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Article

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Dual-Atoms Iron Sites Boost the Kinetics of Reversible Conversion of Polysulfide for High-Performance Lithium-Sulfur Batteries

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ABSTRACT:

Atomically dispersed metal catalysts have offered significant potential for accelerating sluggish kinetics of transformation of lithium polysulfide(LiPS) and inhibiting the shuttle effect to achieve the long-life cycling and high rate of lithium sulfur batteries. However, the end-on adsorption structure between single metal site and polysulfide limits the adsorption capacity and catalytic activity of single atom catalysts. Here, we construct dual-atoms iron sites on nitrogen doped graphene to serve as highly efficient catalyst for lithium sulfur batteries. As expected, the dual-atoms sites can firmly bound polysulfides by forming double Fe-S bonds between polysulfides and the two adjacent iron atoms. Such double-bond adsorption structure is also favorable for the electron transfer and polysulfides activation, so as to reduce the energy barrier and accelerate the reaction

kinetics. As a result, the as-obtained dual-atoms iron catalyst can effectively alleviate the shuttle effect and improve the utilization of active sulfur, thus the batteries present high initial capacity of 1615 mAh g⁻¹ at 0.05 C and long-cycle life with a decay rate per cycle as low as 0.015% at 2C over 1000 cycles.

Introduction

Lithium-sulfur(Li-S) batteries have been acknowledged as promising candidates for a new generation of energy-storage systems owing to their superiority in high energy density(2600 Wh kg⁻¹) and theoretical specific capacity (1672 mAh g⁻¹), low cost and environmental friendliness¹⁻³. Despite great advantages, the practical performances, especially sulfur utilization and long-term stability, are greatly limited by the migration of soluble lithium polysulfide intermediates and sluggish kinetic of sulfur electrochemistry⁴⁻⁶.

In past decades, integrating sulfur with various carbon-based materials or polar compounds were widely applied to physically or electrostatically confine the LiPS in the cathode sides⁷⁻⁹. Those passive strategies could improve the performance to some extent, but failed in the long term, especially at high sulfur loading¹⁰⁻¹². The sluggish redox kinetic of phase change process (transformation of soluble LiPS to insoluble Li₂S₂/Li₂S) causes the accumulation of LiPS and leak to anode, leading to serious shuttle effect. Moreover, the high activation energy barrier of Li₂S makes it hard to be reused, resulting in high polarization and low active material utilization. Recent works demonstrated that introducing electrocatalysts¹³⁻¹⁵ (such as metal sulfides^{16, 17}, carbides¹⁸, nitrides^{19, 20}, and so on) to promote the sophisticated electrochemistry processes of LiPS is an

effectively proactive strategy to fundamentally prevent the shuttle effect and improve the performance of Li-S batteries. However, the reported metal-based catalysts are largely limited by the poor conductivity, low activity and limited amount of active sites²¹⁻²³. Therefore, the development of promising electrocatalysts for advanced Li-S battery still remains a great challenge.

Recently, Atomically dispersed metal catalysts with individually exposed metal centers and tunable electronic structure possess theoretical 100% atom utilization efficiency and utmost catalytic activity, which have demonstrated great application potential in electrocatalysis²⁴⁻²⁶, photocatalysis^{27, 28}, and electrochemical energy storage²⁹⁻³¹. Most recently, our previous work and others have proved that metal single atoms catalysts could also promote the redox kinetic of LiPS in Li-S batteries³²⁻³⁴. However, Efficient catalysts usually require active sites with optimized spatial and electronic structures to match the reactants, achieving strong adsorption capacity and efficient electron transfer. The isolated metal center of single atoms catalysts can only coordinate with one sulfur atom in LiPS to form one Fe-S bond³⁵⁻³⁹, such end-on adsorption structure is unfavorable to the stable anchoring of LiPS. In addition, the end-on adsorption structure limits the activation of S-S bond of LiPS, resulting in high reaction energy barrier. In this regard, Manipulating the spatial and electronic structures of active sites by employing poly-center metal atoms to regulate the adsorption structure with LiPS will be an effective strategy to synergistically optimize adsorption capacity and reaction kinetics.

