Demystifying Activity Origin of M–N–C Single-Atomic Mediators Toward Expedited Rate-Determining Step in Li–S Electrochemistry

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1. Introduction

The sluggish charge transfer kinetics and multi-step conversion of S₈ molecules into Li₂S during sulfur reduction reaction (SRR) inevitably result in limited sulfur utilization, poor rate capability, and short cycle life, thereby greatly hindering the practical application of Li–S batteries.[1–8] As for the sulfur cathode, it undergoes a typical SRR process throughout solid(S₈)-liquid(soluble polysulfides)-solid( insoluble Li₂S₂)-solid( insoluble Li₂S) phase transformation upon discharge. In this sense, S₈ is first reduced through a sequence of lithium polysulfides to Li₂S₄, which delivers 25% of the theoretical capacity. The further reduction of Li₂S₄ to Li₂S, marked as the rate-determining step, contributes to the other 75% of the theoretical capacity.[9] Note that the conversion of sulfur is significantly handicapped by the depression of solid-state diffusion, accordingly inducing the premature end of discharge, which leads to a conspicuous difference between...
the actual capacity and the theoretical value. This phenomenon would become more rampant under elevated sulfur loading conditions. Therefore, designing efficient electrocatalysts to expedite the liquid–solid transformation from Li$_2$S$_4$ to Li$_2$S is strategically meaningful and imperative.

To date, versatile polar metal compounds with ultrathin nanostuctures have been widely explored as electrocatalyst candidates targeting the acceleration of Li$_2$S$_4$ → Li$_2$S conversion.[10,11] Despite the fruitful progress, the fundamentally catalytic insights of Li$_2$S precipitation during SRR remain rather elusive. Meanwhile, the application of such bulk metal-based architectures in the cathode will inevitably reduce the loading ratio of sulfur, which is highly likely to undermine the energy density of the full cells. Along this line, the development of lightweight electrocatalysts affording excellent electrical conductivity and sufficient catalytic activity is desirable to realize the full potential of a sulfur electrode.[12]

Single-atom catalysts (SACs) with atomically dispersed metals stabilized on a suitable support have attracted intensive interest due to their impressive catalytic capability and maximized atom utilization efficiency.[13–20] In the Li–S realm, transition-metal-derived SACs harnessing representative M–N–C configurations (e.g., MN$_4$C$_4$) have readily demonstrated encouraging performances in boosting sulfur electrochemistry.[21–23] Nevertheless, unambiguous identification of exact catalytic moieties in different metal-centered M–N–C SRR electrocatalysts is still lacking. In further contexts, a definitive structure–property correlation in common SACs employed as SRR electrocatalysts has not yet been established.

Herein, we report a universal route to derive representative non-precious metal single-atom modified porous carbon nanofiber films (MSA PCNFs, M = Fe, Co, or Ni) as electrocatalytic hosts to dictate SRR kinetics. The atomistic architectures and coordination configurations of prepared MSA (MN$_4$C$_4$) PCNFs are exhaustively identified by high-angle annular dark field scanning transmission electron microscope (HAADF-STEM) in combination with X-Ray absorption near-edge structure (XANES) and extended X-Ray absorption fine structure (EXAFS). Density functional theory (DFT) calculation is employed to predict the distinctive catalytic properties of MSA PCNFs toward the Li$_2$S precipitation, indicating that the mechanistic pathways rely not only upon a metallic single-atomic center but also neighboring carbon environment. In this regard, MSA PCNFs as efficient electrocatalytic hosts follow the activity order of NISA PCNF > CoSA PCNF > FeSA PCNF, which is further corroborated by electrokinetic measurements and electrochemical performance evaluations.

