Oxidation States Regulation of Cobalt Active Sites through Crystal Surface Engineering for Enhanced Polysulfide Conversion in Lithium–Sulfur Batteries

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In this work, unique Co$_3$O$_4$/N-doped reduced graphene oxide (Co$_3$O$_4$/N-rGO) composites as favorable sulfur immobilizers and promoters for lithium–sulfur (Li–S) batteries are developed. The prepared Co$_3$O$_4$ nanopolyhedrons (Co$_3$O$_4$-NP) and Co$_3$O$_4$ nanocubes mainly expose (112) and (001) surfaces, respectively, with different atomic configurations of Co$^{2+}$/Co$^{3+}$ sites. Experiments and theoretical calculations confirm that the octahedral coordination Co$^{3+}$ (Co$^{3+}$Oh) sites with different oxidation states from tetrahedral coordination Co$^{2+}$ sites optimize the adsorption and catalytic conversion of lithium polysulfides. Specially, the Co$_3$O$_4$-NP crystals loaded on N-rGO expose (112) planes with ample Co$^{3+}$Oh active sites, exhibiting stronger adsorbability and superior catalytic activity for polysulfides, thus inhibiting the shuttle effect. Therefore, the S@Co$_3$O$_4$-NP/N-rGO cathodes deliver excellent electrochemical properties, for example, stable cyclability at 1 C with a low capacity decay rate of 0.058% over 500 cycles, superb rate capability up to 3 C, and high areal capacity of 4.1 mAh cm$^{-2}$. This catalyst’s design incorporating crystal surface engineering and oxidation state regulation strategies also provides new approaches for addressing the complicated issues of Li–S batteries.

1. Introduction

Lithium–sulfur (Li–S) batteries hold great promise as the energy storage systems due to their theoretical specific energy density (2600 Wh kg$^{-1}$), which is much higher than that of conventional lithium-ion batteries.$^{[1-4]}$ However, the practical application of the Li–S batteries has been hindered by several technical issues: the insulating character of sulfur (S$_8$) and lithium sulfide (Li$_2$S), the huge volume change of S$_8$ during charge–discharge process, the notorious lithium polysulfides (LiPSs) shuttle effect, and sluggish sulfur conversion kinetics, which lead to low specific capacity, poor rate capability, and cycle performance.$^{[5-8]}$ In order to solve these problems, various nanostructured carbon materials, such as carbon fibers, graphene oxide (GO), and carbon nanotubes, have been widely used as conductive host materials for sulfur and to confine polysulfides.$^{[9-13]}$ Although non-polar carbon materials can provide a large electrode–electrolyte contact area, cushion volume expansion of sulfur, and shorten diffusion paths of electron and ion transport, they cannot efficiently anchor polar polysulfides, resulting in serious capacity degradation.$^{[14-17]}$ It is reported that nitrogen-doping can facilitate electron conductivity and electrochemical reaction, and effectively improve the surface properties of carbon materials.$^{[18-20]}$ In particular, nitrogen-doping will greatly affect the intrinsic physicochemical properties of graphene, such as lithium storage capacity and conductivity, and inhibit the LiPSs shuttling through coordinating with N atoms.$^{[21-24]}$

Given that LiPSs are polar substances with negative charge, polar host materials have been gradually developed. Compared
with carbon materials, the metal oxides with ample polar sites can strongly bind to LiPSs through Lewis acid–base interaction, polar–polar interaction, and sulfur–chain catenation, so as to adsorb them on the host surface and reduce the loss of active substances. Metal oxides, such as Co$_3$O$_4$, MoO$_3$, and TiO$_2$, have been proved to be effective in improving the stability of Li–S batteries. Moreover, the shuttle effect can also be improved by electrocatalysis. The introduction of catalytic metals (e.g., Co, Pt, and Ni) will significantly accelerate the conversion of high-order LiPSs. It is well known that the performance of catalyst is closely related to its electronic structure. The catalytic performance of the Co$_3$O$_4$ can be remarkably changed when tuning its electronic structure.

