Interconnected CoS₂/NC-CNTs network as high-performance anode materials for lithium-ion batteries

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ABSTRACT Cobalt disulfide (CoS₂) has been considered a promising anode material for lithium-ion batteries (LIBs) due to its high theoretical capacity of 870 mA h g⁻¹. However, its practical applications have been hampered by undesirable cycle life and rate performance due to the volume change and deterioration of electronic conductivity during the discharge-charge process. In this study, an interconnected CoS₂/N-doped carbon/carbon nanotube (CoS₂/NC-CNTs-700) network was successfully prepared to boost its lithium storage performance, in which small-size CoS₂ nanoparticles were confined by N-doped carbon and uniformly decorated on the surface of CNTs. N-doped carbon can effectively accommodate the large volume expansion of CoS₂ nanoparticles. Additionally, the 3D conductive nanostructure design offers adequate electrical/mass transport spacing. Benefiting from this, the CoS₂/NC-CNTs-700 electrode demonstrates a long cycle life (a residual capacity of 719 mA h g⁻¹ after 100 cycles at 0.2 A g⁻¹) and outstanding rate performance (335 mA h g⁻¹ at 5.0 A g⁻¹). This study broadens the design and application of CoS₂ and fosters the advances in battery anode research.

Keywords: metal-organic frameworks, CoS₂, carbon nanotubes, anode, lithium-ion batteries

INTRODUCTION

To reduce the excessive consumption of fossil fuels and meet the growing demands of clean energy, rechargeable batteries with high energy density and power density are being continuously developed. Lithium-ion batteries (LIBs), as one of the most advanced electrochemical storage technologies, have captured tremendous attention in portable electronic equipment and electrical vehicles [1,2]. Currently, graphite is employed as the anode in

LIBs, due to its ability for high reversible charging/discharging under intercalation potentials. However, it possesses a lower theoretical capacity of 372 mA h g⁻¹, which greatly limits its application in LIBs, and cannot meet the demands for advanced electrical vehicles and/or mobile electronic devices [3]. In this respect, over the past decades, tremendous efforts have been made to explore novel anode materials with high specific capacity, such as transition metal oxides, sulfides, carbides, and phosphates [4–7]. Among them, transition metal sulfides (such as FeS₂, CoS₂, and MoS₂) are regarded as promising alternatives due to their high safety and relatively high theoretical capacity [8,9]. In addition, the metal-sulfur bonds of transition metal sulfides are easily broken in the conversion reaction process compared with metal-oxygen bonds, which typically provide enhanced reaction kinetics [10]. The most recent research has been based on cobalt sulfide (CoS₂) due to its excellent electrical conductivity and high theoretical capacity (870 mA h g⁻¹) [11]. Nevertheless, like other transition metal sulfides, CoS₂-based anode materials also met similar obstacles: (1) large volume change in the continuous intercalation-deintercalation process of Li ions, leading to electrode pulverization and poor cycle stability and (2) rapid capacity attenuation due to the dissolution of polysulfide in the electrolyte [12,13]. Particle size reduction to the nanometer level has been shown to significantly reduce the mechanical tension during the transformation reaction and alleviate the pulverization problem. However, the exorbitant surface energy of small nanoparticles usually causes nanoparticle agglomeration [11,14].

It has been reported that carbon substrates, such as graphene, carbon nanotubes (CNTs), and carbon cloth,

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can effectively prevent agglomeration and improve the electrical conductivity of metal sulfide nanoparticles [15,16]. In addition, carbon substrates are capable of shortening the ionic diffusion path and mitigate the volume expansion during the discharge-charge process, thus improving the cycle stability and reversibility [17]. Zhang *et al.* [18] synthesized MoS₂ nanothorns growing on CNTs, which were then coated by amorphous carbon (CNT@MoS₂@C) through a chemical vapor deposition (CVD) method. The obtained CNT@MoS₂@C composite exhibited 0.006% capacity fading at 1.0 A g⁻¹ for 500 cycles, and superior rate capability (707 mA h g⁻¹ at 2.5 A g⁻¹). Zhang *et al.* [19] designed a three-dimensional (3D) CNT network bridged hetero-structured Ni-Fe-S nanocube anode, which exhibited ultra-high specific capacity and cycle stability in lithium-/sodium-/potassium-storage systems.