2. Results and Discussion

The generic fabrication of MSA PCNF affording dispersed metal single-atoms deals with a two-step procedure (Figure 1a). First, a mixed solution containing zeolite imidazolate framework 8 (ZIF-8) and M(NO$_3$)$_2$·6H$_2$O was impregnated into a polycrylonitrile (PAN) host by a typical electrospinning method to form an M$^{2+}$/PAN/ZIF-8 fibrous composite. Upon thorough drying, such a composite was subject to thermal annealing at 800 °C in an Ar atmosphere to derive MSA PCNF. This synthetic strategy can be readily generalized to commonly non-precious metal elements (Fe, Co, or Ni in this case). It is also anticipated to be applicable for the scalable production of M–N–C SACs frameworks with cost-effective features. Note that M CNF or bare PCNF can also be acquired by adopting a similar synthesis strategy merely without the employment of ZIF-8 or M(NO$_3$)$_2$·6H$_2$O precursor. The thus-produced MSA PCNF membrane shows excellent flexibility and mechanical stability on a macrosopic scale, which could remain intact under different bending states (Figure S1, Supporting Information). Extensive transmission electron microscope (TEM) characterizations were performed to inspect detailed morphologies of MSA PCNFs (Figure S2, Supporting Information). As shown in the typical TEM image in Figure 1b, representative NASA PCNF possesses 3D interconnected architecture with uniformly distributed pores throughout the nanofiber, which is beneficial to mass transport during SRR catalytic process. This is in stark contrast to the control sample (Ni CNF) which lacks conspicuous pores (Figure S3, Supporting Information). High-resolution TEM (HRTEM) examination over synthesized NISA PCNF reveals the presence of ample holes and the absence of metal clusters (Figure S4, Supporting Information). The atomically dispersed feature of MSA PCNF was ultimately demonstrated by HAADF-STEM imaging. As displayed in Figure 1c and S5, Supporting Information, Ni, Co, or Fe single atoms are obviously witnessed as bright spots highlighted by red circles.[24] The metal loading within MSA PCNFs was determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES), which reveals similar metal contents of ≈0.5 at% (Table S1, Supporting Information).

Elemental characterization by energy-dispersive X-Ray spectroscopy (EDS) mapping under a STEM mode indicates that C, N, and Ni are homogeneously distributed over NISA PCNF (Figure 1d). The X-Ray diffraction (XRD) patterns of MSA PCNF, Ni CNF, and bare PCNF all manifest two broad peaks centered at 26.2° and 44.0° (Figure 1e), which can be indexed as featured carbon (002) and (100) signals, respectively. Note that diffraction peaks corresponding to metallic and oxidized forms of Ni are absent in these XRD patterns. Compositional analysis of NISA PCNF by X-Ray photoelectron spectroscopy (XPS) suggests the successful incorporation of N and Ni elements (Figure S6, Supporting Information), where the Ni atom is likely to be in an unsaturated low-valent state.[25]

The chemical states and coordination environments of metals were systematically probed via the XANES and EXAFS toolboxes. As for the NISA PCNF, the absorption edge position and white line intensity is located between that of Ni foil and NiO (Figure 1f), implying that the valence state of isolated Ni atoms is between metallic (Ni$^0$) and oxidized (Ni$^{2+}$) status. Moreover, in the Fourier-transformed k$^3$-weighted $\chi(k)$ function of the EXAFS (FT-EXAFS) spectra (Figure 1g), the dominant peak of NISA PCNF at 1.38 Å corresponds to the Ni–N bonding rather than the Ni–Ni bonding at 2.11 Å or the Ni–O bonding at 1.65 Å. The related fitting results suggest that the Ni center is coordinated with four N atoms (Ni–N$_4$) (Figure S7 and Table S2, Supporting Information). In addition, the absorption edge position and white line intensity of CoSA PCNF and FeSA PCNF are also located between those of Co foil/Fe foil and CoO/Fe$_2$O$_3$, indicating that the valence state of isolated Co/Fe atoms is between metallic (Co$^0$)/(Fe$^0$) and oxidized...
Similar observations can be found in the FT-EXAFS spectra of CoSA PCNF and FeSA PCNF with the minor peaks located at 1.32 and 1.53 Å, respectively, which are shifted to the lower direction in comparison with the Co–Co (2.18 Å) and Fe–Fe (2.20 Å) bonding of bulk Fe and Co (Figure S8, Supporting Information). The combination of HAADF-STEM, EXAFS, and XANES analyses upon MSA PCNF has unambiguously determined the incorporation of NiN4C4, CoN4C4, and FeN4C4 moieties in fibrous carbon skeletons.

To investigate the catalytic conversion efficiency toward the rate-determining step of SRR, the activation energies of Li2S4 → Li2S conversion reaction were evaluated for MSA PCNF samples. Figure 2a and S9, Supporting Information manifest cyclic voltammetry (CV) profiles of the thus-derived sulfur cathodes collected at different temperatures (20, 30, and 40 °C). The two featured cathodic peaks appear at 2.3–2.4 and 2.0–2.1 V, which correspond to the generation of soluble LiPSs and insoluble Li2S2/Li2S, respectively. It is evident that NiSA PCNF-derived sulfur cathodes can be used in the Li/S batteries.

