Cofactor-Assisted Artificial Enzyme with Multiple Li-Bond Networks for Sustainable Polysulfide Conversion in Lithium–Sulfur Batteries

Suya Zhou, Shuo Yang, Dong Cai, Ce Liang, Shuang Yu, Yue Hu, Huagui Nie, and Zhi Yang*

Lithium–sulfur batteries possess high theoretical energy density but suffer from rapid capacity fade due to the shuttling and sluggish conversion of polysulfides. Aiming at these problems, a biomimetic design of cofactor-assisted artificial enzyme catalyst, melamine (MM) crosslinked hemin on carboxylated carbon nanotubes (CNTs) (i.e., [CNTs–MM–hemin]), is presented to efficiently convert polysulfides. The MM cofactors bind with the hemin artificial enzymes and CNT conductive substrates through FeN5 coordination and/or covalent amide bonds to provide high and durable catalytic activity for polysulfide conversions, while π–π conjugations between hemin and CNTs and multiple Li-bond networks offered by MM endow the cathode with good electronic/Li+ transmission ability. This synergistic mechanism enables rapid sulfur reaction kinetics, alleviated polysulfide shuttling, and an ultralow (<1.3%) loss of hemin active sites in electrolyte, which is 60 times lower than those of noncovalent crosslinked samples. As a result, the Li–S battery using [CNTs–MM–hemin] cathode retains a capacity of 571 mAh g⁻¹ after 900 cycles at 1 C with an ultralow capacity decay rate of 0.046% per cycle. Even under raising sulfur loadings up to 7.5 mg cm⁻², the cathode still can steadily run 110 cycles with a capacity retention of 83%.

1. Introduction

The electrochemical redox reaction of sulfur in lithium–sulfur (Li–S) batteries undergoes a complicated multiphase evolution.

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the high catalytic activity and high stability of the artificial enzymes are usually difficult to balance, the inactivation and loss problems of the active centers in the artificial enzymes remain a challenge. Recently, with the in-depth research on natural enzymes, it has been found that cofactors, as indispensable participants in enzyme-catalyzed reactions, play an important role in enhancing the catalytic functions and stability of the natural enzymes, especially in catalyzing the diverse, challenging chemical transformations in water environment of life systems,[19] owing to their covalent immobilization of enzyme and strong electronic/ionic transmission through hydrogen-bond networks. The good immobilization capability toward catalytic active sites and perfect electronic/ionic transport are highly desired for an ideal good immobilization capability toward catalytic active sites and steady LiPS conversion and alleviating the shuttle effect in Li–S batteries.

Inspired by the cofactor-assisted enzyme, after combining with the advantages of N-rich melamine (MM) molecules in forming multiple Li-bond networks, we propose a new biomimetic catalyst for highly efficient LiPS conversion, which is realized by crosslinking lithiophilic MM cofactor with the hemin artificial enzyme modified carboxylated carbon nanotubes (CNTs) via an amidation reaction, denoted as [CNTs–MM–hemin]. A series of characterizations, in situ spectroscopic studies, and theoretical calculations reveal: 1) A successful formation of the amide bonds between MM, hemin, and carboxylated CNTs helps to establish a period and covalently crosslinked network structure, inhibiting the dissolution of hemin artificial enzyme in ether-based solvents and thus maintaining the relatively high and stable catalytic activities for LiPS conversions; 2) a FeN4 configuration formed by Fe–N coordination between hemin and MM significantly enhances the conversion of long-chain LiPSs to short-chain LiPSs; 3) a large number of different Li-bonds are formed between LiPSs and hemin and/or MM, constructing multiple Li-bond networks, which is beneficial for accelerating electron transfer/Li+ supplementation in the system and boosting the conversion of short-chain LiPSs to insoluble Li2S2/Li2S. As a result of this synergistic effect, the [CNTs–MM–hemin]-based Li-S batteries exhibit excellent electrochemical performance in terms of cycling stability. While Li-bonds in Li–S chemistry have attracted great attentions, to the best knowledge, the concept of multiple Li-bond networks and the corresponding study are sorely lacked in the rechargeable battery community. This work will pave the way for designing cofactor-assisted artificial enzyme catalysts with multiple Li-bond networks for boosting the electrochemical performance of practical Li–S batteries.

2. Results and Discussion

2.1. Synthesis and Characterization of [CNTs–MM–Hemin] Composite

As schematically illustrated in Figure 1a, [CNTs–MM–hemin] composite was synthesized by a simple condensation method (the detailed synthetic process can be found in the Experimental Section). For comparison, the sample without hemin (denoted as [CNTs–MM]) and the samples without condensation method (denoted as CNTs–MM–hemin and CNTs–hemin, in which hemin is physically bonded to its host) were also prepared. In high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images of the obtained composite (Figure 1b; Figure S1, Supporting Information), the marked brighter points could be corresponded to the well-dispersed Fe. The homogeneous spatial distributions of Fe, N, and C atoms are further evidenced by the energy dispersive X-ray spectroscopy (EDX) elemental mappings (Figure 1b; Figure S2, Supporting Information), indicating hemin molecules are distributed evenly throughout CNT surfaces.