Recently, metal-organic frameworks (MOFs) have been used as precursors to prepare functional materials (such as porous carbon [20,21], metal oxide/carbon [22,23], metal sulfide/carbon [24] and metal phosphates/carbon [25]). Subjected to high-temperature thermal treatment, highly ordered dispersed metal compounds are easier to form by using the superiority of pristine MOFs, which possess highly ordered metal cations and organic linkers [26]. By optimizing and adjusting the MOF morphology and component, various functional composites can be successfully obtained. However, MOFs are normally crystallized with large particle size, which critically weakens their performance for surface physical and chemical processes [27]. Downsizing MOFs to nanoscale more efficiently modifies functional materials and paves new avenues towards nanotechnology application [28].

In this study, CoS₂ nanoparticles (ca. 5 nm) embedded in N-doped CNTs (CoS₂/NC-CNTs) were prepared using ZIF-67 nanoparticles grown on CNTs (ZIF-67-CNTs) as the precursor. ZIF-67 nanoparticles were uniformly attached to CNTs, exhibiting a 3D network structure. After a two-step thermal treatment, ZIF-67-CNTs were converted to CoS₂/NC-CNTs without noticeable aggregation. CoS₂ nanoparticles embedded in N-doped carbon and a 3D network structure can effectively buffer the volume expansion during the discharge-charge process, ensuring a stable electrode structure, and improving the cycle stability and rate performance.

EXPERIMENTAL SECTION

Chemicals

All the chemicals are of analytical grade and used without

further purification.

Preparation of CNTs

The CNTs were obtained by a thermal treatment (700°C for 3 h with a heating rate of 2°C min⁻¹ under 5% hydrogen/argon mixed gas) of the commercial carboxylate-functionalized CNTs.

Preparation of ZIF-67-CNTs and ZIF-67

In a typical synthesis, 100 mg of carboxylate-functionalized CNTs were dispersed in 100 mL of methanol. After sonication for 5 min, 1.176 g of cobalt hexahydrate nitrate (Co(NO₃)₂·6H₂O), and 1.000 g of polyvinylpyrrolidone (PVP) were added and stirred for 3 h. The obtained mixture was marked as solution A. Solution B was obtained by adding 1.325 g of 2-methylimidazole to a mixture solution of 80 μL of triethylamine and 100 mL of methanol followed by stirring for 30 min. After that, solution A was poured into solution B with constant stirring at room temperature for 5 min. Finally, the purple ZIF-67-CNTs were collected by centrifugation and washed with methanol thrice, and then dried in an oven at 60°C for 12 h. For comparison, the pure ZIF-67 was prepared by the similar procedure but without adding CNTs.

Preparation of Co/NC-CNTs-p and Co/NC

ZIF-67-CNTs (200 mg) were heated to a target temperature (600, 700, and 800°C) for 3 h with a heating rate of 2°C min⁻¹ under 5% hydrogen/argon. The obtained products were labeled as Co/NC-CNTs-p (p represents the target temperature). The Co-NC was prepared using ZIF-67 as a precursor under the same condition.

Preparation of CoS₂/NC-CNTs-p and CoS₂/NC

A mixture of 50 mg of Co/NC-CNT-p and 100 mg of sulfur powder were ground, placed in a porcelain boat, and then heated at 300°C for 2 h with a heating rate of 5°C min⁻¹ under argon. After cooling to room temperature, the obtained black powder was collected and denoted as CoS₂/NC-CNTs-p (p represents the target temperature). The CoS₂/NC was prepared by using Co/NC as a precursor with the same method.

Characterization

Powder X-ray diffraction (PXRD) patterns were recorded on a Rigaku MiniFlex600 X-ray diffraction automated with Cu Kα radiation. Field-emission scanning electron microscopy (FESEM) images were obtained on a JSM-7800. Scanning transmission electron microscopy (STEM) was conducted on a JEM-2800. X-ray photo-

electron spectroscopy (XPS) was performed on a Thermo Scientific ESCALAB 250Xi. Nitrogen adsorption/desorption isotherms were recorded on Micromeritis ASAP 2020. Raman spectra were gathered on SR-500I-A with a 532 nm laser.