**Figure 1.** Synthesis and characterization of MSA (MN4C4) porous carbon nanofiber film (PCNF). a) Schematic illustration of the fabrication process of MSA PCNF. b) Transmission electron microscopy (TEM) image of NiSA PCNF. c) High-angle annular dark field scanning transmission electron microscopy (HAADF-STEM) image of NiSA PCNF. d) Energy-dispersive X-Ray spectroscopy (EDS) maps of NiSA PCNF. e) X-Ray diffraction (XRD) patterns of NiSA PCNF, CoSA PCNF, FeSA PCNF, PCNF, and Ni CNF. f) X-Ray absorption near-edge structure (XANES) of NiSA PCNF, Ni CNF, Ni foil, and NiO. g) Fourier-transformed k3-weighted χ(k) function of the EXAFS (FT-EXAFS spectra in R space of NiSA PCNF, Ni CNF, Ni foil, and NiO. Scar bars: b) 100 nm. c) 2 nm. d) 100 nm.
cathode possesses a higher redox current in comparison with those of (Fe)SA PCNF-based counterparts, suggesting superior catalytic performance. Considering that the Li₂S₄ → Li₂S conversion process contributes ~75% of the theoretical capacity, the activation energy was calculated by the relevant peak appearing at 2.0–2.1 V. The intensity of peak current \( j \) as a function of temperature can be fitted by using the Arrhenius equation:

\[
 j \propto A e^{-E_a/RT}
\]

In this equation, \( E_a \) is the activation energy, \( R \) is the gas constant, \( A \) is a pre-exponential factor, and \( T \) is the temperature. The slope of the curve plotted in Figure 2b represents the activation energy for the Li₂S₄ → Li₂S conversion reaction. NiSA PCNF electrode exhibits the lowest activation energy quantity (17.33 kJ mol⁻¹), indicating advantageous catalytic capability. Likewise, the NiSA PCNF electrode presents a smaller Tafel slope value of 69.98 mV dec⁻¹ as compared to CoSA PCNF (73.04 mV dec⁻¹) and FeSA PCNF electrodes (80.56 mV dec⁻¹), indicating faster reaction kinetics of Li₂S₄ → Li₂S process (Figure 2c).

In further contexts, Li-ion diffusivity of NiSA PCNF-, PCNF-, and Ni CNF-based sulfur electrodes was evaluated by CV tests with variable scan rates. As depicted in Figure S10, Supporting Information, NiSA PCNF electrode presents a faster Li-ion diffusion rate in contrast to its counterparts.[26]

The precipitation of solid Li₂S product on carbon paper (CP)-MSA PCNF was further examined via chronoamperometric nucleation test. CP-NiSA PCNF harvests the highest Li₂S nucleation capacity of 285.2 mAh g⁻¹ and reaches the position of the peak current in the shortest duration, implying prompted SRR reaction kinetics (Figure 2d–f and S11, Supporting Information). To inspect the morphology of Li₂S deposition, post-mortem scanning electron microscopy (SEM) observations show that the CP-NiSA PCNF surface is fully covered by Li₂S precipitation, whereas the CP-Fe(Co)SA PCNF presents a relatively low Li₂S coverage (Figure 2d–f inset).[27–30] Encouragingly, NiSA PCNF...
not only induces the largest Li$_2$S nucleation capacity but also enables the earliest peak time, indicative of the most favorable liquid–solid conversion kinetics during the SRR process (Figure 2g).

To comprehensively explore the catalytic ability of MSA catalyst with respect to the full SRR process, CV profiles of MSA PCNF, PCNF, and Ni CNF symmetric cells were collected in the presence/absence of Li$_2$S electrolyte at a scan rate of 0.5 mV s$^{-1}$ (Figure S12, Supporting Information). Obviously, NiSA PCNF enables an advanced electrochemical activity among the tested materials.$^{[31]}$ CV measurements of such symmetric cells at 50 mV s$^{-1}$ between −1.0 and 1.0 V were also carried out (Figure 2h), again confirming the superior catalytic performance of NiSA PCNF.$^{[33]}$ The schematic illustration in Figure 2i demonstrates the expedited SRR process catalyzed by NiN$_4$C$_4$ sites, in which polysulfide conversion and Li$_2$S precipitation are greatly accelerated on the NiSA PCNF.