The [CNTs–MM–hemin] composite was further examined by Fourier transform infrared (FTIR) and X-ray photoelectron spectroscopy (XPS) to confirm the association of MM to hemin and carboxylated CNTs. In Figure 1c, the strong peaks (at 1704 cm−1) assigned to the carboxylic stretch of carboxylic group of hemin (C=O (acidic))[20] are observed in hemin and CNTs–MM–hemin, and the sharp peaks (at 3300–3500 cm−1) ascribed to the amino groups of MM can be clearly found in MM and CNTs–MM–hemin. Whereas, the peaks at 1704 and 3300–3500 cm−1 in [CNTs–MM–hemin] are significantly weakened, while the C=O (amide) peak[20] at ≈1656 cm−1 is enhanced. These findings suggest a successful formation of the covalent amide bond when the amino group of MM reacts with the carboxylic group of the hemin and carboxylated CNTs via condensation reaction, which is also confirmed by the amide peak at ≈400.8 eV in the N 1s XPS spectra of [CNTs–MM–hemin] and [CNTs–MM] (Figure 1d). In Figure 1e, compared with hemin, the Fe 2p peaks of CNTs–hemin and CNTs–MM–hemin significantly shift to higher binding energy, indicating that the physical π–π conjugation interaction between CNTs and hemin/MM successfully occurs.[21] For [CNTs–MM–hemin], it is found that its Fe 2p peaks significantly shift to lower binding energy compared with those of CNTs–MM–hemin (Figure 1e), and its Cl 2p peaks disappear (Figure S3, Supporting Information), combined with the theoretical calculation of dechlorination reaction energy (Figure S4, Supporting Information), which suggests that the weak Fe–Cl bond in hemin is easily cleaved during condensation reaction and the N-rich MM facilitates the coordination with Fe atom of hemin through N1 site, probably forming an unique FeN4 site.[21]

To explore the immobilization effect of the multiple connections, including covalent amide bond, physical π–π conjugation, and Fe–N coordination bond, on the highly soluble hemin in ether-based electrolyte, UV–vis absorption spectroscopic studies were carried out on hemin, CNTs–hemin, CNTs–MM–hemin, and [CNTs–MM–hemin] in a binary solvent of 1,3-dioxolane (DOL) and dimethyl ether (DME) (DOL/DME, v/v = 1:1). Figure 1f and Figure S5 in the Supporting Information give the intensity variation in soret band[22] for hemin (≈390 nm, as shown in Figure 1g) with the added hemin concentration (1–30 μg mL−1). Clearly, [CNTs–MM–hemin] exhibits an extremely low solubility of hemin (<1.3%) among the three composites, which is around 60 times lower than those of noncovalent crosslinked samples (76% for CNTs–MM–hemin, and 79.5% for CNTs–hemin), manifesting [CNTs–MM–hemin] has a
Figure 1. Schematic illustration and structural and stability characterization of [CNTs–MM–hemin] composites. a) Schematic of the synthetic route for [CNTs–MM–hemin] composite and the amplification of physical interaction, covalent, and coordinated sites of the resulting composite. b) HAADF-STEM image and the corresponding EDX elemental mapping images of C, Fe, and N for [CNTs–MM–hemin]. c) FTIR spectra of hemin, [CNTs–MM–hemin], CNTs–MM–hemin, and MM. d) N 1s XPS spectra of [CNTs–MM–hemin], CNTs–MM–hemin, [CNTs–MM–hemin], and MM. e) Fe 2p XPS spectra of [CNTs–MM–hemin], CNTs–MM–hemin, and hemin. f) Dependence of the hemin addition on the UV–vis absorbance peak at different composites in a binary solvent of DOL and DME (v/v = 1:1). g) UV–vis absorption spectrum of hemin dissolved in the DOL/DME solvent.

The robust ability to immobilize hemin and inhibit its dissolution in ether-based solvents.

On the basis of the above spectral results, it is reasonable to conclude that in [CNTs–MM–hemin], MM acts as a cofactor to grab hemin artificial enzyme and carboxylated CNTs with covalent amide bonds, a FeN5 configuration is formed by Fe–N coordination between hemin and MM, and the physical \( \pi-\pi \) interactions between CNTs and the molecules (hemin and MM) also exist to accelerate electron transfer in the system, as presented in Figure 1a. With the aid of the multiple (covalent, coordinated, physical) connections, [CNTs–MM–hemin] with a periodic covalent network structure can efficiently inhibit the dissolution of hemin in ether-based solvents.