Herein, we constructed atomically dispersed dual-atoms iron sites supported on nitrogen doped graphene (denoted as Fe DAs-NG), and applied to Li-S batteries to explore its electrocatalytic reactivity and mechanism for the conversion of LiPS for the first time. Density functional theory(DFT) calculations revealed that the two adjacent Fe atoms in dual-atoms Fe site can form

two Fe-S with two adjacent S atoms of one LiPS molecular, separately, so as to exhibit strong LiPS adsorption capacity and strong driving force for S-S bond breaking. Moreover, the dual-atoms Fe sites could activate Li_2S molecule and reduce its decomposition energy barrier. As a result, the obtained Fe DAs-NC exhibit superior catalytic activity in the sluggish reversible conversion processes of LiPS, and effectively reduced the shuttle effect and irreversible capacity loss. The Li-S batteries with Fe Ds-NC/S cathode display a greatly improved initial capacity of 1615 mAh g^{-1} and outstanding cycle stability with a low decay rate per cycle of 0.015% at 2C. Even at a high sulfur areal loading of 7.9 mg cm^{-2} , the Fe Ds-NC/S cathode could deliver high capacity of 6.6 mAh cm^{-2} over 200 cycles at 0.2 C.

Results and discussion

Material characterization

In this work, we constructed isolated dual-atoms iron sites on nitrogen doped graphene by a two-step impregnation method. This method is based on the chemical interaction between single atom Fe sites and polar Fe species. In detail, the isolated atomic Fe doped graphene (Fe SAs-NC) was first obtained by thermal reduction of a mixture of Graphene oxide and Fe (III) chloride under ammonia (NH_3) gas flow. Then the single Fe atoms sites served as chemisorption sites to anchor the subsequently impregnated Fe species. Following by heat treatment at NH_3 atmosphere, the adsorbed Fe species were reduced and bonded with the neighboring Fe atoms to form dual-atoms Fe sites on the surface of carbon. The detailed geometric structure of Fe SAs-NC and Fe DAs-NC materials were investigated by scanning electron microscope (SEM) and transmission electron microscopy (TEM) images. As shown in Figure 1a, b and S1a, b, the Fe DAs-NC maintains graphene-like ultra-

thin layered structure and shows a wrinkled surface, indicating that the graphene sheets did not agglomerate during the drying and calcination process and maintained large specific surface area(Figure S2). In addition, no obvious nanoparticles were observed. The corresponding elemental mapping profiles of Fe DAs-NC and Fe SAs-NC in Figure 1c, S1c demonstrated the random distribution of Fe and N atoms in carbon matrix without distinct aggregation. Moreover, No characteristic diffraction peak of Fe-based compounds was found in X-ray diffraction (XRD) patterns (Figure S3) of Fe DAs-NC, further verified the the absence of large Fe-based nanoparticles. To investigate the existential form of Fe atoms, the aberration-corrected high-angle annular dark-field STEM (HAADF-STEM) was performed. As shown in Figure 1d, lots of bright dots homogeneously distributed on the carbon matrix. As expected, most of the bright dots appear in pairs with a distance of 2.2-2.3 Å(Figure 1e, f), suggesting the successful fabrication of Fe-Fe dimer structure^{40, 41}. Some of them were tagged by red circles. As a contrast, the HAADF-STEM image of Fe SAs-NC shows isolated bright dots in Figure S1d, suggesting the single atomic dispersion structure of Fe SAs-NC.

Figure 1 (a) SEM and (b) HRTEM images and (c) EDS elemental mapping profiles of Fe DAs-NC. (d) Aberration-corrected HAADF-STEM and (e) magnified images marked in d and (f) corresponding intensity profiles.

