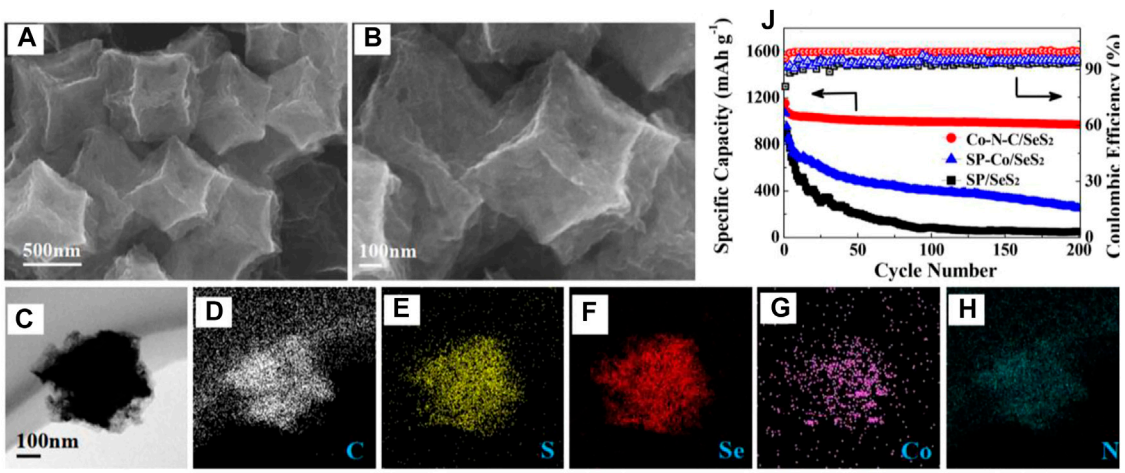

FIGURE 6 | SEM images of **(A)** Co-N-C and **(B)** Co-N-C/SeS_2 composites. The TEM image of a single Co-N-C/SeS2 polyhedron **(C)** and the corresponding elemental mapping images of **(D)** C **(E)** S **(F)** Se **(G)** Co, and **(H)** N **(J)** Cyclic stability of the SP/SeS_2, SP-Co/SeS_2, and Co-N-C/SeS_2 cathodes at 0.2 C for 200 cycles. Reproduced with permissions from the ref (He et al., 2018). Copyright © 2018 the Royal Society of Chemistry.

METAL ATOM-DECORATED CARBON MATERIALS FOR ENHANCING LI-SE BATTERY PERFORMANCES

Although a large number of literature have suggested using heteroatom doping carbon materials and metal compounds as selenium carriers for enhancing Li-Se battery performance (Li and Yin, 2015; Yi et al., 2015; Jin et al., 2017; Lv et al., 2017; Choi et al., 2018; Gu et al., 2018; He et al., 2018; Yang et al., 2018; Zhao et al., 2018; Gu et al., 2019; Gu and Lai, 2019; Du et al., 2020), there are few reports about metal atom-doped carbon materials simultaneously catalyzing LiPSe redox reaction and chemically trapping LiPSe.

In 2017, He's group first reported a 3D porous N-doped graphitic carbon-Co scaffold (C-Co-N) derived from metal-organic frameworks (as shown in **Figures 5A,B**) as a conductive Lewis base matrix to host selenium for the Li-Se battery (He et al., 2017). They employed the DFT calculation to calculate the adsorption energy of LiPSe (**Figure 5C**) on this C-Co-N material, which indicated that the C-Co-N matrix had excellent chemical confinement for LiPSe. As a result, the resulted C-Co-N/Se electrode demonstrated excellent cycling stability (capacity fading of only 0.07% per cycle) and rate capabilities (196.9 mAh g^{-1} at 10 C, 1C = 675 mA g^{-1}) as shown in **Figures 5D,E**.

METAL ATOM-DECORATED CARBON MATERIALS FOR ENHANCING LI-SES$_X$ BATTERIES PERFORMANCES

The Se_xS_y cathodes own the advantages of both Se and S, such as low cost and high reversible capacity, etc. But they also face the same issue as pure S and Se cathodes. Thus, in recent years, researchers also utilized the metal atom-decorated carbon materials to address the challenges of Li-SeS_x batteries (He et al., 2018; Wang et al., 2020d; Jin et al., 2020).