SRR process undergoes a complicated multiple-step evolution. Note that the liquid–solid conversion from Li$_2$S$_4$ to Li$_2$S is extremely sluggish and recognized as the rate-determining step of the SRR process.$^{[35]}$ In this sense, the rational design of electrocatalysts to accelerate the Li$_2$S$_4$!Li$_2$S conversion is an effective maneuver to maximize sulfur utilization. It is generally received that moderate adsorption (neither too strong nor too weak) of LiPSs on the catalytic sites is a key prerequisite for an efficient catalysis in sulfur electrochemistry.$^{[29]}$ This would guide the theoretical simulations to predict the catalytic activity and reaction pathways of SRR process based on the analysis of metal centers and surrounding N/C atoms in M–N–C moieties. To ulteriorly gain insight into the SRR catalytic activity of representative MN$_4$C$_4$ (M = Fe, Co, or Ni), DFT calculation was employed and MN$_4$-incorporated graphene configurations were constructed beforehand (Figure S13, Supporting Information). Considering that the final solid–solid reaction is the slowest step, such a process (Li$_2$S$_2$ + 2Li$^+$ + 2e$^-$ ! 2Li$_2$S) was accordingly simulated with the aim to examine the catalytic properties of different adsorption sites. Along this line, a LiS* radial intermediate solvated by 1,3-dioxolane (DOL) molecule was modeled by considering the factually chemical environments (Figure S14, Supporting Information).$^{[39]}$ We then considered four possible adsorption sites, namely the metal atom (M) site, the nitrogen atom (N) site, and two carbon atom sites in the five-membered ring (C$_5$)/six-membered ring (C$_6$) adjacent to the N atom.$^{[40]}$ It is noted that the LiS* radical shuttles from N site to the M site after relaxation, in contrast to the scenarios at C$_5$ and C$_6$ sites. Figure 3a depicts optimized adsorption configurations of LiS* intermediate, with the corresponding adsorption Gibbs free energy values ($\Delta G_{\text{ads}}$) summarized in

\begin{figure}
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\includegraphics[width=\textwidth]{figure3}
\caption{Theoretical simulations of solid–solid reaction process (Li$_2$S$_2$ + 2Li$^+$ + 2e$^-$ ! 2Li$_2$S) on MN$_4$-graphene. a) Optimized adsorption configurations of solvated LiS* intermediate with the first explicit solvation shell (DOL molecule) on three representative sites, e.g., one metal site and two carbon sites in the five-membered (C$_5$) and six-membered ring (C$_6$). b) Volcano curve between the negative overpotential and adsorption free energy of LiS* on the above active sites (triangles, squares, circles, and hexagon indicates the M, C$_5$, C$_6$ site of MN$_4$C$_4$ and C site of pristine graphene, respectively). c) Bader charge analysis of M, C$_5$, and C$_6$ site in the MN$_4$-graphene. d) Chemical-bonding analysis of d orbitals belonging to the metal site of MN$_4$C$_4$ and p orbitals of S atom from LiS* using pCOHP method. Horizontal dashed line indicates the Fermi level.}
\end{figure}
Table S3, Supporting Information. In comparison with a bare graphitic framework, the implant of heterogeneous MN₄ groups apparently improves the radical anchoring on M–N–C moieties throughout interactions between M/C₅/C₆ sites and S atoms. In terms of a fixed metal type, the trend of the adsorption strength for different sites follows: M > C₅ > C₆. As for MN₄-incorporated graphene based on distinct single metal-atoms, the binding strength of LiS° follows the order of Fe > Co > Ni.