To further analysis the coordination structure and local electronic environment of dual-atoms Fe sites, the Fe DAs-NC was characterized by extended X-ray absorption fine structure (EXAFS) and Fe K-edge X-ray absorption near-edge structure (XANES) measurement in comparison with Fe SAs-NC, Fe₂O₃ and Fe foil. As shown in Figure 2a, the Fourier transform of EXAFS spectra of both Fe DAs-NC and Fe SAs-NC show a main peak at ~ 1.5 Å, which could be attributed to Fe-N(O) bonds in the first shell²⁴. In addition, there is also a minor peak of Fe-Fe scattering path in Fe DAs-NC at 2.4 Å, which is absent in Fe SAs-NC. Table S1 revealed the coordination numbers and bond length of Fe-N and Fe-Fe bonds by fitting K-edge EXAFS curves. The coordination numbers of Fe-Fe bond for Fe DAs-NC was 1.1, suggesting that the adjacent Fe atoms tend to form dimer which is consistent with results of the AC-STEM images. In addition, Fe DAs-NC showed an Fe-N

coordination number of 3.4, which means that most Fe atoms bonded with three N atoms to form Fe-N₃ structure. Above results confirmed that the coordination structure of dual-atoms Fe sites in Fe DAs-NC is Fe₂-N₆(Figure 2b)^{42, 43}. In comparison, the Fe-N coordination numbers of Fe SAs-NC was 4.2, which is consistent with typical Fe-N₄ structure⁴⁴. As shown in Figure 2c, the pre-edge XANES spectra suggested that Fe atoms in Fe DAs-NC and Fe SAs-NC show positive valence between Fe foil and Fe₂O₃, and the dual-atoms Fe sites possess lower oxidation state compared with single Fe sites, which is facilitated the electron transfer through Fe-N bonding. The corresponding X-ray photoelectron spectroscopy(XPS) spectrum revealed similar result (Figure S4). In Figure 3d, the two major peaks at 710.8 and 724.5 eV ascribing to the Fe²⁺ 2p_{3/2} and Fe²⁺ 2p_{1/2}. Moreover, the negatively shifted bonding energy of dual-atoms Fe also suggested a lower oxidation state of Fe (Figure S5)⁴⁵. In addition, the N 1s XPS spectrum of both Fe DAs-NC and Fe SAs-NC shows similar four characteristic peaks at ~398.1, 398.8, 399.8 and 401.4 eV, corresponding to pyridine N, Fe-N, pyrrole N and graphitized N, respectively(Figure S6)^{46, 47}. According to the XPS quantitative analysis results the N content of Fe DAs-NC was as high as 15.3 wt.%, which is not only beneficial to loading a large number of Fe atoms, but also to providing additional polar sites for LiPS adsorption. The Fe content of Fe DAs-NC was determined to be 5.6 wt.% according to the inductively coupled plasma optical emission spectrometry (ICP-OES). For comparison, the Fe SAs-NC has a similar Fe content of 4.8 wt.%. Above results confirmed that the dual-atoms Fe site with Fe₂-N₆ coordination structure was successfully constructed.

Figure 2 (a) Fe K-edge XANES spectra and (b) FT-EXAFS spectra of Fe DAs-NC, FeSAs-NC, Fe₂O₃ and Fe foil.

(c) EXAFS fitting curve and top view of the optimized Fe DAs-NC(inset). Magenta, blue and brown balls

represent Fe, N and C atoms, respectively. (d) XPS spectra of Fe 2p.