2.2. Interaction between Polysulfides and [CNTs–MM–Hemin]

Encouraged by the exciting immobilization capability of [CNTs–MM–hemin] toward catalytic active sites of hemin, its adsorption and catalytic effects on LiPSs were evaluated experimentally and theoretically. Theoretical calculations based on density functional theory (DFT) were performed to model the adsorption of \( \text{Li}_2\text{S}_n \) molecules (\( n = 8, 6, 4, 2, 1 \)) on the surfaces of hemin–MM, hemin, and MM with \( N_1 \) and \( N_2 \) site configurations, respectively. The most favorable optimized local atomic structure and conformation of adsorbed \( \text{Li}_2\text{S}_n \) (\( n = 8, 6, 4, 2, 1 \)) on the four surfaces are shown in Figure S6 in the Supporting Information. It is found that MM binds with hemin via a Fe–N bond, and the \( \text{Li}_2\text{S}_n \) molecule (\( n = 8, 6, 4, 2, 1 \)) adsorbs onto the hemin–MM surface with the adsorption energy (\( E_{\text{ads}} \)) of \(-0.87 \) to \(-2.32 \) eV, which are generally lower than those of hemin (\(-0.82 \) to \(-2.45 \) eV) and MM (\(-0.68 \) to \(-0.89 \) eV), indicating that hemin–MM theoretically has the strongest chemical entrapment ability toward sulfur species mainly due to the Fe–S and Li–N bonds, and should have a positive effect for
suppressing the shuttle effect. Further, the LiPS chemisorption capabilities of CNTs, [CNTs–MM], and [CNTs–MM–hemin] composites were experimentally characterized by soaking the three composites into Li2S6 solution (Figure S7, Supporting Information). A decolorized Li2S6 solution is observed in the presence of [CNTs–MM–hemin], while the solution with [CNTs–MM] still demonstrates light yellow color, and that with CNTs keeps dark yellow in color. Such a remarkable contrast indicates that [CNTs–MM–hemin] catalyst has the best adsorbability for LiPSs, completely consistent with the above DFT calculations (Figure 2a; Figure S6, Supporting Information). To further analyze the intrinsic chemical interaction of LiPSs with [CNTs–MM–hemin], ex situ XPS study was executed after Li2S6 adsorption for 24 h. The S 2p peak of Li2S6-treated [CNTs–MM–hemin] at 167.2 eV (Figure S8, Supporting Information) is in accord with the binding energy of thiosulfate, suggesting an effective polysulfide conversion on the [CNTs–MM–hemin] surface.[23] The Fe 2p peaks for [CNTs–MM–hemin] display significant changes after Li2S6 treatment (Figure 2b). Two new peaks at 708.8 and 722.2 eV could be ascribed to Fe–S bond,[24] which results from the interaction between the Fe atom of heme and the S atom of LiPSs. The Li 1s peak of Li2S6-treated [CNTs–MM–hemin] is shifted toward lower binding energy by 0.7 eV compared with that of the pure Li2S6 (56.1 eV; Figure 2c), as expected, its N 1s peak is shifted toward higher binding energy (Figure 2d), implying a strong electron transfer from the N atoms of heme and/or MM to Li+ or LiPSs that results in Li-bond formation, namely the formation of the Li···N bond, according to previous reports.[25] A 7Li NMR investigation of the different Li···N bonds was further conducted since different types of N environment exist in heme and MM. The narrow signal due to the soluble Li+ appears at ≈2.0 ppm in the spectrum of the Li,S6 solution (Figure S9, Supporting Information). In the case of Li,S6-treated CNTs, no chemical shift is observed expect for a peak broadening, while the downshifts of the 7Li resonance in different degrees for Li,S6-treated [CNTs–MM] and Li,S6-treated CNTs–hemin in Figure 2e indicate that the Li nucleus is more shielded by different N environments (forming different Li···N bonds) in MM and heme.[26] In case of Li,S6-treated [CNTs–MM–hemin], both 7Li signals of [CNTs–MM] and CNTs–hemin remain, demonstrating the formation of multiple Li···N bonds between the [CNTs–MM–hemin] and LiPSs. According to the principle of NMR,[27] the solid Li2S components generally result in broader signals in NMR spectra due to the presence of anisotropic interactions. However, the interactions are averaged out on the NMR time scale by fast tumbling of the soluble polysulfide species, generally resulting in narrow line widths for the solution components. Thus, the narrowing in the 7Li peak at ≈1.3 ppm could be attributed to the higher Li+ mobility in [CNTs–MM–hemin]. The above findings demonstrate that [CNTs–MM–hemin] can effectively adsorb LiPSs through the Fe–S and multiple Li···N bonds, not only avoiding the LiPS shuttling but also ensuring a faster Li+ migration/supplement in the system.

The catalytic effect of the [CNTs–MM–hemin] on the LiPS redox kinetics was also revealed by the cycle voltammogram (CV) profiles in the Li,S6 symmetric cells (Figure S10, Supporting Information). All the Li,S6 symmetric cells show more obvious current response in contrast to the CNT symmetric cell without Li,S6 electrolyte. Particularly, the electrodes with heme, including CNTs–hemin, CNTs–MM–hemin, and [CNTs–MM–hemin], exhibit higher redox currents than those of [CNTs–MM] and CNTs, meanwhile, the redox currents between CNTs–MM–hemin and CNTs–hemin (or between [CNT-MM] and CNT) are almost comparable, implying superiority of heme, but not MM, in catalyzing LiPS redox kinetics. Impressively, the [CNTs–MM–hemin]
Figure 3. Electrochemical performances of Li–S batteries with different catalysts. a) The fourth cycle of CVs for the cathodes containing [CNTs–MM–hemin], CNTs–MM–hemin, CNTs–hemin, [CNTs–MM], and CNTs, respectively. Right inset is higher magnification of the reduction current between 2.01 and 2.09 V. b) The rate capabilities of the five cathodes. c) The long-term cycling performance of the cathode containing [CNTs–MM–hemin] and CNTs over 900 cycles at 1C. d) Cycling stability of the cathode containing [CNTs–MM–hemin] with a sulfur mass loading of 4.1 mg cm$^{-2}$ measured at a rate of 0.1C for 200 cycles.