The surface atomic configurations vary in different lattice planes of Co$_3$O$_4$ nanocrystals, leading to differences in the surface atomic density, surface electronic structures, geometric bonding, and chemical reactivity, which have a significant impact on physicochemical properties and electrochemical performances of crystal surfaces. It is worth noting that through crystal surface engineering, exposing different crystal faces and adjusting the catalytic sites on the Co$_3$O$_4$ surface can enable appropriate bond strength between substrates and active sites, thus improving the catalytic performance. From the atomic arrangements of Co$_3$O$_4$ (001) and Co$_3$O$_4$ (112) surfaces, the (001) surface contains only tetrahedral coordination Co$^{2+}$ (Co$^{2+}_t$) sites, while the (112) surface contains both Co$^{2+}_t$ and octahedral coordination Co$^{3+}$ (Co$^{3+}_o$) sites. It can be predicted that the Co$_3$O$_4$ (001) and Co$_3$O$_4$ (112) will exhibit different catalytic behaviors due to the regulation of oxidation states, which is able to enhance the LiPSs catalytic conversion toward amplified Li–S electrochemistry.

Herein, we have designed the Co$_3$O$_4$ nanopolyhedron (Co$_3$O$_4$-NP) and Co$_3$O$_4$ nanocube (Co$_3$O$_4$-NC) with different dominant lattice planes on N-doping reduced graphene oxide (N-rGO) by a simple hydrothermal method as sulfur electrocatalysts in Li–S batteries. Experimental results and theoretical calculations show that the Co$_{3+}$ species have stronger coupling and catalytic effect on LiPSs than Co$_{2+}$ species, which is attributed to the different oxidation states of the two components. Accordingly, compared with Co$_3$O$_4$-NC (001), Co$_3$O$_4$-NP (112) crystal planes, which consist abundant Co$_{3+}$ ions, can not only provide potent sulfur immobilization to effectively inhibit shuttle effect, but also dynamically accelerate LiPSs catalytic conversion to realize superior sulfur redox kinetics, giving rise to amplified Li–S performance.

**2. Results and Discussion**

The preparation process and formation mechanism of S@Co$_3$O$_4$/N-rGO composites are schematically illustrated in Figure 1. By simply adjusting the amount of ammonia, the Co$_3$O$_4$ crystals supported on GO can transform from nanocube to nanopolyhedron. At a high concentration of NH$_3$·H$_2$O, the Co(NH$_3$)$_6^{2+}$ in the solution will be oxidized by oxygen to Co(NH$_3$)$_6^{3+}$, forming a stable colloidal CoOOH solution rather than layered Co(OH)$_2$. In comparison with green Co(OH)$_2$, the presence of Co$_{3+}$ ions in brown CoOOH intermediates is proposed to explain the formation of the (112) plane oriented Co$_3$O$_4$-NP crystals. Meanwhile, in the hydrothermal reaction, the ammonia acts as a nitrogen source to convert GO to N-rGO. The N-rGO can offer sufficient growing sites for metal oxide nuclei to generate Co$_3$O$_4$/N-rGO composites. As shown in Figure 2, the morphology and crystal structure of the obtained Co$_3$O$_4$ crystals were investigated by electron
The clear lattice fringes observed in high-resolution transmission electron microscopy (HRTEM) and inverse fast Fourier transformation (FFT) patterns reveal the crystallographic nature of the spinel structure. The Co$_3$O$_4$-NC crystals are monodispersed on the rGO with a uniform size of 20 nm which also demonstrates perfect edges and clear surfaces. The lattice resolved HRTEM image shows the (220) and (400) crystal planes with 2.85 and 2.02 Å $d$-spacings. When the observed interface angle is 45°, it indicates that the projected direction is (001), which confirms that the dominant exposed surfaces of Co$_3$O$_4$-NC crystals are (001) planes (Figure 2e–g and Figures S2 and S3, Supporting Information).

The main exposed surface of Co$_3$O$_4$-NP crystals with an average size of about 18 nm is the (112) surface. We can observe the (311) and (111) crystal planes along the (112) zone axis, which have 2.43 and 4.67 Å lattice spacing, respectively (Figure 2i–k and Figures S4 and S5, Supporting Information). In addition, the energy-dispersive X-ray spectra of Co$_3$O$_4$/N-rGO composites are depicted in Figure 2d,l, which show the uniformed distribution of C, Co, and O elements. Scanning electron microscopy (SEM) images also confirmed the morphologies of these two kinds of nanomaterials (Figure 2a,b).