Electrochemical measurements

The working electrodes were prepared using a slurry method by mixing the active material, conductive Ketjen black, and polyvinylidene fluoride (PVDF) with a weight ratio of 8:1:1 in *N*-methyl-2-pyrrolidinone (NMP), which was cast onto the copper foil and dried at 110°C under vacuum overnight. The CR2025 coin-type cells, assembled in an argon-filled glove box ($[O_2] < 0.1$ ppm, $[H_2O] < 0.1$ ppm), were used to test the electrode electrochemical performance. The cells were prepared by assembling the anode electrode (active material), Li-metal foil as the counter and reference electrodes, and separator (Celgard 2400). The electrolyte was a solution of ethylene carbonate (EC)/diethyl carbonate (DEC)/dimethyl carbonate (DMC) ($v:v:v = 1:1:1$) with 1.0 mol L^{-1} $LiPF_6$. The cells were charged and discharged in the voltage range of 0.01 to 3.00 V (vs. Li/Li^+) at room temperature by using LAND-CT2001A battery testers. Cyclic voltammetry (CV) was conducted in the range of 0.01 to 3.00 V (vs. Li/Li^+) at a scan rate of 0.1 mV s^{-1} on a VersaSTAT 4 electrochemical workstation.

RESULTS AND DISCUSSION

The synthesis of CoS_2/NC -CNTs is shown in Fig. 1a. First, Co ions were adsorbed on the surface of the car-

boxylate-functionalized CNTs *via* ultrasonic dispersion. Then, a mixture solution of 2-methylimidazole-dissolved trimethylamine/methanol was added, in which triethylamine accelerated nucleation and inhibited the grain growth of the ZIF-67 nanoparticles. Second, ZIF-67-CNTs were transformed to Co/NC -CNTs under hydrogen/argon during the thermal treatment. Finally, CoS_2/NC -CNTs were obtained by a low-temperature sulfurization reaction of Co/NC -CNTs.

PXRD was conducted to analyze the composition of the as-prepared samples. As shown in Fig. S1, the PXRD patterns of the as-synthesized ZIF-67 and ZIF-67-CNTs precursors were consistent with the simulated results [24], indicating that ZIF-67 with high crystallinity was successfully synthesized and combined with CNTs. ZIF-67 nanoparticles exhibit high size homogeneity with an average diameter of approximately 40 nm (Fig. S2a, b). This can be attributed to the added triethylamine for accelerated nucleation and grain growth inhibition [29]. When carboxyl-modified CNTs were introduced in the synthesis process, ZIF-67 nanoparticles were anchored on CNTs and arranged in a linear manner (Fig. S2c), suggesting that the ZIF-67 nanoparticles were successfully assembled *in-situ* on the CNTs' surface. Compared with ZIF-67 nanoparticles, ZIF-67-CNTs show a unique bead-like 1D structure with high dispersion and are loosely entangled with many nanopores (Fig. S2d).

Calcination temperature plays an important role in affecting morphology, composition, specific surface area, and porosity. Temperatures of 600, 700, and 800°C were chosen as targets to calcine ZIF-67-CNTs to balance the

Figure 1 The preparation process of CoS_2/NC -CNTs network.

graphitization of carbon with a stable porous structure and a number of heteroatoms [30]. Through the following thermal treatment at different temperatures, the phase of ZIF-67 changes, as shown in Fig. S3. The indexed characteristic peaks of Co-NC and Co/NC-CNTs-p located at 44.4° , 51.6° , and 76.0° are in good agreement with the (111), (200), and (220) planes of Co (JCPDS No. 15-0806), respectively [31]. In addition, the XRD patterns of Co/NC-CNTs-600, Co/NC-CNTs-700, and Co/NC-CNTs-800 exhibit an obvious peak around 26° , which can be attributed to the (002) plane of graphitic carbon (JCPDS No. 41-1487). An extra peak appears at 47.6° in the XRD pattern of Co/NC-CNTs-800, corresponding to the (101) plane of Co (JCPDS No. 05-0727), resulting from a phase transformation at 800°C . Numerous Co nanoparticles were loaded on the surface of CNTs, presenting a clear 3D network structure of Co/NC-CNTs-700 (Fig. S4b). Comparatively, serious agglomeration of Co nanoparticles in the Co/NC composite appears in Fig. S4a.