The electrode demonstrates the largest redox current, verifying that the special FeN$_5$ configuration in [CNTs–MM–hemin] significantly enhances the LiPS conversion reaction kinetics. This point can be further confirmed by the in situ UV–vis absorption spectroscopic results. Figures S11–S13 in the Supporting Information present the in situ UV–vis absorption spectra of various dissolved LiPS species ($Li_2S_n$, $n = 8, 6, 4$) at the four electrodes, respectively, while Figure 2f–h displays the normalized intensities of the absorbance peaks at 492, 475, 420, and 617 nm, corresponding to the $S_8^{2−}, S_6^{2−}, S_4^{2−}$, and $S_3^{2−}$ ions,$^{[28]}$ respectively, as a function of potential. According to the drastically decreased intensities of $S_8^{2−}$ and $S_6^{2−}$ and increased intensity of $S_3^{−}$ on the electrodes containing hemin (CNTs–hemin and [CNTs–MM–hemin]) and the comparable intensities of $S_8^{2−}, S_6^{2−},$ and $S_3^{−}$ between [CNTs–MM] and CNTs during discharge (Figure 2f,g), it is deduced that compared to MM, hemin has better catalytic capability to covert long-chain LiPSs ($S_8^{2−}$ and $S_6^{2−}$) to $S_3^{−}$ radicals, especially when a FeN$_5$ configuration is formed in [CNTs–MM–hemin]. For the conversion of short-chain LiPSs ($S_4^{2−}$), although both hemin and MM show very limited catalytic effect (as found in purple and orange dots in Figure 2h), after the condensation reaction, [CNTs–MM–hemin] also manifests an amazing catalytic potential in converting short-chain $S_4^{2−}$ ions to $S_3^{−}$ radicals (as shown with the pink dots in Figure 2h).

2.3. Electrochemical Performance

To verify the beneficial effect of the [CNTs–MM–hemin] catalyst on improving the performance of Li–S batteries, CVs, galvanostatic charge/discharge voltage profiles, and rate performance of the batteries using [CNTs–MM–hemin], CNTs–MM–hemin, CNTs–hemin, [CNTs–MM], and CNTs modified cathodes are compared in Figure 3 and Figures S14 and S15 in the Supporting Information. The reduction/oxidation peaks for the cathodes containing hemin (CNTs–hemin, CNTs–MM–hemin, and [CNTs–MM–hemin]) are more positive/negative than those of [CNTs–MM] and CNTs modified cathodes, indicating that hemin artificial enzyme as a catalyst may efficiently facilitate the catalytic conversion between sulfur and $Li_2S_2/Li_2S$, in agreement with our previous reports.$^{[21,29,30]}$ The CV plot of the battery with [CNTs–MM–hemin] cathode presents the sharpest and most positive/negative reduction/oxidation peaks, the smallest voltage hysteresis ($ΔV$) and the highest collection coefficient ($I_L/I_{li}$).
All charge/discharge profiles of the five batteries at 0.2 C exhibit two distinct discharge and one charge plateaus (Figure S15a, Supporting Information), corresponding to the typical multistep conversion reactions of sulfur, in consistent well with the above CV results (Figure 3a; Figure S14, Supporting Information). Obviously, the charge/discharge curves of the battery with CNTs–MM–hemin cathode reveal lowest plateaus and lowest polarization voltage (ΔE; Figure S15b, Supporting Information), reflecting the capacity improvement and faster reaction kinetics contributed by the catalysis of CNTs–MM–hemin composites. In Figure 3b, the discharge capacities of CNTs–MM–hemin cathode are 1490, 1196, 1100, 1038, and 982 mAh g⁻¹ at 0.2 C, 0.3 C, 0.5 C, 0.8 C, and 1 C (1 C = 1675 mAh g⁻¹), respectively. As the current density is restored to 0.2 C, a specific capacity of 1172 mAh g⁻¹ is recovered, which is substantially higher than those of the CNTs–MM–hemin, CNTs–hemin, [CNTs–MM] and CNT cathodes. The ultrahigh reversible capacity of the [CNTs–MM–hemin] cathode strongly indicates the enhanced sulfur utilization and accelerated redox kinetics of LiPSs at [CNTs–MM–hemin] cathode surface. For the long-term cycling performance, the [CNTs–MM–hemin], CNTs–MM–hemin, and CNT cathodes with sulfur loading of ∼1.4 mg cm⁻² were further evaluated at 1 C (Figure 3c; Figure S16, Supporting Information). The [CNTs–MM–hemin] cathode shows the best cycling stability among them. It delivers the initial and retained discharge capacities of 978 and 571 mAh g⁻¹ after 900 cycles, corresponding to a capacity decay ratio of 0.046% per cycle. To the best of our knowledge, such a good cycling stability of [CNTs–MM–hemin] cathode has rarely been reported in recent literatures related to Li–S batteries (as compared in Table S2 in the Supporting Information). By contrast, the CNTs–MM–hemin and CNT cathodes only provide initial discharge capacities of 899 and 681 mAh g⁻¹, dropping rapidly to 350 (capacity decay ratio: 0.068%) and 88 mAh g⁻¹ (capacity decay ratio: 0.098%) after 900 cycles, respectively (Figure 3c; Figure S16, Supporting Information). It is further confirmed that [CNTs–MM–hemin] with a periodic covalent network structure plays an important role in accelerating surface reaction kinetics. When increasing the sulfur mass loading to ∼4.1 mg cm⁻², the [CNTs–MM–hemin] cathode exhibits a high capacity retention of 87% and an areal capacity of 2.14 mAh cm⁻² over 200 cycles (Figure 3d). Even at the ultrahigh sulfur mass loading of 7.5 mg cm⁻², the [CNTs–MM–hemin] cathode still reveals the high capacity retention of 83% after 110 cycles (Figure S17, Supporting Information), further demonstrating the long cycle lifespan of [CNTs–MM–hemin] cathode and its potentials in practical application of Li–S batteries.