The phase and composition of the products were characterized by X-ray diffraction (XRD) patterns and Raman spectra. Despite variations in shape, the identified peaks are indexed as the fcc spinel type Co$_3$O$_4$ (JCPDS No. 74-2120) and the patterns display high crystallinity and purity of the Co$_3$O$_4$ crystals (Figure 3a). In addition, some diffraction peaks of S@Co$_3$O$_4$/N-rGO composites are basically consistent with orthorhombic sulfur (JCPDS No. 08-0247) (Figure S6, Supporting Information). The SEM images and element mapping presented in Figure S7, Supporting Information, further demonstrate the uniform sulfur distribution. As revealed by Raman results (Figure 3b), two peaks at 1590 and 1350 cm$^{-1}$ can be attributed to the G bands (graphitic sp$^2$ stretching) and D bands (disordered sp$^3$) of graphene, respectively.

In the range from 400 to 800 cm$^{-1}$, three distinct bands at 478 (E$_{2g}$), 521 (F$_{2g}$), and 686 cm$^{-1}$ (A$_{1g}$) can be observed, corresponding to the feature of spinel Co$_3$O$_4$. According to the intensity ratios of D-band to G-band ($I_D/I_G$) of GO, Co$_3$O$_4$-NC/N-rGO, and Co$_3$O$_4$-NP/N-rGO (0.94, 1.02, and 1.07), the graphite structure in rGO becomes more disordered obviously. Furthermore, three sharp peaks appearing below 500 cm$^{-1}$ in the Raman spectrum can be ascribed to elemental sulfur, confirming the formation of...
To examine the surface composition and chemical bonding of Co₃O₄/N-rGO composites, X-ray photoelectron spectroscopy (XPS) characterization was performed (Figure S9, Supporting Information). The high-resolution XPS spectra of N 1s show two peaks related to the pyrrolic (399.7 eV) and pyridinic (397.9 eV) nitrogen, which proves that nitrogen atoms are successfully doped into graphene.[52–54] According to Table S1, Supporting Information, the XPS survey spectra of Co₃O₄-NC/N-rGO and Co₃O₄-NP/N-rGO show similar elemental compositions of C, Co, O, and N. The atomic ratio of nitrogen/carbon (N/C) is about 2.1%, indicating that the N doping rates of the two composites are the same. There are two peaks located at 795.5 and 780.2 eV in the Co 2p spectra, corresponding to the Co 2p¹/₂ and Co 2p₃/₂ orbits. The energy difference between Co 2p¹/₂ and Co 2p₃/₂ splitting is about 15 eV, indicating the existence of low spin Co²⁺.[55,56] Besides, the high resolution of Co 2p₃/₂ in Co₃O₄-NP/N-rGO can be deconvoluted into two peaks at 782.1 and 780.1 eV, which can be ascribed to Co²⁺ and Co³⁺ species.[47,57] The peaks at 797.5 and 795.5 eV can be attributed to the spin–orbital properties of Co 2p¹/₂. Obviously, the Co₃O₄-NP/N-rGO has a higher relative area ratio of Co³⁺ to Co²⁺ (Figure S10, Supporting Information), implying the Co₃O₄-NP (112) surface with more Co³⁺ ions. As shown in Figure 3c, two peaks located at 531.7 and 530.1 eV in the O 1s spectra can be ascribed to adsorbed oxygen (O_ads) and crystal lattice oxygen (O_latt) of Co₃O₄, individually.[58] The C 1s peaks at binding energies of 287.5, 285.2, and 284.7 eV derive from contributions of different C–N, C=N, and C=C type species of N-doped graphene (Figure 3e).[59] In addition, the Co₃O₄-NC/N-rGO and Co₃O₄-NP/N-rGO materials exhibit similar specific surface area, which enables us to exclude the effect of specific surface area on the performance and pay more attention to the role of Co active sites in the electrocatalytic behaviors (Figure S11, Supporting Information).