For example, He et al. used a cobalt- and nitrogen-doped porous carbon (Co-N-C) polyhedron to encapsulate the SeS_2 and investigated its electrochemical performances as shown in **Figure 6** (He et al., 2018). As can be seen from the SEM, TEM, and corresponding element mapping images, the SeS_2 have been encapsulated into the unique hollow of the cobalt- and nitrogen-doped porous carbon, and were distributed homogenously. As a result, the Co-N-C/SeS_2 composite with a high loading (66.5 wt%) of SeS_2 delivered a reversible capacity of 1,165.1 mAh g^{-1} and an 84.1% capacity retention of the initial capacity (970.2 mAh g^{-1}) with a nearly 100% Coulombic efficiency after 200 cycles, which were superior to that of the Super P/SeS_2 (SP/SeS_2) and Super P-Co/SeS_2 (SP-Co/SeS_2) composite cathodes.

CONCLUSION

In terms of the cathode problems of Li-S and Li-Se batteries, the sluggish redox reaction kinetics as well as the easy solubility of intermediates are major causes for the shuttle effect of LiPS/LiPSe. Therefore, it is indispensable to incorporate catalytic materials with strong adsorption and catalysis toward LiPS/LiPSe.

Metal atom-decorated carbon materials exhibited multifunctional roles, i.e., enhancing the electrode conductivity, accommodating high loading and volume expansion, adsorbing the LiPS/LiPSe, and overwhelmingly accelerating the reaction rate, which are beneficial to promote battery performance, and has shown great potential as the advanced materials for state-of-the-art energy storage devices.

Current investigations have demonstrated that metal atom-decorated carbon materials, particularly the single metal atom doping carbon, exhibited high activity on the adsorption-diffusion-conversion of LiPSs. According to previous reports, the noble metal atom-decorated carbon materials did not improve the electrochemical performances of Li-S batteries compared to the iron series metal atom-decorated carbon materials, even though they have been verified to have excellent catalytic properties in the fields of HER, OER, and CO_2 reduction, etc. In contrast, other transition metal atom-decorated carbon materials, such as vanadium and samarium-decorated carbon materials, demonstrated great potential on improving the electrochemical performances of Li-S batteries. However, we should pay attention to the fact that the roles of metal atom-decorated carbon materials on LiPSe still need investigating. Future investigations could pay more attention to constructing suitable transition metal atom-decorated carbon materials for Li-Se batteries.

What is more, an in-depth understanding of the chemical scission of S-S or Se-Se bonds induced by these catalysts is still out of reach. In order to clearly understand the conversion process of sulfur/selenium redox, the in-situ characterizations, i.e., *in-situ* Raman/X-ray absorption spectroscopy/TEM, are suggested to observe and trace the full chemical reaction.

Another problem that cannot be ignored is the safety of the lithium anode, as it is well known that the lithium anode suffers from severe lithium dendrite problems during reduction (Ju et al., 2020). Recently, quite a few studies have reported that building lithium alloys could effectively inhibit lithium dendrite growth (Yan et al., 2016; Xue et al., 2018; Zhu et al., 2018; Wan et al., 2020). Thus, using active metal atoms in decorated carbon materials to react with lithium, form lithium alloys, and then incorporate them into the carbon framework would be a promising strategy.

Finally, for commercial application, the cost should be taken into consideration too. Low-cost and large-scale production of metal atom-decorated carbon materials are highly recommended. Presently, it is undeniable that this kind of material, especially single metal atom-doped carbon materials still cannot realize large-scale production, and the cost is still high due to the complex synthesis process. Therefore, the design structure of cost-effective metal atom-decorated carbon materials needs to be carefully considered. Anyhow, metal atom-decorated carbon materials are still promising and worth looking forward to.

AUTHOR CONTRIBUTIONS

XG and LD conceived the idea and co-wrote the manuscript. XR and XG discussed the results and commented on the manuscript.

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