Cycle-dependent UV–vis investigations of different composites in electrolyte solution were performed, aiming to find out the underlying reasons for the excellent cycling performance of the [CNTs–MM–hemin] cathode, as shown in Figure S18 in the Supporting Information. It shows that the [CNTs–MM–hemin] sample exhibits the lowest hemin concentration in solution during cycling, clearly suggesting the [CNTs–MM–hemin] possesses the most robust immobilization capability to hemin through the multiple (covalent, coordinated, physical) connections. On the contrary, the significant increases in the hemin concentration in solution were observed in CNTs–MM–hemin and CNTs–hemin during cycling, implying a weak immobilization ability of CNTs–MM–hemin and CNTs–hemin to hemin only through the physical connection (π–π interaction). The results were further confirmed by a high Fe retention rate (≥92%) in [CNTs–MM–hemin] cathode and a low Fe retention rate (≤53.0% and 29.5%, respectively) in CNTs–MM–hemin and CNTs–hemin cathodes after 500 cycles in inductively coupled plasma-mass spectrometry (ICP-MS) analysis (Figure S19, Supporting Information). The positive role of the [CNTs–MM–hemin] in high sulfur utilization and enhanced reaction kinetics was further verified in the electrochemical impedance spectra (EIS) measurement. These spectra in Figure S20a–e in the Supporting Information were analyzed using the equivalent circuit model in Figure S20f in the Supporting Information, where R_e is electrolyte resistance, R_1 is interfacial charge transfer resistance, and R_2 is the mass transportation resistance of the solid-state layer of the accumulated insoluble Li_2S_2/Li_2S_3/Li_2S_4 composite to hemin. Meanwhile, the most stable and lowest R_e (Figure S21b, Supporting Information) and R_2 (Figure S21c, Supporting Information) are also observed in [CNTs–MM–hemin] cathode, demonstrating sustainable and efficient charge/mass transportation for sulfur redox reactions during long-term cycling.}

### 2.4. Catalytic Mechanisms

To gain insight into the catalytic effect of the composite cathode on mitigating LiPS shuttle at the microscale, the Raman spectra were measured in situ during the second discharge of the five cathodes, as shown in Figure 4a–e. The potential dependences of the peak intensities are provided in Figure 4f–j. As the cathodes are discharged from 2.6 to 2.2 V, the intensity depletion of the strong S₈ peaks (pointed by green stars) [35] and the intensity enhancement of long-chain LiPS (Li₂S₈/Li₂S₆) peaks (pointed by red stars) [36] are observed on the five cathodes, signifying the S₈ rings are opened to form a large quantity of long-chain LiPSs. Subsequently, the cell potential was held at 2.2 V, where long-chain LiPSs are further reduced to short-chain LiPSs (Li₄S₇/Li₂S/Li₂S₃), and Raman spectra from the cathodes were acquired for each 15 min in order to reveal the role of catalysts in suppressing the LiPS migration. There is no much intensity change of both long-chain and short-chain LiPSs observed with increasing time for [CNTs–MM] and CNT cathodes, but the cathodes with hemin (CNTs–MM–hemin, CNTs–hemin, and [CNTs–MM–hemin] cathode) exhibit a progressive intensity increase of short-chain LiPS peaks and a considerable intensity loss of long-chain LiPS peaks during the time, particularly CNTs–MM–hemin cathode shows the largest intensity variation. These results clearly evident that hemin can effectively mitigate LiPS shuttle through catalyzing long-chain LiPSs to short-chain LiPSs (Li₄S₇/Li₂S₃ + nLi^+ + ne⁻ → Li₂S₄/Li₂S₃/Li₂S), especially in the Fe₃N₄ configuration in the [CNTs–MM–hemin] cathode. The findings correspond well to the symmetric cell (Figure S10, 2104205 (6 of 13) © 2021 The Authors. Advanced Science published by Wiley-VCH GmbH
Figure 4. In situ Raman investigation of different cathodes during discharge. In situ Raman spectra of the a) [CNTs–MM–hemin], b) CNTs–MM–hemin, c) CNTs–hemin, d) [CNTs–MM], and e) [CNTs–MM] cathodes during the second discharge, where the cell potentials were scanned from 2.6 to 2.2 V, and kept at 2.2 V for a long time. Time dependence of the normalized peak intensity of different sulfur species at the f) [CNTs–MM–hemin], g) CNTs–MM–hemin, h) CNTs–hemin, i) [CNTs–MM], and j) [CNTs–MM] cathodes.
Figure 5. Semi-in situ S 2p and Li 1s XPS spectra. Semi-in situ S 2p XPS spectra of a) [CNTs–MM–hemin], b) CNTs–MM–hemin, c) CNTs–hemin, d) [CNTs–MM], and e) CNT cathodes after discharging to specific states. Semi-in situ Li 1s XPS spectra of f) [CNTs–MM–hemin], g) CNTs–MM–hemin, h) CNTs–hemin, i) [CNTs–MM], and j) CNT cathodes after discharging to specific states.