To verify that the Co₃O₄-NP/N-rGO composites have stronger adsorption ability toward LiPSs, the same amount of two host materials were added into Li₂S₆ solutions separately. Clearly, after adsorption by Co₃O₄-NP/N-rGO, the color of Li₂S₆ solution gradually faded, while the color of the one with Co₃O₄-NC/N-rGO slowly changed to light yellow. The UV–vis spectroscopy was also used to analyze the concentration changing of Li₂Sₓ (x = 4–8) solution. The intensity of absorption peak located at about 425 nm in the spectra can indicate the amount of S₄²⁻ species.[60] The solution with Co₃O₄-NP/N-rGO delivers a much lower absorbance peak intensities than those containing Co₃O₄-NC/N-rGO or blank (Li₂S₆ solution), confirming its stronger LiPSs adsorability (Figure 4a). As a result, the effective exposure of the Co³⁺ active sites is beneficial to LiPSs adsorption, which provides a better chemical constraint for LiPSs shuttle inhibition. In addition to LiPSs adsorbability, the catalytic effect also plays an important role in improving the electrochemical performance of sulfur cathode. Symmetrical cells using identical Co₃O₄/N-rGO as electrodes were assembled with the electrolyte containing LiₓSₓ. The cyclic voltammetry (CV) profile apparently exhibits larger and sharper redox peaks with the smaller polarizations for Co₃O₄-NP/N-rGO, suggesting the more efficient LiPSs transformation and faster reaction kinetics (Figure 4b). Different scan rate CV curves and the linear relations between peak current (Iₚ) and square root of scanning rate (ν¹/₂) were shown in Figure 4b. The results indicated that Co₃O₄-NP/N-rGO exhibited better electrochemical performance than Co₃O₄-NC/N-rGO due to the optimized structure and stronger catalytic activity.
rate ($v^{0.5}$) demonstrate that the Li$^+$ diffusion coefficient ($D_{Li^+}$) of Co$_3$O$_4$-NP/N-rGO electrode is higher than that of Co$_3$O$_4$-NC/N-rGO (Figure S12, Supporting Information). Moreover, the electrochemical impedance spectroscopy (EIS) was carried out, which shows a smaller charge transfer resistance for the Co$_3$O$_4$-NP/N-rGO cathode, proving the facile sulfur reactions and its fast charge/mass-transfer process (Figure 4c).

Apart from that, the oxidation behaviors of Li$_2$S on different catalytic planes and catalytic activity of Co$_3$O$_4$/N-rGO composites were investigated by linear sweep voltammetry in a three-electrode configuration (Figure 4d and Figure S13, Supporting Information). The Co$_3$O$_4$-NP/N-rGO electrode delivers a lower onset potential of $-0.36$ V and smaller Tafel slope of $113$ mV dec$^{-1}$ in comparison to Co$_3$O$_4$-NC/N-rGO ($-0.21$ V, $202$ mV dec$^{-1}$), evidencing its lower overpotential for Li$_2$S oxidation and the kinetic enhancement. The redox kinetics of sulfur also can be reflected by the deposition behavior of Li$_2$S.$^{[61,62]}$ Remarkably, the cell based on Co$_3$O$_4$-NP/N-rGO exhibits higher precipitation capacity (297 mAh g$^{-1}$) compared with the Co$_3$O$_4$-NC/N-rGO (188 mAh g$^{-1}$) and stronger current response, indicating the lower energy barriers for the nucleation and growth of Li$_2$S on Co$_3$O$_4$-NP/N-rGO surface (Figure 4e,f).

Previous studies have proved that the catalytic activity of metal oxide nanoparticles came from ion pairs (catalytic sites in two different oxidation states)$^{[63]}$. The surface layer of Co$_3$O$_4$ (001) plane contains Co$^{2+}$ ions, without any Co$^{3+}$ ions, but there are two Co$^{3+}$ ions in the sub-layer which are usually active sites for catalysis.$^{[64]}$ However, it is difficult for substrate to contact with the Co$^{3+}$ ions of Co$_3$O$_4$ nanocube in a catalytic reaction. The Co$_3$O$_4$ nanopolyhedron predominantly exposes the (112) surface with ample Co$^{3+}$ active sites, promoting the chemical interactions between Co$_3$O$_4$ and LiPSs. At the same time, the Co$^{2+}$ cations act as catalytic sites to expedite the LiPSs conversion and contribute significantly to reaction. Consequently, the Co$_3$O$_4$-NP enclosed by (112) plane exhibits higher catalytic activity than the Co$_3$O$_4$-NC with (001) plane.

