# A $Co_9S_8$ microsphere and N-doped carbon nanotube composite host material for lithium-sulfur batteries

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# ABSTRACT

Lithium-sulfur batteries have emerged as extraordinarily favorable energy storage devices due to their high specific capacity and energy density, safety and low cost. Unfortunately, the wide applications of lithium-sulfur batteries are hampered by several issues, such as the low electronic conductivity and slow redox kinetics, serious volumetric expansion and polysulfide “shuttle effect”. To overcome these issues, in our work, we design and synthesize a composite sulfur host material of $Co_9S_8$ microspheres and N-doped carbon nanotubes, where the metallic sulfide $Co_9S_8$ with a good conductivity enables the immobilization of the polar lithium polysulfides owing to the strong polar chemisorptive capability, and the one dimensional N-doped carbon nanotubes can provide channels for fast electron and lithium-ion transport. As the lithium polysulfides are well confined, and the redox conversions are promoted, the $Co_9S_8$@N-CNTs/S-based lithium-sulfur battery possesses a superior energy storage performance, exhibiting a large specific capacity of 1233 mAh $g^{-1}$ at 0.1 C and an outstanding cyclic performance, with a low decay of 0.045% per cycle and a Coulombic efficiency of more than 99% after 1000 cycles.

**Keywords:** Metal sulfides; N-doped carbon nanotube; Cathode material; Lithium-sulfur battery.

## 1. Introduction

The increase in the energy consumption and global warming has accelerated research on electrochemical energy storage devices for electric vehicles and electronic equipment [1-6]. Lithium-sulfur batteries are promising energy storage devices due to their high theoretical energy density (2600 Wh/kg) and specific capacity, natural abundance, low cost, and safety [7-11]. Unfortunately, there are some essential challenges hindering their wide applications, including the insulating nature of sulfur, the large volume change that occurs during cycling, and the dissolution and shuttling behaviors of the intermediate polysulfides, which result in poor sulfur utilization and fast capacity fading [12-15].

To overcome the abovementioned issues, researchers have adopted different strategies to construct sulfur host materials and improve the cathode performance. Various carbon nanostructures, for instance porous carbon [16], carbon nanofibers and nanotubes [17, 18] and graphene [19-30], have been used as the sulfur matrix via physical confinement. However, as nonpolar carbon materials weakly interact with sulfur, some soluble lithium sulfides may migrate from the cathode to the anode and result in decreased active material utilization and low electrode performance. Recently, some polar compounds, such as $TiO_2$ [31], $Ti_4O_7$ [32], $MnO_2$ [33], $V_2O_5$ [34], $NiS_2$ [35] and $SnS_2$ [36], have been explored to effectively confine the intermediate polysulfides by the strong chemical affinity/adsorption of polysulfides. Nevertheless, most of the polar compounds possess a poor conductivity, leading to sluggish interface redox reaction kinetics and reduced rate performances. Therefore, combining the polar compound with nanocarbon to form a host material capable of strong adsorption and with a high conductivity is beneficial to increase the conductivity, improve the electrolyte contact and provide more effective chemical and physical confinements for polysulfides, which will greatly increase the performance of lithium-sulfur batteries [37, 38].

Recently, polar $Co_9S_8$ has been proven to provide strong chemical adsorption to confine polysulfides and possess a high catalytic activity to accelerate redox reactions and polysulfide conversion [39]. For example, $Co_9S_8$ nanotube-based cathodes demonstrate a stable cycle life and a high discharge capacity for lithium-sulfur batteries due to the enhanced conduction of electrons and Li ions and inhibition of polysulfides [40, 41]. In addition, heterojunctions based on $Co_9S_8$ and hybrids of $Co_9S_8$ and nanocarbon materials (e.g., CNTs, carbon nanofibers, hollow carbon spheres, etc.) display remarkable electrochemical performances for lithium-sulfur batteries due to the well-defined interfaces, the cooperative chemisorption of polysulfides and the synergistic dual-confinement effects [42-46]. Compared to pristine CNT, doping CNTs with N can enhance their electronic conductivity, as more electron carriers are provided by the dopants in the conduction band. The introduced nitrogen-containing functional groups can increase the surface polarity, and the defects and nonuniformities in the N-CNTs may serve as active sites for the adsorption of S and polysulfides and the deposition of $Li_2S$. Moreover, the N-CNT networks may also tightly connect and confine the sulfur substances to enhance the structural integrity of the composite electrode and serve as the steady “highways” to accelerate electron transport [47, 48]. In this work, the composite of $Co_9S_8$ microspheres and N-CNTs was synthesized by a facile solvothermal method and subsequent annealing. The synthesis process is convenient, and a three-dimensionally interconnected network structure with the $Co_9S_8$ microspheres tightly attached to the N-CNTs is formed. In this composite, the polar metal sulfide $Co_9S_8$ enables a superior lithium polysulfide absorptivity via the polar chemical bond, which decreases polysulfide dissolution and the shuttle effect and increases the specific capacity and cyclic performance, while the N-doped carbon nanotubes can assist to increase the electronic conductivity and enlarge the interface between the electrode and electrolyte to further enhance the rate performance. Meanwhile, the N-CNTs/S composite and the $Co_9S_8$@N-CNTs/S composites with different contents of N-CNTs have been studied and compared. The unique $Co_9S_8$@N-CNTs composite-based sulfur cathode displays an outstanding overall electrochemical performance, making it promising for applications in lithium-sulfur batteries.