Supporting Information) and in situ UV–vis absorption spectroscopy results (Figure 2f–h; Figures S11–S13, Supporting Information).

Beside the evolution micromechanism of the adsorbed LiPSs, the structural dynamics of the cathode material itself during discharge is also a noteworthy issue. As shown in Figure S22a in the Supporting Information, the Fe 2p$_{1/2}$ and Fe 2p$_{3/2}$ peaks due to hemin in [CNTs–MM–hemin] cathode gradually shift to lower binding energy upon discharge, which suggests that Fe in hemin is gaining electron density from both S atom of LiPSs and N atom of hemin or MM, giving rise to stronger Fe–S and Fe–N bonds, but weaker S–S and C–N bond in molecules. As a result, the S–S bond in long-chain LiPSs easily breaks to form short-chain LiPSs, and the C–N Raman peak shifts to a lower wavenumber during the sulfur reduction reaction on [CNTs–MM–hemin] cathode (Figure S22b,c, Supporting Information).

The catalytic abilities toward short-chain LiPS conversion of the aforementioned catalysts were further evaluated by the potentiostatic Li,S deposition measurements. As shown in Figure S23 in the Supporting Information, the amounts of the Li,S precipitation on the electrodes are in the order of [CNTs–MM–hemin] (261.4 mAh g$^{-1}$) > [CNTs–MM–hemin] (221.7 mAh g$^{-1}$) > [CNTs–MM] (194.7 mAh g$^{-1}$) > CNTs–hemin (170.5 mAh g$^{-1}$) > CNTs (132.8 mAh g$^{-1}$), whereas their precipitation time is totally in a reverse order ([CNTs–MM–hemin] (6744 s) < CNTs–MM–hemin (7146 s) < CNTs–hemin (8236 s) < [CNTs–MM] (9032 s) < CNTs (10650 s)), revealing the most vigorous Li$_2$S nucleation kinetics on [CNTs–MM–hemin] owing to a synergistic catalytic effect of covalent, coordinated, and physical interactions in the system on the conversion of short-chain LiPSs.$^{[37]}$

The reaction mechanisms of [CNTs–MM–hemin] catalysts were also clarified by a semi-in situ XPS study. The S 2p signals of the Li salts and their decomposition products in different degree are observed at 167.0–170.5 eV$^{[38,39]}$ on all the cathodes of discharge states, since the Li salts were not removed from the extracted cathodes surface in order to obtain the full information of the sulfur species (Figure 5a–e). At fully charged state (2.8 V), the S$_8$ signals dominate the low binding energies of all the cathodes. After discharging to 2.05 V, the S$_8$ signals are severely attenuated and the LiPS (Li$_2$S$_n$, 4 ≤ n ≤ 8) signals are enhanced prominently. When the cathodes are fully discharged to 1.6 V, the reduction of Li$_2$S$_n$, (4 ≤ n ≤ 8) signals and the...
increase of Li$_2$S$_2$/Li$_2$S signals are observed at the five cathodes. The findings are the typical reduction process of S$_n$ to form Li$_2$S$_n$ ($4 \leq n \leq 8$) then to Li$_2$S$_2$/Li$_2$S on the cathode. On careful analysis, the cathodes containing hemin ([CNTs–MM–hemin], CNTs–MM–hemin, and CNTs–hemin) exhibit the stronger S$_n$ and Li$_2$S$_n$ ($4 \leq n \leq 8$) signals at 2.8 and 2.05 V, respectively, than the hemin-free cathodes ([CNTs–MM] and CNTs), substantiating the good catalytic effect of hemin on long-chain LiPSs conversion again.[40] Moreover, the cathodes with MM ([CNTs–MM] or CNTs–MM–hemin) display larger proportions of Li$_2$S$_2$/Li$_2$S than the MM-free cathodes (CNTs or CNTs–hemin) at 1.6 V, suggesting MM can catalyze the conversion from Li$_2$S$_n$ ($4 \leq n \leq 8$) to insoluble Li$_2$S$_2$/Li$_2$S. Upon the catalytic effect of both hemin and MM along with a special FeN$_5$ configuration, the [CNTs–MM–hemin] cathode exhibits the strongest Li$_2$S$_2$/Li$_2$S signals and the smallest proportions of Li$_2$S$_n$ ($4 \leq n \leq 8$) at 1.6 V, manifesting its extraordinary ability to catalyze the LiPSs conversion, in good accordance with the foregoing in situ Raman (Figure S22, Supporting Information) and Li$_2$S nucleation results (Figure S23, Supporting Information).