Reaction Kinetics

To evaluate the catalytic activities of Fe DAs-NC on the redox conversion of LiPS, various electrochemical measurements have been studied as shown in Figure 3. The symmetric cells were first constructed using identical catalysts as working and counter electrodes and Li₂S₆ solution (0.15 M) as electrolyte. The cyclic voltammetry (CV) profiles of the assembled symmetric cells at a scan rate of 1 mV s⁻¹ are showed in Figure 2a, which exhibited two pairs of obvious redox peaks. The reduction peaks arise from the reduction of Li₂S₆ to short-chain LiPS(peak a) and then Li₂S₂/Li₂S(peak c), the oxidation peaks are due to the oxidation of Li₂S₆ to long-chain LiPS(peak b)

and final sulfur(peak d)⁴⁸. Compared with Fe SAs-NC, the CV curve of Fe DAs-NC electrodes exhibited higher response peak current density, suggesting a faster interfacial reactivity of the LiPS electrochemistry facilitated by the dual-atoms Fe sites. In particular, the significantly higher c peak indicated that the Fe DAs-NC electrodes could greatly promote the deposition of Li₂S. The strong interfacial interaction and fast interface electron transfer are essential preconditions for a redox conversion. As the Nyquist plot shown in Figure S7, the Fe DAs-NC electrodes exhibited a lower charge transfer impedance (14.5 Ω) than that of Fe SAs-NC electrodes (30.9 Ω). The reduced interfacial impedance is attributed to the good conductivity and excellent catalytic activity of dual-atoms Fe sites.

To further confirm the enhanced catalytic properties of Fe DAs-NC in the sluggish phase change process, Li₂S₈ cells with Fe DAs-NC cathode and Li metal anode were employed to explore the deposition and dissolution behavior of Li₂S during charge and discharge process. The galvanostatic discharge curves at C/24 shows a voltage dip at the beginning of the second discharge plateaus (Figure S8) and a voltage jump at the initial charging plateaus (Figure 3d), from which the overpotential for the deposition and decomposition of Li₂S₂/Li₂S could be estimated, respectively^{49, 50}. Noteworthy, the Fe DAs-NC cathode shows lower overpotential in the reversible conversion of soluble Li₂S₄ to insoluble Li₂S₂/Li₂S, indicating that the dual-atoms Fe sites can accelerate the significant liquid-solid-liquid phase change processes. In addition, the Fe DAs-NC cathode showed an earlier and higher discharging current peak in the potentiostatic nucleation experiment (Figure 3b), which indicated an easier and faster Li₂S nucleation and growth process in the surface of Fe DAs-NC. Moreover, the potentiostatic curves also revealed a promoted Li₂S dissolution process (Figure 3c). Above results confirmed that the dual-atoms Fe sites can effectively promote the

sluggish phase transition processes during the charging and discharging process of Li-S batteries, which is conducive to inhibiting the shuttle effect and improving the utilization of active materials.

Owing to the high specific surface area, favorable electrical conductivity and electrocatalytic reactivity, the Fe DAs-NC was applied as sulfur host material of Li-S batteries with sulfur content of 80% and areal loading of 1.8 mg cm^{-2} . The electrocatalytic reactivity was investigated by CV in Figure 3e, the CV profiles of Li-S battery with Fe DAs-NC cathode displayed higher reduction potential and lower oxidation potential than those of Fe SAs-NC cathode, suggesting the lower reaction energy barrier in the each step of reversible conversion of LiPS. In addition, the peak current of peak a (corresponding to the liquid-solid deposition of soluble LiPS to insoluble $\text{Li}_2\text{S}_2/\text{Li}_2\text{S}$) was increased by 83%, the peak current of peak b (corresponding to the solid-liquid conversion of Li_2S to short-chained LiPS) heightened by 66%, suggesting that Fe DAs-NC can efficiently accelerate the conversion kinetics of phase change process in a working Li-S battery. Moreover, The corresponding Tafel slop of Fe DAs-NC cathode in initial reduction (53 mV dec^{-1}) and oxidation process (81 mV dec^{-1}) were lower than those of Fe SAs-NC cathode (58 and 97 mV dec^{-1} , respectively), which further verified the enhanced kinetic conversion of the LiPS (Figure 3f). The charge/discharge profiles at 0.05 C also reflected matched results. As shown in Figure S9, the polarization voltage of Fe DAs-NC cathode (119 mV) was lower than that of Fe SAs-NC cathode (183 mV). Moreover, the plateau capacity ratio ($Q_{\text{low}}/Q_{\text{high}}$) is a key descriptor for evaluating conversion efficiency of LiPS to Li_2S . The Fe DAs-NC/S cathode showed a $Q_{\text{low}}/Q_{\text{high}}$ value of 2.98 (the theoretical value is 3), which is much higher than that (2.29) of Fe SAs-NC/S cathode. Thus, the Fe DAs-NC/S cathode delivered a higher initial discharge capacity of 1615 mAh g^{-1} compared with that of Fe SAs-NC/S cathode (1284 mAh g^{-1}). The enhanced kinetic, inhibited shuttle effect and