## 2. Experimental

### *2.1 Preparation of $Co_9S_8$ and $Co_9S_8$@N-CNTs*

The $Co_9S_8$@N-CNTs composite host was prepared using a solvothermal process. First, 27 mg of the N-CNTs was ultrasonically dispersed into 30 mL of ethylene glycol and 10 mL of distilled water to form a suspension. $CoCl_2 \cdot 6H_2O$ (0.7138 g) and thiourea (0.4567 g) were added with stirring, and the ratio of $CoCl_2$:thiourea was fixed as 60:40. The obtained solution was then subjected to a hydrothermal reaction for 12 h at 180 °C. The product was filtered, adequately washed, and vacuum-dried for 24 h at 80 °C. The obtained precursor was annealed for 3 h at 500 °C in $H_2$/Ar (10%:90%). The obtained sample is denoted as $Co_9S_8$@N-CNTs. The pristine $Co_9S_8$ material was also prepared using the same processes but without adding the N-CNTs. The other $Co_9S_8$@N-CNTs composites with different contents of N-CNTs (13.5 mg and 40.5 mg) were prepared by a similar procedure. Hereafter, these obtained samples with different N-CNT contents are denoted as $Co_9S_8$@N-CNTs-1 and $Co_9S_8$@N-CNTs-2.

### *2.2 Synthesis of S-impregnated materials*

Sulfur is loaded by a vapor diffusion method. The S-impregnated materials were obtained by mixing both sublimed sulfur and the $Co_9S_8$@N-CNTs (1:4) in a Teflon-lined stainless steel autoclave filled with Ar, which was subsequently heating for 10 h at 180 °C. For comparison, either pristine $Co_9S_8$ or the N-CNTs was also loaded with sulfur using the same procedure to obtain the composites.

### *2.3 Characterization*

The powder X-ray diffraction (XRD) analysis was performed with an X-pert Pro MPD diffractometer. The morphology and structure were observed using scanning electron microscopy (SEM, PHILIPS-XL30TMP) and transmission electron microscopy (TEM, FEI

Tecnai-G20, 200 kV). A VG Multilab 2000 apparatus was used to perform X-ray photoelectron spectroscopy (XPS), thermogravimetric analysis (STA449/6/G, NETZSCH) was performed to determine the carbon and sulfur contents, and a Shimadzu UV3600 instrument was used to obtain the ultraviolet-visible absorption spectra.

### 2.4 Electrochemical measurements

The cathode slurry comprising 70 wt% of the synthesized materials, 20 wt% of Super-P, and 10% of PVDF was made by mixing in NMP and coated onto an Al film before vacuum drying for 24 h at 60 °C. The separator was a Celgard 2400 polypropylene membrane, the counter electrode was a Li foil, and the electrolyte was 1 M LiTFSI + 0.1 M $LiNO_3$ dissolved in dimethoxyethane and 1,3-dioxolane (1:1). The coin cells (2032 type) were assembled in a glove box filled with argon. A Neware battery test system (5V5mA) was used to obtain the charge/discharge profiles at various rates within 1.7-2.8 V and the capacities were calculated based on the mass of sulfur. A CHI 660D electrochemical workstation was used to obtain the cyclic voltammetry (CV) curves within 1.7-2.8 V and the electrochemical impedance spectroscopy (EIS) between 10 mHz~1 MHz.