To gain further insight into the experimental mechanism, density functional theory calculation was carried out with the optimized geometries of Li$_2$S$_6$ adsorption on ideal Co$_3$O$_4$ (001) and Co$_3$O$_4$ (112) surfaces. According to the charge accumulate (red) and dissipate (green) position, the electrons tend to transport from Co and Li to S and O atoms (Figure 5a,b). More charge transfer can be observed in Co$_3$O$_4$ (112) facet than the Co$_3$O$_4$ (001) facet, which confirms that the exposure of high-valent (+3) Co cations can attract more electrons and effectively boost the electron transfer. The adsorption configuration of Li$_2$S$_6$ on Co$_3$O$_4$ (001)-Co$^{2+}$ exhibits chemical interaction by forming Co–S bond with a bond length of 2.44 Å. In stark contrast, shorter bond length of Co–S (2.18 Å) can be found in Li$_2$S$_6$-Co$_3$O$_4$ (112)-Co$^{3+}$, implying much stronger interaction than that on Co$_3$O$_4$ (001)-Co$^{2+}$ (Figure 5c,d and Figure S14, Supporting Information). Evidently, the adsorption energies of Li$_2$S$_6$ on Co$_3$O$_4$ (001) and Co$_3$O$_4$ (112) surfaces are $-2.06$ and $-3.47$ eV respectively, suggesting the stronger surface affinity of Co$_3$O$_4$ (112) for LiPSs and chemical sulfur immobilization. Different coupling strengths between Co-3d and anion p orbitals in these two geometries can also be seen from the density of states (Figure 5e and Figures S15–S18, Supporting Information). Compared with Co$_3$O$_4$ (001), the d-band center of Co 3d in Co$_3$O$_4$ (112) ($-3.1122$ eV) has a distinct upshift with respect to Fermi level, revealing the
Figure 5. Charge density difference for the geometrical configurations of Li$_2$S$_6$ molecules interacting with Co sites at different oxidation states: a) Li$_2$S$_6$-adsorbed Co$_3$O$_4$ (001)-Co$^{2+}$, b) Li$_2$S$_6$-adsorbed Co$_3$O$_4$ (112)-Co$^{3+}$. The bond length of Co-S and Li-O in stable configurations of Li$_2$S$_6$ adsorption on c) Co$_3$O$_4$ (001) and d) Co$_3$O$_4$ (112) surfaces. e) Total and partial DOS of Co$_3$O$_4$ (001), Co$_3$O$_4$ (112) surfaces, Li$_2$S$_6$-Co$_3$O$_4$ (001), and Li$_2$S$_6$-Co$_3$O$_4$ (112).

favorable charge transfer and higher charge density during sulfur catalytic processes of the Co$_3$O$_4$ (112). After adsorption of Li$_2$S$_6$, the partial density of states (PDOS) of Li$_2$S$_6$-Co$_3$O$_4$ (001) as well as Li$_2$S$_6$-Co$_3$O$_4$ (112) also displays similar characteristics and the Fermi level lies below the valence band edge which means that the conductivity of the Co$_3$O$_4$ surface is enhanced. The PDOS shows a reduced energy gap between the anion p and Co 3d band centers of Li$_2$S$_6$-Co$_3$O$_4$ (112) compared to Li$_2$S$_6$-Co$_3$O$_4$ (001). This further leads to reduced antibonding orbitals, increased energy of bonding states, higher electron energy, and electrochemical activity, thereby inducing stronger chemisorption with LiPSs and modulating the electron exchange to promote the interfacial S$_{2+}$/S$^{2-}$ redox dynamics. In addition, more peaks appear around the Fermi level mainly due to the orbital contribution of the S atoms. The Co$_3$O$_4$ (112) achieves a higher electronic concentration at Fermi level after adsorbing Li$_2$S$_6$, proving that Co$_3$O$_4$ (112) has better conductivity than Co$_3$O$_4$ (001). Hence, the oxidation state of Co (+3 or +2) determines the electron distribution of the Co-3d orbit, which remarkably changes the interaction mode of Li$_2$S$_6$ toward Co and affects its catalytic properties. The presence of Co$^{3+}$ improves the adsorption energy and strengthens electron exchange with sulfur-containing intermediates, indicating the enhanced catalytic activity of Co$_3$O$_4$ (112).