promoted specific capacity are ascribed to the superior catalytic activity of the unique dual-atoms Fe sites.

Figure 3 (a) CV curves of the symmetric cells at a scan rate of 1 mV s⁻¹. (b) Potentiostatic nucleation curves, potentiostatic charge curves and (d) Charge overpotential of Fe DAs-NC and Fe SAs-NC electrodes. (e) CV curves and (f) corresponding Tafel plots of initial discharge and charge process.

The Fe DAs-NC with high catalytic reactivity for the conversion of LiPS and the nucleation, deposition and decomposition of Li_2S can effectively prevent the shuttle effect and reduce the irreversible capacity loss of polysulfide to greatly improve the rate capacity and cycle stability of Li-S batteries. As shown in Figure 4a, the Fe DAs-NC/S cathode exhibited excellent rate of 1435, 1300, 1188, 1073, 884 and 706 mAh g⁻¹ at 0.1, 0.2, 0.5, 1, 2 and 5 C, respectively. By contrast, the Fe SAs-NC/S cathode delivered lower capacities especially at a high rate (78.7% and 69% of Fe DAs-NC/S at 2C and 5C, respectively). In particular, when the current density decreased back to 0.2 C, the Fe DAs-NC/S cathode still maintained an average capacity of 1289 mAh g⁻¹, suggesting

an excellent rate stability. In addition, the galvanostatic discharge-charge profiles of Fe DAs-NC/S (Figure 4b, S10) revealed smaller voltage polarization (Figure S11) and higher plateau capacity ratio(Figure S12) at different current density, suggesting that the improved rate performance is attributed to the superb catalytic activity of dual-atoms Fe sites. Furthermore, as shown in Figure 4c, the Fe DAs-NC/S cathode could maintain an excellent cycle stability at a low rate of 0.5 C, the battery delivered a stable discharge capacity of 1021 mAh g⁻¹ after 400 cycles with a capacity decay rate of 0.038% per cycle, which is much lower than that of Fe SAs-NC/S cathode(0.13%). Even at a high rate of 2 C for 1000 cycles, the Fe DAs-NC/S cathode could still reach a high capacity retention of 84.5% with an average Coulombic efficiency of 99.5 %, demonstrating an low capacity decay rate of 0.015% per cycle(Figure 4d). The enhanced capacity retention benefits from the strong LiPS interactions and electrocatalysis effects of dual-atoms Fe sites. To demonstrate the potential of Fe DAs-NC/S in practical applications, Li-S batteries with high sulfur area loading were assembled. As shown in Figure S13, even the S loading increase to 7.9 mg cm⁻² in Fe DAs-NC/S cathode, the battery still reached a high initial capacity of 7.6 mAh cm⁻² at 0.2 C, and maintained a good reversible capacity of 6.6 mAh cm⁻² after 200 cycles. This excellent electrochemical performance directly demonstrate the positive role of the catalytic effect of dual-atoms Fe sites.

Figure 4 (a) Rate performance and (b) corresponding galvanostatic charge-discharge curves (c) Cycle performance at 0.2 C and (d) 2 C of batteries with Fe DAs-NC/S and Fe SAs-NC/S cathode.