### *2.5 $Li_2S_6$ adsorption capability*

Sulfur powder and $Li_2S$ (5:1) were dissolved in dimethoxyethane and 1,3-dioxolane (1:1) and stirred for 48 h at 80 °C to form the $Li_2S_6$ solution. Then, 30 mg of $Co_9S_8$, N-CNTs or the $Co_9S_8$@N-CNTs were separately added to the obtained $Li_2S_6$ solution (5 mL) to investigate the absorption ability of the polysulfides.

## 3. Results and discussion

The preparation of the $Co_9S_8$@N-CNTs microspheres and $Co_9S_8$@N-CNTs/S composite is illustrated in Fig. 1. The $Co_9S_8$ microsphere precursor with interconnected N-CNTs was first prepared by a solvothermal process, during which the $Co^{2+}$ ions would be absorbed on the surface of the N-CNTs to form uniformly distributed $Co_9S_8$ due to the electrostatic attraction effect [34]. After annealing in a reducing atmosphere, the $Co_9S_8$@N-CNTs were successfully obtained. Finally, a vapor diffusion process was used to load sulfur and form the $Co_9S_8$@N-CNTs/S composite. The morphology and structure of the as-synthesized materials were observed by SEM, as shown in Fig. 2(a-d). Fig. 2(a) shows that the $Co_9S_8$ microspheres (approximately 3~8 μm) are mainly composed of secondary nanoparticles with sizes of approximately 10 nm. Fig. 2(b) shows the SEM image of the $Co_9S_8$@N-CNTs, showing that the N-CNTs (11.2%, as shown in Fig. S1) spread throughout and interconnect with the monodisperse $Co_9S_8$ microspheres. Such a 3D network structure is favorable to transport electrons and ions. After loading with sulfur, some agglomerations of melted sulfur and the $Co_9S_8$ microspheres are observed for the pristine $Co_9S_8$ material (Fig. 2(c)), while the structure and morphology of the $Co_9S_8$@N-CNTs are basically retained, and sulfur is homogeneously deposited, as shown in Fig. 2(d). The TEM image (Fig. 3(a)) and the EDX elemental mapping image of the $Co_9S_8$ microspheres (Fig. 3(b) and (c)) exhibit the homogenous distribution of Co and sulfur elements. Fig. 3(d) shows the high-resolution TEM image, where the lattice distance is 0.3 nm and corresponds to the (311) plane of $Co_9S_8$, implying the high crystallinity of the $Co_9S_8$ material [35].

Fig. 4 shows the XRD patterns of the materials. As shown in Fig. 4(a), the diffraction peak of the N-CNTs at 26.1° is attributed to the graphitic carbon. All the diffraction peaks of $Co_9S_8$ and $Co_9S_8$@N-CNTs are assignable to cubic *Fm-3m* $Co_9S_8$ (JCPDS card no. 19-0364) [36], indicating the good crystallinity of both materials and the negligible effect of the N-CNTs on the $Co_9S_8$ structure. As the percentage of the N-CNTs is relatively low (～11.2%), the peak corresponding to the N-CNTs at approximately 26° might be shielded/overlapped by the stronger diffraction peak of $Co_9S_8$. Therefore, the peak corresponding to the N-CNTs was not observed for the $Co_9S_8$@N-CNTs sample. As shown in Fig. 4(b), the strong orthorhombic peaks for sulfur are observed in the XRD patterns of $Co_9S_8$/S and the $Co_9S_8$@N-CNTs/S (JCPDS card No.08−0247), indicating that sulfur has been successfully incorporated, and the good crystallinity is probably due to the vapor diffusion process (180 °C, 10 h) used to load sulfur [37]. The XRD peaks of $Co_9S_8$ in the composites after loading sulfur are not evident, probably because of the shielding/overlapping effects induced by the relatively high sulfur loading (～70%). Fig. 5 displays the TGA profiles of the sulfur, N-CNT/S, $Co_9S_8$/S, $Co_9S_8$@N-CNTs/S, $Co_9S_8$@N-CNTs-1/S and $Co_9S_8$@N-CNTs-2/S composites. The weight loss of all the samples ends at approximately 350 °C. The sulfur content is ～70% for $Co_9S_8$/S and ～75% for all of the $Co_9S_8$@N-CNTs/S composites. The higher sulfur ratio of the $Co_9S_8$@N-CNTs/S composites may result from the penetration of sulfur inside the N-CNTs from the $Co_9S_8$@N-CNTs composite network, which is consistent with the SEM results.