We then introduced a descriptor of thermodynamic overpotential (η) to qualitatively evaluate the catalytic activity of diverse adsorption sites in the two-step Li₂S₂ → Li₂S conversion reaction. (Step 1: 3DOL + Li₂S₂ + Li⁺ + e⁻ + \* → 3DOL – LiS° + Li₂S; Step 2: 3DOL – LiS° + Li⁺ + e⁻ + \* → 3DOL + LiS + \*). Figure 3b displays the relationship between the negative overpotential and free energy of adsorbed LiS° intermediate, which appears as a volcano plot. On the left side of the volcano profile, the determination of potential is limited by reaction Step 2 due to the more negative ΔG_{ads} at Fe (−3.83 eV) and Co (−3.40 eV) sites. On the right side, the potential is otherwise determined by reaction Step 1. It is known that the peak position of the volcano profile represents the site affording optimal catalytic activity. As shown in the plot, MN₄-graphene falling in the proximity of the optimal of the plot follows the order of C₅ site in CoN₄-graphene, Ni site in NiN₄-graphene, and C₆ site in FeN₄-graphene according to the minimized overpotential by 0.02, 0.06, and 0.15 V, respectively. Even though the C₅ site of CoN₄-graphene possesses a lower overpotential value than the Ni site in NiN₄-graphene by 0.04 V, the ΔG_{ads} of LiS° on the Co site is obviously higher than that on the C₅ site by 1.17 eV. In this sense, it would be preferable for the solvated LiS° radical to occupy the Co site rather than the C₅ site on the CoN₄-graphene, suggestive of a single-site catalytic mechanism, and likewise, the FeN₄-graphene. In contrast, the ΔG_{ads} of LiS° over the Ni site shows a slight disparity from that over the C₅ and C₆ sites, thereby implying a multi-site catalytic pathway for NiN₄-graphene. Collectively, our theoretical prediction indicates that NiSA PCNF harvests superior catalytic activity in terms of boosting Li₂S₂ → Li₂S conversion to the CoSA PCNF and FeSA PCNF counterparts.

To further unveil the origin of high SRR catalytic activity, we modeled the atomic charge distribution at the MN₄-graphene framework according to the Bader scheme. As presented in Figure 3c, all the M, C₅, and C₆ sites possess positive charges, with the values ranked in descending order of M > C₅ > C₆ owing to the larger electronegativity of heteroatom N compared with metal atom and C atom. Considering the polar bonding configuration of LiS° radical with S atom owning negative charges, MN₄-graphene carrying a more positive charge would induce the formation of stronger binding of LiS° because of higher Coulomb interactions, which is consistent with the calculation results of adsorption energy. This signifies that atomic charge redistribution by the introduction of a heterogeneous MN₄ group can enhance the anchoring effect of LiS°. The projected density of states (pDOS) of MN₄-graphene was additionally calculated (Figure S15 and S16, Supporting Information). In comparison with pristine graphene, there exists a high population of density of states around the Fermi level in MN₄-graphene, which are conducive to augmenting the electrical conductivity. Supplementary spin-charge density simulations also reveal that Fe(Co)N₄-graphene possesses magnetism, mainly contributed by the dₓz orbital of Fe atom and dₓz orbital of Co atom with the magnetic moment of 1.93 and 0.82 \(\mu\)B, respectively (Figure S17, Supporting Information). The occurrence of magnetism might also help promote the capture of LiS° intermediates.

According to classical bonding theory, the binding strength of LiS° over the metal site is related to the energy level differences between \(p\) orbitals of S atom in LiS° and \(d\) orbitals of metal atom in MN₄-graphene. The higher number of \(d\)-electrons (\(N_d\)) for metals, i.e., Fe (\(N_d = 6\)), Co (\(N_d = 7\)), and Ni (\(N_d = 8\)), would trigger lower d-band center locations of the active site. In response, the anti-bonding states harvest lower energy and higher occupancy, resulting in weaker interactions between adsorbed LiS° and metal adsorption site, and vice versa. Quantitative chemical-bonding analysis was further carried out by pDOS and projected crystal orbital Hamilton population (pCOHP) method for the S atom of LiS° and adjacent metal atom (Figure 3d and S18, Supporting Information). The integrated pCOHP values up to the Fermi level for Fe–S, Co–S, and Ni–S are −1.24 and −1.99 eV, −1.13 and −1.13 eV, −0.54, and −0.73 eV with spin-up and spin-down state, respectively, suggesting that the sequence of bonding strength between S atom and metal atom follows Fe–S > Co–S > Ni–S. Along this line, NiN₄-graphene affords moderate binding strength with LiS°, which is ultimately helpful to promote SRR catalytic activity. Taken together, theoretical insight was gained into the identification of active sites of single-atomic M–N–C moieties with respect to catalyzing rate-determining step of the SRR process, especially the decisive solid–solid conversion.