The deep mechanism of the improved conversion kinetics of LiPS was further investigated by first-principles calculations. As shown in Figure S14, the stable coordination structure models of Fe DAs-NC and Fe SAs-NC were constructed, according to the XAS and XPS results. The chemical interaction between LiPS and dual-atoms Fe site was reflected by the calculated binding energies

(E_b) ($E_b = E_{Fe\ DA} + E_{LiPS} - E_{LiPS+Fe\ DA}$). As shown in Figure 5a, the E_b of LiPS (S_8 , Li_2S_8 , Li_2S_6 , Li_2S_4 , Li_2S_2 and Li_2S) absorbed on dual-atom Fe site were higher than those on single-atom Fe site, demonstrating the superiority of dual-atoms Fe site in confining LiPS and restricting shuttle effect. Visual experiment was performed to further verify the actual adsorption effect in Figure S15(inset). The Fe DAs-NC powder was added into the yellow Li_2S_4 solution and stood for 12 h, the color of the solution gradually became nearly transparent, in contrast, the solution with the addition of Fe SAs-NC remained light yellow, indicating that the dual-atoms Fe site possess stronger chemical affinity and higher adsorption capacity for Li_2S_4 . The efficient adsorption for Li_2S_4 on Fe DAs-NC was also reflected by the corresponding UV/vis spectra. The strong interaction has a positive effect on LiPS activation. As shown in Figure 5b, the optimized adsorption configuration of Li_2S_4 on Fe DAs-NC surface suggested that Li_2S_4 is bonded on dual-atoms Fe site by two Fe-S bonds. In addition, the charge density differences shows that two adjacent sulfur atoms of Li_2S_4 have intense electron transfer between the two Fe atoms of dual-atoms Fe site, respectively. Such double-bond adsorption structure is of great benefit to efficient adsorb and active the Li_2S_4 . As a contrast, there is only one Fe atom at single Fe atom site to bind the terminal S of Li_2S_4 , causing limited the electron transfer. Moreover, the density of states (DOS) of Li_2S_4 adsorbed on Fe DAs-NC also confirmed the strong interaction between Fe 3d electron and S 2p electron (Figure 5c). And the DOS of Fe DAs-NC is nearer to Fermi level, demonstrated the higher electrical conductivity than Fe SAs-NC, which is conducive to the electron transfer during subsequent electrochemical conversion. The double-bond adsorption configuration also exists between dual-atoms Fe sites and Li_2S_8 , Li_2S_6 and Li_2S_2 (Figure S16, 17, 18, 19). Noteworthily, the Li_2S_2 anchored on dual-atoms Fe site showed more stretched S-S bond than that on single Fe atom site, suggesting that the Li_2S_2 molecule is more

effectively activated on dual-atoms Fe site, which could accelerate the conversion of Li_2S_2 to Li_2S .

Figure 5 (a) Binding energies between the Li_2S_x and Fe DAS-NC, Fe SAS-NC. (b) Side view for charge density

difference of Li_2S_4 adsorption on Fe DAS-NC and Fe SAS-NC, The yellow and blue isosurfaces represent the

electron accumulate and depletion, the iso-surface is set to $0.003 \text{ eV}/\text{\AA}^3$. (c) DOS of Fe 3d and S 2p after Fe DAS-

NC and Fe SAS-NC adsorb Li_2S_4 . (d) Free-energy profiles for the reduction of polysulfides on Fe DAS-NC and Fe

SAS-NC.

The discharging process of Li-S batteries involves stepwise reduction reaction from S_8 to Li_2S , including the initial lithiation of S_8 , the liquid-liquid conversion of Li_2S_8 to Li_2S_4 , liquid-solid conversion of Li_2S_4 to Li_2S_2 and the further reduction of Li_2S_2 . The Gibbs free energy of each reaction steps were calculated on Fe DAS-NC and Fe SAS-NC surface in Figure 5d. The Gibbs free energy values of the lithiation of S_8 and liquid-liquid conversion process is either negative or very small, indicating that those processes are favorable in thermodynamics. In contrary, the larger Gibbs free energy values of the last two conversion steps on both Fe DAS-NC and Fe SAS-NC surface suggested that the liquid-solid conversion and subsequent reduction process are the rate-determining