To compare the polysulfide absorptivity, the $Co_9S_8$, N-CNTs and $Co_9S_8$@N-CNTs materials were separately put into a $Li_2S_6$ solution. As displayed in Fig. 6(a) and Fig. S3, at the beginning, all of the solutions are the same yellow color. The yellow solution obtained with the addition of the $Co_9S_8$@N-CNTs turns colorless after 1 hour, indicating the strong chemisorption between $Li_2S_6$ and the $Co_9S_8$@N-CNTs [49]. In contrast, the solutions obtained with the addition of $Co_9S_8$ or the N-CNTs still display slight yellow colors. Fig. 6(b) shows the UV-vis absorption spectra obtained for the $Li_2S_6$ solutions without or with the addition of $Co_9S_8$ and the $Co_9S_8$@N-CNTs. The $Li_2S_6$ solution shows an obvious polysulfide absorption peak at approximately 411 nm, while both peaks are negligible for the $Li_2S_6$ solution soaked with $Co_9S_8$ and the $Co_9S_8$@N-CNTs. Moreover, the peak intensity of the $Co_9S_8$@N-CNTs is weaker than that of $Co_9S_8$, implying the stronger absorption ability of the $Co_9S_8$@N-CNTs composite, which may effectively suppress the dissolution and shuttling effect of polysulfide during cycling [50]. The XPS survey spectrum of the $Co_9S_8$@N-CNTs composite was recorded and shown in Fig. 7(a), where the distinct peaks corresponding to Co 2p, S 2p, C 1s, N 1s and O 1s are observed. The Co $2p_{3/2}$ spectrum shown in Fig. 7(b) is decomposed into five peaks in the range of 771-789 eV, which not only indicates the presence of $Co^{3+}$ and $Co^{2+}$ at binding energies of approximately 778.4 eV and 781.9 eV, corresponding to the cobalt ion in the octahedron and tetrahedron sites in

$Co_9S_8$ [51-55], but also includes two additional peaks at 780.56 eV and 783.2 eV, corresponding to the Co-S and Co-N bonds. Fig. 5(c) shows that the S 2p spectrum is decomposed into six peaks. The S $2p_{3/2}$ and S $2p_{1/2}$ components at 162.4 eV and 163.4 eV suggest the existence of S-S species [35]. In addition, the other three peaks appearing at 161.5 eV, 164.4 eV and 166.5 eV correspond to the Co-S, C-S and S-N bonds. The $SO_4^{2-}$ component may be caused by the slight oxidation of the sample surface. The spectrum of C 1s shown in Fig. 7(d) includes three main peaks at binding energies of 284.2, 284.6 and 285.5 eV, corresponding to C-S, the $sp^2$ carbon of C=C, and C-N, respectively [56-58], confirming the incorporation of the N-CNTs and the interaction between $Co_9S_8$ and the N-CNTs. The N 1s spectrum shown in Fig. 7(e) can be fitted by four components at 402.0, 400.6, 399.6, and 398.4 eV, which are attributed to graphitic N, pyrrolic N, amine N and pyridinic N, respectively. Due to the unique crystal and electronic structure of $Co_9S_8$, there might be a strong chemical interaction between $Co_9S_8$ and the polysulfides, as the Li atoms in polysulfides can form bonds with the S on the $Co_9S_8$ surfaces, and the S in the polysulfides can also form bonds with the Co on the $Co_9S_8$ surfaces because of the anion-cation Coulomb interactions. In addition, the introduced nitrogen-containing functional groups can increase the surface polarity of the CNTs, which is beneficial to further increasing the adsorption and confinement of lithium polysulfides. Therefore, the polar surface and the various chemical states of the composite may contribute to the strong interactions and adsorption of lithium polysulfides [59].

To evaluate the performances of the $Co_9S_8$@N-CNTs/S composite material, coin cells with the $Co_9S_8$@N-CNTs/S cathodes and Li anodes were assembled and compared to the $Co_9S_8$/S cathode. Fig. 8(a) exhibits the initial charge-discharge profiles obtained for $Co_9S_8$/S and the $Co_9S_8$@N-CNTs/S at 0.1 C. The specific discharge capacities of the $Co_9S_8$@N-CNTs/S and $Co_9S_8$/S are 1233 and 1016 mAh $g^{-1}$, respectively, indicating that the nitrogen-doped carbon nanotube network can efficiently improve the specific capacity. The rate performance of the cathodes was observed at various current rates of 0.1-2 C (Fig. 8(b)).