We continued our path to probe the mechanistic features of SRR reaction involving the NiSA PCNF by conducting on-site instrumental characterizations. The operando Raman spectroscopy and in situ XRD analysis were employed to detect the phase evolution of sulfur species upon discharge/charge. In general, long-chain LiPSSs can be monitored by Raman spectroscopy, where a Li–S cell with a transparent window was assembled to allow in situ detection (Figure S19, Supporting Information). As for our S/NiSA PCNF cathode, Raman intensities of Li₂S₈ and Li₂S₆ peaks gradually decline in the discharge process and regenerate during charging (Figure 4a), supportive of good reversibility of sulfur electrochemistry.[41, 42] This is in stark contrast to the scenario of the control S/Ni CNF cathode, where related Raman signals do not show the conspicuous change (Figure S20, Supporting Information). In situ XRD measurement was further carried out to witness the efficient sulfur redox conversion during the discharge/charge. As shown in Figure 4b, an obvious diffraction pattern at \(\approx 13.6^\circ\) appears at the end of the discharge process, which can be identified as the formation of Li₂S. During charging, the intensity of the Li₂S signal gradually declines and finally disappears.[43, 44] We performed ex situ XPS studies to further examine any change in surface chemistry of NiSA PCNF electrocatalyst during the first charge/discharge cycle. Figure 4c manifests the ex situ Ni 2p spectra of NiSA PCNF. The spectrum at the initial stage shows two characteristic peaks at 854.7 and 872.1 eV, corresponding to the Ni 2p₁/₂ and 2p₃/₂ of a single Ni atom, respectively. Note that the binding energy of Ni downshifts with the increasing depth of the discharge process and reversibly shifts back upon charging, implying the chemical stability of Ni single atoms during the
sulfur redox reaction. When discharging to 2.08 V, a new peak at 862.0 eV in the spectrum is detected, which can be attributed to the formation of Ni–S bonding.\(^\text{[45]}\) Collectively, the potential catalytic mechanisms of liquid–solid conversion via the introduction of MN\(_4\)C\(_4\) moiety are sketched in Figure 4d. We propose whether the C atom sites participate in catalyzing the rate-determining step of SRR is associated with \(N_d\). As for Fe \((N_d = 6)\) and Co \((N_d = 7)\), the Li\(_2\)S precipitation is catalyzed throughout a single-site mechanism at the sole M site. In contrast, with respect to Ni \((N_d = 8)\), it is likely that multi-site (M, C\(_5\) and C\(_6\) sites) catalysis occurs for the conversion of Li\(_2\)S\(_4\) to Li\(_2\)S, thereby maximizing sulfur utilization. This represents a solid example of unambiguous identification in the active sites of MN\(_4\)C\(_4\)-based M–N–C catalysts harnessing varied electrocatalytic activity toward SRR.

We next proceeded to validate the SRR activities of MSA PCNFs by evaluating the electrochemical performances of derived cathodes. As for the three types of S/MSA PCNF electrodes, Figure 5a manifests their rate performances under a typical sulfur loading of 1.8 mg cm\(^{-2}\). At varied current densities of 0.2, 0.5, 1.0, 2.0, and 3.0 C, the discharge capacities of S/NiSA PCNF cathode reach 1498.6, 1399.0, 1228.1, 1077.5, and 950.1 mAh g\(^{-1}\), respectively. These are markedly superior to those of S/FeSA PCNF and S/CoSA PCNF counterparts, indicating improved rate performance of S/NiSA PCNF. Such an outstanding rate capability compares favorably with those of reported SACs-derived cathodes in the Li–S realm, especially at a high-rate (e.g., 3.0 C) condition (Table S4, Supporting Information). The catalytic superiority of NiSA PCNF was further verified by the galvanostatic charge/discharge (GCD) test at a constant current density of 0.2 C (1.0 C = 1675 mA g\(^{-1}\)). As shown in Figure 5b, all MSA PCNF cathodes manifest two discharge plateaus. The valley that appears between the first plateau and the second plateau was defined as the Li\(_2\)S nucleation point. The potential gap between the Li\(_2\)S nucleation point and the tangential line of the potential plateau is used to evaluate the Li\(_2\)S nucleation. Obviously, the NiSA PCNF cathode possesses a low overpotential of 11.8 mV, suggesting a low interfacial energy barrier existed for Li\(_2\)S nucleation and deposition on the surface of NiSA PCNF. The increased Li\(_2\)S formation during the discharging process is further evidenced by the onset potential of charge curves. A lower onset potential and longer active time could be observed for NiSA PCNF cathode, indicating more Li\(_2\)S produced during the discharging process. The voltage gap of the NiSA PCNF cathode remains the lowest value of only 0.17 V, suggesting a kinetically favorable reaction process. Notably, the NiSA PCNF electrode enables the highest capacity at the final solid–solid conversion step, which might originate from the advanced electrocatalytic effect modulated by the multi-site electrocatalytic mechanism that is proposed aforementioned.