The diffusion behavior of Li$^+$ can also be used to evaluate the potential kinetic improvement by crystal surface engineering. Diffusion diagrams and corresponding diffusion paths of lithium ions on different crystal planes are described in Figure 6a–c. Obviously, the diffusion barrier energy of Li$^+$ on Co$_3$O$_4$ (112) surface is 0.32 eV, which is lower than the 0.53 eV on Co$_3$O$_4$ (001) surface, indicating that the crystal surface engineering promotes ion transfer. It is well known that random deposition of Li$_2$S is the cause of rapid decay of battery capacity. To investigate the kinetic process, the climbing-image nudged elastic band method is applied to calculate the activation energies of Li$_2$S decomposition. Figure 6e,f shows the geometric configuration of the initial structure (IS), transition structure (TS), and final structure (FS) for Li$_2$S decomposition on Co$_3$O$_4$ (001) and Co$_3$O$_4$ (112) surfaces. In the energy profiles, the decomposition energy barrier (0.45 eV) of Li$_2$S on Co$_3$O$_4$ (112) plane is lower than that on Co$_3$O$_4$ (001) plane (0.85 eV), proving the facilitated Li$_2$S transformation kinetics by exposing Co$^{3+}$ active sites (Figure 6d).

The electrochemical properties of the obtained S@Co$_3$O$_4$-NP/N-rGO electrodes were investigated. According to the TGA curves (Figure S19, Supporting Information), the weight loss of about 75% from 30 to 300 °C is due to the sulfur, the weight loss of ≈7% between 300 and 750 °C owes to the oxidation of carbon, and the remaining 18% over 750 °C originates from Co$_3$O$_4$. Typical
CV was carried out at a slow scan rate of 0.1 mV s\(^{-1}\) to analyze the electrochemical behaviors of electrodes (Figure 7a). The cathodic peaks occurring at 2.3 and 2.05 V are due to the formation of high-order LiPSs (Li\(_2\)S\(_n\), 4 \(\leq n \leq 8\)) and further reduction to short-chain insoluble Li\(_2\)S/LiS. In contrast, one peak at \(\approx 2.3–2.4\) V implies oxidation process of LiPSs returning to S.\(^{[66]}\) The peak positions of S@Co\(_3\)O\(_4\)-NP/N-rGO cathode are almost unchanged during the first three cycles, indicating the highly reversibility and stability of LiPSs oxidation/reduction process. Besides, the cell with S@Co\(_3\)O\(_4\)-NP/N-rGO displays the higher slopes (the peak current \(I_p\) vs \(v^{0.5}\)) for all redox peaks and smaller polarizations than S@Co\(_3\)O\(_4\)-NC/N-rGO in Figure S20, Supporting Information, which proves its more favorable Li\(^+\) diffusion process. The charge–discharge profiles of the sulfur cathodes at different cycles under 0.2 C exhibit a charging slope and two distinctive discharge plateaus, which are consistent with the CV plots based on multistep polysulfide conversion reactions (Figure 7b). In addition, the S@Co\(_3\)O\(_4\)-NP/N-rGO electrode shows 337 mAh g\(^{-1}\) at the high discharge plateau and an initial discharge capacity of 1087 mAh g\(^{-1}\). As shown in Figure 7c, the S@Co\(_3\)O\(_4\)-NP/N-rGO electrode delivers a higher capacity retention of 84.1% than that of S@Co\(_3\)O\(_4\)-NC/N-rGO electrode (67.4%) after 100 cycles.

The rate performance of the S@Co\(_3\)O\(_4\)-NP/N-rGO electrode at various current densities is illustrated in Figure 7d,e. Clearly, the S@Co\(_3\)O\(_4\)-NP/N-rGO cathode shows discharge capacities of 1050, 915, 824, 702, and 569 mAh g\(^{-1}\) at the current rates of 0.2, 0.5, 1, 2, and 3 C, respectively. Even at the high current density of 3 C, the charge and discharge curves of the S@Co\(_3\)O\(_4\)-NP/N-rGO electrode still exhibit two discharge platforms, confirming its limited electrochemical overpotential and excellent reaction kinetics. The S@Co\(_3\)O\(_4\)-NP/N-rGO reveals the lower charge-transfer resistance in Nyquist plots (Figure 7f), indicating the enhanced ion/electron transfer attributed to the atomic arrangements and surface electronic structures of Co\(_3\)O\(_4\)-NP (112).