The $Co_9S_8$/S material exhibits specific discharge capacities of 1016, 826, 689, 635 and 543 mAh $g^{-1}$ at 0.1, 0.2, 0.5, 1 and 2 C, respectively. In contrast, the specific discharge capacities of the $Co_9S_8$@N-CNTs/S at 0.1 0.2, 0.5, 1 and 2 C are 1233, 1066, 925, 841 and 713 mAh $g^{-1}$, respectively, which are higher than those of $Co_9S_8$/S. When switched back to 0.1 C, more than 88% of the original capacities were recovered for the $Co_9S_8$@N-CNTs/S cells (Fig. 8(b)), indicating the fast reaction kinetics of the $Co_9S_8$@N-CNTs/S electrode. The superior rate capability of the $Co_9S_8$@N-CNTs/S may result from the accelerated ion transport and electron transfer from the three dimensional N-CNT and $Co_9S_8$ composite network structure.

The $Co_9S_8$/S and $Co_9S_8$@N-CNTs/S cathodes were cycled for 1000 cycles at 0.5 C to study their cyclic performance, and the results are shown in Fig. 8(c). The $Co_9S_8$@N-CNTs/S electrode initially exhibits a capacity of ~950 mAh $g^{-1}$, which is higher than the capacity of $Co_9S_8$/S, 788 mAh $g^{-1}$. After 300 cycles, the capacities of 652 and 480 mAh $g^{-1}$ were retained for the $Co_9S_8$@N-CNTs/S and $Co_9S_8$/S, respectively, which corresponds to a retention of 68.63% and 60.91% at the end of 300 cycles. After 1000 cycles, the $Co_9S_8$@N-CNTs/S cathode still maintains the specific capacity of 522 mAh $g^{-1}$, the Coulombic efficiency is higher than 99%, and the average decay is approximately 0.045% for one cycle [60]. In contrast, the $Co_9S_8$/S cathode exhibits a much lower discharge capacity (273 mAh $g^{-1}$), higher decay (0.065% after one cycle) and lower Coulombic efficiency (97%). As shown in Fig. 8(c), during the long-term cycling at 0.5 C, both of the synthesized samples experienced a rapid decay and a less rapid decay. There are some mono-dispersed $Co_9S_8$ microspheres/sulfur in the composite, which may suffer from volume expansion and sulfur dissolution during the continuous charging-discharging and cause fast capacity decay during the first 300 cycles. However, the decay that occurred for the $Co_9S_8$@N-CNTs/S composite is relatively slow compared to that of the $Co_9S_8$/S composite after 300 cycles, which is probably because the stronger chemical interaction between the polysulfides and the former effectively inhibited the “shuttle effect” and reduced the capacity decay. Meanwhile, an N-CNTs/S cathode was also evaluated and delivered a discharge capacity of 500 mAh g$^{-1}$ in the first cycle, after which the capacities were gradually reduced to 100 mAh g$^{-1}$ in the 1000th cycle performed at 0.5 C, which is a worse cycling performance compared to that of the $Co_9S_8$@N-CNTs/S composite, as shown in Fig. S4. The increased performance of the $Co_9S_8$@N-CNTs/S may result from the strong chemical interaction and binding between the $Co_9S_8$ and N-CNT composite and polysulfides, which can effectively suppress the dissolution and shuttling effect of polysulfide during cycling. To investigate the structure stability, additional SEM images of the $Co_9S_8$@N-CNTs/S electrode were obtained before and after cycling, as shown in Fig. S5(a) and (b). Fig. S5(b) demonstrates that the active material in the cycled electrode basically retains the morphology of the initial composite before cycling (Fig. S5(a)), indicating the good structure stability during high current density cycling. Compared to the XPS spectra of the $Co_9S_8$@N-CNTs/S electrode in the charge state, a new peak at 164 eV was observed in the discharged state, as shown in Fig. S7, which is attributed to the Li-S bond and indicates the formation of the new Li-S bond after the discharging process. These results indicate that the lithium polysulfides are firmly confined on the electrode surface and further confirm the interaction between the cathodes and lithium polysulfides. Compared to other reported sulfur cathodes based on metal oxides and sulfides, as listed in Table S1, the $Co_9S_8$@N-CNTs/S cathode shows a relatively higher rate capability and cycling performances [61-66].