steps of the overall reaction. The sluggish liquid-solid conversion would cause the accumulation of Li_2S_4 in electrolyte, which is the culprit causing the shuttle effect. The Gibbs free energy values on Fe DAs-NC are much lower than those on Fe SAs-NC, implying the faster kinetic conversion of the LiPS, which are ascribed to the effective activation of dual-atoms Fe site. Apart from the discharge process, the charge process of Li_2S oxidation is also accelerated by the electrocatalysis of dual-atoms Fe sites. As shown in Figure S20, the longer Li-S bond (2.38 Å) and larger Li-S-Li bond angle (118.4°) of Li_2S molecular absorbed on the Fe DAs-NC than those (2.23 Å, 102°, respectively) on single Fe atom site indicate that dual-atoms Fe sites can effectively weaken Li_2S and facilitate the decomposition process. The above results indicate that the synergistic double-bond adsorption structure between LiPS and the two adjacent Fe atoms can effectively anchor and activate LiPS and promote the subsequent conversion.

Conclusion

In summary, we successfully constructed dual-atoms Fe sites on the surface of nitrogen doped graphene as efficient catalyst for boosting conversion kinetics of LiPS. Combining results from theory calculations and experiment, we demonstrated that the unique dual-atoms Fe sites can firmly anchor and effectively activate LiPS molecules by double-bond adsorption structure, which benefit to accelerate the reversible conversion of LiPS as well as suppress the shuttle effect. Therefore, the initial discharge capacities, rate performance and long-term cycle stability of Li-S batteries based on Fe DAs-NC/S cathode are greatly improved. Even at a high sulfur areal loading of 7.9 mg cm^{-2} , the batteries could still maintain high capacity of 6.6 mAh cm^{-2} at 0.2 C over 200 cycles. This double-bond adsorption strategy for activating LiPS could open up a new direction for the further application of isolated central electrocatalysts in Li-S batteries.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available. Structure characterization, and electrochemical properties of Fe DAs-NC and Fe SAs-NC along with additional supporting data.

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Notes

The authors declare no competing financial interest.

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Figures

Figure 1

(a) SEM and (b) HRTEM images and (c) EDS elemental mapping profiles of Fe DAs-NC. (d) Aberration-corrected HAADF-STEM and (e) magnified images marked in d and (f) corresponding intensity profiles.

Figure 2

(a) Fe K-edge XANES spectra and (b) FT-EXAFS spectra of Fe DAs-NC, FeSAs-NC, Fe₂O₃ and Fe foil. (c) EXAFS fitting curve and top view of the optimized Fe DAs-NC(inset). Magenta, blue and brown balls represent Fe, N and C atoms, respectively. (d) XPS spectra of Fe 2p.

Figure 3

(a) CV curves of the symmetric cells at a scan rate of 1 mV s⁻¹. (b) Potentiostatic nucleation curves, potentiostatic charge curves and (d) Charge overpotential of Fe DAs-NC and Fe SAs-NC electrodes. (e) CV curves and (f) corresponding Tafel plots of initial discharge and charge process.

Figure 4

(a) Rate performance and (b) corresponding galvanostatic charge-discharge curves (c) Cycle performance at 0.2 C and (d) 2 C of batteries with Fe DAs-NC/S and Fe SAs-NC/S cathode.

Figure 5

(a) Binding energies between the LiPS and Fe DAs-NC, Fe SAs-NC. (b) Side view for charge density difference of Li₂S₄ adsorption on Fe DAs-NC and Fe SAs-NC, The yellow and blue isosurfaces represent the electron accumulate and depletion, the iso-surface is set to 0.003 eV/Å³. (c) DOS of Fe 3d and S 2p after Fe DAs-NC and Fe SAs-NC adsorb Li₂S₄. (d) Free-energy profiles for the reduction of polysulfides on Fe DAs-NC and Fe SAs-NC.

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