The performance of electrode under raised sulfur loading was further assessed. In Figure 7h, the S@Co\(_3\)O\(_4\)-NP/N-rGO cathodes deliver a high areal capacity of 3.2 and 4.1 mAh cm\(^{-2}\) at an electrolyte/sulfur ratio of 8.8 and 5.3 mL g\(^{-1}\), respectively. These results fully demonstrate that S@Co\(_3\)O\(_4\)-NP/N-rGO electrode can effectively catalyze sulfur redox reactions, which offers significantly improved sulfur utilization and restrained LiPSs shuttle effect.
Figure 7. a) CV plots and b) charge–discharge profiles of S@Co$_3$O$_4$-NP/N-rGO. c) Cycling performance at 0.2 C, d,e) rate capability, f) EIS spectra, and g) long-term cycling stability at 1 C of different electrodes. h) High-loading cycling behavior of S@Co$_3$O$_4$-NP/N-rGO electrode at 0.1 C.

Figure 8. The operando X-ray diffraction patterns of S@Co$_3$O$_4$-NP/N-rGO electrode.

In situ XRD studies of S@Co$_3$O$_4$-NP/N-rGO electrode were performed to investigate and determine structural changes during cycling. As shown in Figure 8 and Figure S21, Supporting Information, the characteristic patterns of Co$_3$O$_4$ can be clearly observed during the entire discharge/charge process, and its lattice parameters almost remain unchanged, while there is no featured peak of CoO phase (PDF No. 43-1004), which indicates the high stability of Co$_3$O$_4$ as catalytic materials for Li–S battery cathodes.

3. Conclusion

In summary, we developed the Co$_3$O$_4$/N-rGO composite via crystal surface engineering, which can be employed as an effective sulfur electrocatalyst to inhibit shuttle effect and accelerate the catalytic conversion of LiPSs. Co$_3$O$_4$ crystals enclosed by different planes with various Co$^{2+}$/Co$^{3+}$ catalytic active sites are prepared to regulate the oxidation states of cobalt, the surface...
electronic structures, and the adsorption and catalytic capability. Compared with CoO$_2$-NC crystals enclosed by (001) surfaces, the (112) lattice planes oriented CoO$_2$-NP crystals with ample Co$^{4+}$ active sites strengthen the LiPSs affinity of CoO$_2$ and further enhance the LiPSs catalytic conversions. Meanwhile, the nitrogen-doped rGO can effectively improve the electronic conductivity and electrolyte accessibility. Moreover, the CoO$_2$/N-rGO composite architecture serves as a conductive framework to provide rich active interfaces and accelerate electron/ion transportation, rendering enhanced sulfur utilization, improved electrocatalytic behavior, and facilitated polysulfide conversion. Attributed to the structure superiorities, the S@Co$_3$O$_4$-NP/N-rGO electrode shows high specific capacity of 1087 mAh g$^{-1}$ at 0.2 C, good rate performance, excellent cycling stability at 1 C corresponding to an exceptionally low capacity fading rate of 0.058%, and high areal capacity under raised sulfur loading. This work provides a perspective for synthesis of highly adsorptive and catalytic sulfur host materials and the development of practical Li–S batteries.

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

Acknowledgements
R.X. and D.L. contributed equally to this work. This work was supported by the Department of Science and Technology of Guangdong Province (2019C011L203 and 2020B0909030004), Science and Technology Program of Guangzhou (No. 2019050001), Natural Science Foundation of Guangdong Province, China (2022A1515010615), Start Foundation of South China Normal University, the China Postdoctoral Science Foundation (No. 2021M691087), and the Vacuum Interconnected Nanotech Workstation (Nano-X), Suzhou Institute of Nano-Tech and Nano-Bionics, Chinese Academy of Sciences (CAS). The authors also thank the support from the Guangdong Innovative and Entrepreneurial Team Program (2016ZT06CS17), Program for the Outstanding Young Talents of Hebei Province, China, and Natural Sciences and Engineering Research Council of Canada, University of Waterloo and Waterloo Institute for Nanotechnology.

Conflict of Interest
The authors declare no conflict of interest.

Data Availability Statement
The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords
crystal surface engineering, lithium–sulfur batteries, oxidation states, polysulfide conversion