The lithium storage performances of the $Co_9S_8$@N-CNTs/S composite cathodes with different contents of N-CNTs (8.8% for N-CNTs-1 and 14.9% for N-CNTs-2, as shown in Fig. S1) were measured, and the results are shown in Fig. S6. The N-CNTs-1 and N-CNTs-2 cells delivered discharge capacities of approximately 385 and 400 mAh g$^{-1}$ at 0.5 C, respectively, which are lower compared to of the $Co_9S_8$@N-CNTs/S composite cathode at the same rate. Fig. 8(d) displays the CV curves of the $Co_9S_8$/S and $Co_9S_8$@N-CNTs/S electrodes within 1.7-2.8 V at 0.1 mV/s. Both curves show one oxidation peak and two reduction peaks. During the cathodic scanning process, the first peak is associated with the reduction of cyclic $S_8$ molecules to long chain polysulfides ($Li_2S_n$, $4 \leq n \leq 8$), and the second peak is related to the transformation of the long $Li_2S_n$ chain to the short $Li_2S_2$/$Li_2S$ chain [67]. During the anodic scanning process, the anodic peak is ascribed to the transformation of $Li_2S_2$/$Li_2S$ back to $S_8$. Both reduction peaks at approximately 2.30 and 2.05 V appear for the $Co_9S_8$/S and $Co_9S_8$@N-CNTs/S electrodes, but the peaks of the $Co_9S_8$@N-CNTs/S are sharper and have a higher intensity than those of the $Co_9S_8$/S electrodes. In addition, the anodic peaks appear at 2.40 V and 2.38 V for $Co_9S_8$/S and $Co_9S_8$@N-CNTs/S, respectively. The oxidation peak of the $Co_9S_8$@N-CNTs/S electrode is also sharper, has a higher intensity and is negatively shifted compared to that of $Co_9S_8$/S, indicating the higher reversibility of the $Co_9S_8$@N-CNTs/S cathode.

Fig. 8 (e) shows the Nyquist plots obtained for the $Co_9S_8$/S and $Co_9S_8$@N-CNTs/S cathodes. Both plots show a high-frequency semicircle, a medium-frequency semicircle and a low-frequency inclined line, which correspond to the solid interface layer of the electrode surface, the charge-transfer process, and the Warburg impedance within the cathode, respectively [68]. The charge-transfer resistance of the $Co_9S_8$@N-CNTs/S cathode is approximately 53 $\Omega$, which is much lower compared to that of $Co_9S_8$/S (64 $\Omega$). These results imply that the $Co_9S_8$@N-CNTs/S electrode exhibits increased ion and charge transfer rates and higher material utilization than $Co_9S_8$/S, which may contribute to the improved energy storage performance of the $Co_9S_8$@N-CNTs/S [69-74].

The outstanding lithium storage characteristics of the $Co_9S_8$@N-CNTs/S may be ascribed to the unique composite structure and properties. As shown in Fig. 8(f), the $Co_9S_8$/N-CNTs composite possesses an open and porous three-dimensional structure, which provides sufficient space for electrolyte penetration and an adequate interface for Li-ion transport [75]. Both the $Co_9S_8$ microspheres and N-CNTs can immobilize polysulfides by chemical bonds to suppress polysulfide dissolution and thus increase the sulfur utilization.

Specifically, the polysulfides can be strongly adsorbed on the $Co_9S_8$ surfaces due to the coexistence of Co−S and Li−S bonds, which results in electron transfer from the polysulfides to the Co atoms and accelerates the reaction kinetics of the polysulfides decomposing to the final insoluble products on $Co_9S_8$, and the electrochemical reaction kinetics could be greatly increased during the discharge/charge processes occurring in Li–S batteries [52, 53]. In addition, the N-CNTs not only promote the electronic conductivity but also buffer the volume expansion of elemental sulfur. Therefore, a remarkable increase in the discharge capacity, rate performance and cyclic stability of the lithium-sulfur battery is achieved [76].