Cyclic stability of the three types of S/MSA PCNF electrodes was also tested. As depicted in Figure 5c, the S/NiSA PCNF electrode manages to deliver an initial capacity of 1122.9 mAh g\(^{-1}\) with a low capacity decay of 0.12% per cycle over 150 cycles at
0.2 C, indicative of the advanced ability of NiSA PCNF to restrain the "shuttle effect" as compared to Fe(Co)SA PCNFs and Ni CNF (Figure S21 and S22, Supporting Information). In this sense, our experimental evaluation results of electrochemical performances are in good agreement with theoretical simulations, corroborating the impressive SRR activity of NiSA PCNF.

To envisage practical applications, Li–S cells based on the representative S/NiSA PCNF cathode with elevated sulfur loadings (5.0–10.2 mg cm\(^{-2}\)) were constructed. When the sulfur loading reaches 5.1 mg cm\(^{-2}\), S/NiSA PCNF cathode delivers an initial capacity of 1005.8 mAh g\(^{-1}\) and maintains a capacity of 849.1 mAh g\(^{-1}\) after 100 cycles at 0.2 C (Figure 5d). Such a cathode also enables an excellent rate capability: when cycled at 0.1, 0.2, 0.5, and 1.0 C, it harvests discharge capacities of 1059.2, 939.1, 869.6, and 509.1 mAh g\(^{-1}\), respectively (Figure S23, Supporting Information). As shown in Figure 5e, under an elevated sulfur loading of 10.2 mg cm\(^{-2}\) and a lean-electrolyte condition (E/S ratio \(\approx 5.5 \mu L mg^{-1}\)), S/NiSA PCNF cathode with a thickness of 150 \(\mu m\) achieves a high initial areal capacity of 14.12 mAh cm\(^{-2}\) and still maintains a capacity of 10.58 mAh cm\(^{-2}\) after 40 cycles at 0.05 C (Figure S24, Supporting Information), readily surpassing the typical benchmark value of commercial Li-ion battery (\(\approx 4 \text{ mAh cm}^{-2}\)). More impressively, as shown in Figure 5f, this outstanding areal capacity exhibits an overwhelming advantage over the previously reported sulfur cathodes based on SACs.\(^{[46–51]}\) In terms of long cycling performance, S/NiSA PCNF cathode is able to retain a high capacity of 754.4 mAh g\(^{-1}\) and achieve a low capacity decay rate of 0.09% per cycle after 500 cycles at 1.0 C, indicative of excellent cyclic stability (Figure 5g). In addition, a 2.0 cm \(\times\) 3.0 cm pouch cell was further assembled based on a S/NiSA PCNF cathode at a sulfur loading of \(\approx 2.0 \text{ mg cm}^{-2}\), upholding the continuous powering of a light emitting diode (LED) indicator under different bending states (Figure S25, Supporting Information).

3. Conclusions
In summary, a universal route was developed to synthesize MSA PCNFs (M = Fe, Co, or Ni) as electrocatalytic hosts to steer the...
rate-determining step of the SRR process. The coordination configurations of $\text{MN}_4\text{C}_4$ moiety have been identified by HAADF-STEM, XANES, and EXAFS, which aid in elucidating the structure of obtained single atoms at the atomic level. Based on exhaustive theoretical simulations and electrokinetic analysis, it is disclosed that NiS PA CF exhibits a robust electrocatalytic effect on SRR affording a close collaboration of Ni atomic center and adjacent carbon atoms. This unique multi-site catalytic mechanism is distinct from the single-site modulation of Fe(Co)SA PCNF, accordingly endowing the NiSA PCNF with excellent electrocatalytic performances toward the liquid–solid redox conversion. The thus-constructed Li–S cells deliver a high capacity of 950.1 mAh g$^{-1}$ at 3.0 C. This work offers a meaningful roadmap for guiding the rational design of single-atom catalysts to boost sulfur electrocatalysis, holding promise in the pursuit of practical Li–S systems.

Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest
The authors declare no conflict of interest.

Data Availability Statement
Research data are not shared.

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Li–S batteries, M–N–C, rate-determining step, single-atomic mediator, sulfur reduction reaction

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