The Li element is further visualized by the signals at binding energy of $\approx 55.5$ eV in the XPS spectra (Figure 5f–j). At fully charged state (2.8 V), the Li 1s signal due to Li–S bond of LiPSs from pristine CNTs is at slightly higher binding energy than other four cases, indicating less electron loss in other cases, which in turn suggests the electron from N of hemin or MM might transfer to Li$^+$, forming a “Li-bond-like” S–Li$^+$ bridging configuration. One thing to be noted is that the other four Li 1s peaks are located at different binding energies, which is probably attributed to the discrepancy in forming Li–N bond or S–Li$^+$ bridging configuration between Li$^+$ and different N species in various catalytic molecules, in good agreement with the $^7$Li NMR results (Figure 2e). As the cathode is discharged to 2.05 V, the significant shifting toward lower binding energy in Li 1s signal is witnessed at CNTs–hemin cathode, but the shifting stops when the cathode is further discharged to 1.6 V. This directly proves that hemin artificial enzyme as a catalyst does have the strong catalytic conversion ability to long-chain LiPSs, but not to short-chain LiPSs. Almost no Li 1s shifting at CNTs–MM surface during discharge is the evidence that MM hardly converts short-chain LiPSs via Li-bonds without the aid of hemin for accelerating the conversion of long-chain LiPSs, although MM is beneficial for the conversion of short-chain LiPSs (as proved by XPS in Figure 5). Despite both hemin and MM are included in the CNTs–MM–hemin cathode, the extent of shifting at 2.05 V is much more significant than that at 1.6 V, as observed at CNTs–hemin, largely due to the discontinuous and uneven distribution of hemin and MM on the surface of the CNTs, where the long Li$^+$ diffusion path from the hemin to the nearby MM surface limits the conversion kinetics of short-chain LiPSs. In [CNTs–MM–hemin] cathode, MM can not only enhance the catalytic activity of hemin toward long-chain LiPSs and molecular uniform distribution, but also shorten the electron/Li$^+$ migration distance between the two molecules through covalent and coordinated bonds, as a result, a fast and smooth catalytic conversion and nucleation of LiPSs can be realized at the interface. That is why a gradual shifting toward lower binding energy of the Li 1s signal during discharge (Figure 5f) and the highest Li$^+$ diffusivity in the redox reaction ([Figure 6a,b; Figure S24 and Table S3, Supporting Information] are detected at [CNTs–MM–hemin] surface.

Given rich and diverse Li–N bonds exist in the system and easily form Li-bond networks, a periodic hemin–MM configuration was established here, as shown in Figure 6c and Figure S25 in the Supporting Information, where one end of MM molecule attaches to the Fe center atom of hemin via Fe–N coordination and the other end (amino group) of MM binds with adjacent hemin through forming covalent amide bond. Based on this model, the migration paths of Li$^+$ on the surfaces of periodic hemin–MM and hemin were calculated by climbing image nudged elastic band (CI-NEB) method, respectively, and are given in Figure 6d,e. The calculated energy barrier of Li$^+$ along the diffusion coordinate on hemin surface is 2.38 eV (Figure 6f). Surprisingly, it decreases to 0.87 eV for hemin–MM (Figure 6f), where the Li atoms are preferentially adsorbed on O atoms of amide group and N atoms of MM and form a large number of Li-bonds (Li–N and Li–O bonds), even Li-bond networks. The results demonstrate that the multiple Li-bonds and Li-bond networks are favorable for reducing the energy barrier of Li$^+$ diffusion and enhancing the nucleation kinetics of LiPSs, which is confirmed by the above Li$_2$S deposition, Li 1s XPS and Li$^+$ diffusivity experiments.

The above analysis can give an overall picture of what is happening in this system. Hemin artificial enzyme inherits strong adsorption and catalytic activity to long-chain LiPSs via Li–N bond and Fe–S coordinated bond. In the process of discharge, hemin fights for electrons from long-chain LiPSs through Fe–S bond, promoting the cleavage of the S–S bond in long-chain LiPSs and the generation of the short-chain LiPSs. With the help of physical π–π interactions between the CNTs and the molecules (hemin and MM), amide bonds between MM and hemin/CNTs, and Fe–N coordination between hemin and MM, MM cofactor not only acts as a stabilizer for easy-lost hemin, but also has high adsorption ability to Li$^+$ for a fast solid Li$_2$S nucleation. The foregoing short-chain LiPSs trapped on hemin surface rapidly diffuse to adjacent MM and form abundant and various Li-bonds (multiple Li–N bonds), even Li-bond networks, between them, accelerating electron/Li$^+$ transfer in the system and boosting the conversion of short-chain LiPSs to insoluble Li$_2$S$_2$/Li$_2$S. With the synergistic effect of covalent, coordinated and physical interactions between hemin, MM and CNTs, the [CNTs–MM–hemin] catalyst guarantees the smooth sulfur catalytic conversion to mitigate the shuttle effect of LiPSs effectively and improve the electrochemical performance of Li–S batteries.

3. Conclusion

In conclusion, a new cofactor-assisted artificial enzyme with multiple Li-bond networks, i.e., [CNTs–hemin–MM], was proposed to accelerate the SRR kinetics and suppress the polysulfide shuttle in Li–S batteries. A large number of well-dispersed FeN$_5$ sites as catalytic active centers of hemin and perfect Li-bond electronic transmission networks offered by MM cofactors on CNT conductive substrates fully realize the efficient and stable catalytic superiorities to promote both long-chain and short-chain LiPS conversions. Comprehensive spectroscopic and electrochemical characterizations combined with theoretical calculations elaborate the catalytic effects and reaction mechanisms on LiPS conversion at [CNTs–hemin–MM] cathodes, particularly the
synergistic functions of the covalent amide bonds, coordinated FeN₅ configurations and physical π–π conjugations formed between hemin, MM, and CNTs. The high and sustained catalytic effects toward LiPSs decide outstanding electrochemical performances of Li–S batteries, exhibiting impressive stability and high sulfur loading performance. The present work opens up a new and sustainable avenue on the design of cofactor-assisted artificial enzyme and multiple Li-bond networks to achieve efficient sulfur conversion for advanced rechargeable lithium batteries. It is believed that the concept of multiple Li-bond networks may also inspire the understanding of Li⁺ transport properties and growth behavior of Li dendrites and propel the development of high-performance lithium secondary battery systems.