To explore the contribution of the spherical metal sulfide $Co_9S_8$ to the capacity of the composites, the lithium storage behaviors of the $Co_9S_8$ microsphere (without impregnation of sublimed sulfur) and the N-CNTs (without impregnation of sublimed sulfur) were measured within 1.7–2.8 V, as shown in Fig. 9 and Fig. S8. The pristine $Co_9S_8$ and N-CNTs cathodes display a low initial specific capacity of 23 and 26 mAh $g^{-1}$, and retain capacities of 9.6 and 7 mAh $g^{-1}$ after 200 cycles at 0.2 C, respectively, suggesting the negligible contribution of $Co_9S_8$ and the N-CNTs to the capacity of the $Co_9S_8$/S and $Co_9S_8$@N-CNTs/S composite cathodes. Therefore, the N-CNTs can promote the electronic conductivity and provide the additional adsorption and confinement of the polysulfides to prevent shuttling and synergistically increase the charge/discharge cycling performance of the S composite cathodes with $Co_9S_8$.

## 4. Conclusions

A unique sulfur host material composed of $Co_9S_8$ microspheres and interlaced N-CNTs has been designed and realized. In this novel structure, the polar chemical bond in $Co_9S_8$ can strength the confinement of the soluble lithium polysulfides and mitigate the shuttle effect, and the nitrogen-doped carbon nanotubes interconnected with the metallic sulfide enable a highly conductive network and a high specific interface for the rapid transfer of charges. As a result, the $Co_9S_8$@N-CNTs/S composite exhibits superior lithium storage characteristics of improved specific discharge capacity, outstanding cyclic and rate performance. The $Co_9S_8$@N-CNTs/S cathode displays a good cycling capability and a high Coulombic efficiency for up to 1000 cycles at 0.5 C, demonstrating that the novel composite structure is a potential sulfur host material for practical applications in lithium-sulfur batteries.

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# Figure Captions

**Fig. 1** Schematics of the synthesis of the $Co_9S_8$@N-CNTs/S: (a) dispersion of the N-CNTs in an ethylene glycol (EG) solution, (b) precursor of $Co_9S_8$ with the N-CNTs, (c) solvothermal reaction performed at 180 °C for 12 h, (d) calcination of the $Co_9S_8$@N-CNT composite at 500°C for 3 h, and (e) impregnation of sulfur on the $Co_9S_8$@N-CNT composite ($Co_9S_8$@N-CNT/S).

**Fig. 2** SEM images of $Co_9S_8$ (a), $Co_9S_8$@N-CNTs (b), $Co_9S_8$/S (c) and $Co_9S_8$@N-CNTs/S (d).

**Fig. 3** TEM image of $Co_9S_8$ (a), EDX image of Co (b) and S (c), and HRTEM image of $Co_9S_8$ (d).

**Fig. 4** XRD patterns of (a) $Co_9S_8$, N-CNTs and the $Co_9S_8$@N-CNT composite and (b) sulfur, $Co_9S_8$/S, and the $Co_9S_8$@N-CNT/S.

**Fig. 5** TGA profiles of sulfur, $Co_9S_8$/S, $Co_9S_8$@N-CNTs-1/S, $Co_9S_8$@N-CNTs/S and $Co_9S_8$@N-CNTs-2/S.

**Fig. 6** Optical photographs showing the color change of the $Li_2S_6$ solution after adding $Co_9S_8$ and $Co_9S_8$@N-CNTs: (1) $Li_2S_6$ solution, (2) $Li_2S_6$ solution with added $Co_9S_8$, and (3) $Li_2S_6$ solution with the added $Co_9S_8$@N-CNTs (a). UV-vis absorption spectra collected for the $Li_2S_6$ solution soaked with $Co_9S_8$ and the $Co_9S_8$@N-CNTs (b).

**Fig. 7** XPS survey spectrum of $Co_9S_8$@N-CNTs (a), core level XPS spectra of Co $2p_{3/2}$ (b), S 2p (c), C 1s (d) and N 1s (e) of $Co_9S_8$@N-CNTs.

**Fig. 8** Discharge/charge curves (0.1 C) (a), rate performances (b), cyclic performance (0.5 C) (c), CV profiles (d), and EIS plots (e) of the $Co_9S_8$/S and $Co_9S_8$@N-CNTs/S cathodes respectively, and depiction of the accelerated polysulfide adsorption and conversion of $Co_9S_8$@N-CNTs (f).

**Fig. 9** Discharge-charge profiles of the $Co_9S_8$ electrode (without the impregnation of sulfur) at 0.2 C (a), and cycling performance of the $Co_9S_8$ electrode (without the impregnation of sulfur) at 0.2 C (b).