4. Experimental Section

Material Synthesis: [CNTs–MM–hemin] composite was fabricated using the previously reported method.[41] First, 10 mg hemin (>95%, Alfa Aesar) and 10 mg carboxylated multiwalled CNTs (>99.9%, inside diameter: 3–5 nm, Aladdin) were dispersed in anhydrous ethanol (5 mL, >99.5%, Aladdin) under ultrasonication. The 7 mg 1-ethyl-3(dimethylaminopropyl) carbodiimide (EDC, >97%, Sigma-Aldrich) and 7 mg N-hydroxysulfosuccinimide sodium salt (Sulfo-NHS, >98%, Sigma-Aldrich) were further injected into the above mixture and stirred for 2 h to activate the carboxylic groups of hemin and CNTs. Subsequently, a MM (>99%, Alfa Aesar) solution (10 mg of MM dissolved in 3 mL of anhydrous ethanol) was introduced into the mixture and stirred overnight for producing amide bonds by a condensation reaction between the carboxylic acid group of hemin/CNTs and the amino groups of MM. The obtained dispersion was then centrifuged at 3000 rpm for 5 min. This procedure was repeated three times. The resulting wet [CNTs–MM–hemin] composite was allowed to evaporate at 55 °C in vacuum to dryness. The average Fe content in [CNTs–MM–hemin] composite was measured to be ≈91% of hemin molecules was effectively attached onto the CNTs. For comparison, the composite without hemin (denoted as [CNTs–MM]) was fabricated under the same condition of [CNTs–MM–hemin]. The composites without condensation method (denoted as CNTs–MM–hemin and CNTs–hemin, in which hemin is physically bonded to its host) were fabricated by ultrasonication of CNTs, hemin, and MM in a mass ratio of 1:1:1 or CNTs and hemin in a mass ratio of 1:1 in N-methyl-2-pyrrolidinone (NMP, >99.5%, Aladdin) followed by hot drying treatment at 55 °C for 8 h.

Material Characterization: HAADF-STEM images and EDX elemental mappings of [CNTs–MM–hemin] were collected at 200 kV using a FEI-Thermis Z instrument equipped with a probe corrector, a high-angle annular dark-field detector, and EDX detector. Thermo Fisher Scientific K-Alpha instrument served as X-ray photoelectron spectrometer (Excitation source: Al Ka). FTIR spectra were recorded using a Fourier transform

Figure 6. Li⁺ diffusion study. a) CV curves of [CNTs–MM–hemin] cathode at different scan rates. b) Corresponding linear fits of the peak current in panel (a) based on Equation (1). c) Side view of periodic hemin–MM configuration. Side views of Li⁺ migration routes on d) periodic hemin–MM and e) hemin surfaces. f) The relevant energy barrier of Li⁺ diffusion on periodic hemin–MM and hemin surfaces. The light blue, brown, pink, rose pink, red, blue, and green balls are N, C, H, Fe, O, Cl, and Li atoms, respectively.
Galvanostatic charge–discharge, rate performance, and cycle life measurements were characterized by a Neware battery testing system (CT-4008T-5V20mA-164, Shen Zhen Netware Technology) between 1.6 and 2.8 V (vs Li/Li⁺) at room temperature. All the electrochemical measurements mentioned previously were conducted at ambient temperature (30 °C). All current and capacity were calculated based on the sulfur mass of the cathode.

\[i_0 = (2.65 \times 10^{-5}) n^{1.5} S_{Li}^{0.5} C_{Li}^{0.5}\]  

(1)

In this equation, \(i_0\) is the peak current, \(n\) is the charge transfer number, \(S\) is the electrode area, and \(i_{Li}^0\) is the diffusion coefficient of \(Li^+\) through Equation (1).
concentration in the electrolyte, and  is the scan rate. Since , , and are constant,  has a linear relation with and  can be obtained from the slopes of curves.

**Computational Methods:** DFT calculations were conducted using the Vienna Ab initio Simulation Package (VASP 5.3.5) with the projector augmented wave (PAW) and Perdew–Burke–Ernzerhof (PBE) exchange–correlation functional. The plane-wave cutoff energy was set as 450 eV. For hemin-based structure optimizations, a  1 Monkhorst–Pack (MP)  grid was used to sample the Brillouin zone. The adsorption energies  for LiPSs on surfaces were determined by Equation (2)

$$E_{\text{ads}} = E_{\text{total}} - E_{\text{surf}} - E_{\text{LiPS}}$$

where  and  represent the total energies of the adsorbed systems, pristine substrates, and the isolated LiPS clusters, respectively.

**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.

**Keywords**

biomimetic catalysts, covalent amide bonds, FeN5 coordination structures, lithium–sulfur batteries, multiple Li-bond networks
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