The XRD patterns of CoS_2/NC and $\text{CoS}_2/\text{NC-CNTs-p}$ are shown in Fig. S5. The peaks of CoS_2/NC and $\text{CoS}_2/\text{NC-CNTs-p}$ centered at 32.3° , 36.2° , 39.8° , 46.5° , 54.9° , 57.6° , 60.1° , and 62.7° can be assigned to the (200), (210), (211), (220), (311), (222), (230), and (321) planes of CoS_2 (JCPDS No. 41-1471) [32]. There are no additional diffraction peaks from residues and impurities, indicating that both Co/NC and Co/NC-CNTs-p were successfully converted to CoS_2/NC and $\text{CoS}_2/\text{NC-CNTs-p}$ after the sulfurizing process with high purity. Compared with the dominate broad peaks of (002) diffraction of CNTs and Co/NC-CNTs-700, the peak of $\text{CoS}_2/\text{NC-CNTs-700}$ exhibits no obvious angle change, indicating that the following sulfurizing process does not change the interlayer distance of carbon, further confirming no S doping [33,34].

The morphology and nanostructure of CoS_2/NC and $\text{CoS}_2/\text{NC-CNTs-700}$ were examined based on SEM and TEM images. As shown in Fig. S6, severe aggregation of CoS_2/NC is obvious, while the original ZIF-67 structure disappears. Comparably, the introduction of CNTs builds 3D space in $\text{CoS}_2/\text{NC-CNTs-700}$ and prevents them from aggregation (Fig. 2a, b). Furthermore, the TEM image of $\text{CoS}_2/\text{NC-CNTs-700}$ shows that 5 nm-diameter CoS_2 nanoparticles were uniformly distributed and loaded on the surface of CNTs (Fig. 2c, d). Meanwhile, thin-layered carbon with a thickness in the range of 2–3 nm covers the CoS_2 nanoparticles and anchors them on the surface of CNTs. This suggests that the volume expansion of CoS_2 can be greatly relieved in the discharge-charge process for cycle stability improvement [35]. Energy-dispersive X-ray

Figure 2 (a, b) SEM, (c) TEM, (d) high resolution TEM, and (e) STEM and EDS mapping images of $\text{CoS}_2/\text{NC-CNTs-700}$.

spectroscopy (EDS) mapping images further confirm the hierarchical structure of $\text{CoS}_2/\text{NC-CNTs-700}$, where the N, C, Co, and S elements are uniformly distributed. Particularly, the Co and S signals mainly locate on the particles, in accordance with the SEM and TEM results (Fig. 2e).

N_2 adsorption-desorption measurements were performed to investigate the surface areas and pore size distributions of $\text{CoS}_2/\text{NC-CNTs-700}$ and CoS_2/NC . Typical type-IV isotherms and H3-type hysteresis loops were observed in Fig. S7, suggesting the coexistence of micropores and mesopores in $\text{CoS}_2/\text{NC-CNTs-700}$ and CoS_2/NC , confirmed by the pore size distributions [36]. The calculated Brunauer-Emmett-Teller (BET) specific surface area of $\text{CoS}_2/\text{NC-CNTs-700}$ is $76.1 \text{ m}^2 \text{ g}^{-1}$, much larger than that of CoS_2/NC ($38.8 \text{ m}^2 \text{ g}^{-1}$). In addition, $\text{CoS}_2/\text{NC-CNTs-700}$ shows rich mesopores and pore size distributions highly concentrated in the range of 2–32 nm (Fig. S7). Enough space and abundant channels in $\text{CoS}_2/\text{NC-CNTs-700}$ favor the Li-ion diffusion and storage, and

the active materials ensure sufficient contact with the electrolyte.

To verify the composition and chemical state of $\text{CoS}_2/\text{NC-CNTs-700}$, XPS was adopted. Obvious signals of Co 2p, S 2p, C 1s, N 1s, and O 1s were detected in the XPS survey spectrum (Fig. S8). The high-resolution XPS spectrum of the Co 2p deconvolutes into two satellites (denoted as sat.) and four peaks (Fig. 3a). The Co 2p_{3/2} peaks located at 779.4 and 781.7 eV can be assigned to Co–Co and Co–S, respectively. The Co 2p_{1/2} peaks located at 798.4 and 794.6 eV can be assigned to Co–Co and Co–S, respectively. The result indicates the coexistence of Co^{2+} and Co^{3+} ions [37]. In the high-resolution S 2p spectrum, the characteristic S 2p peaks at 168.6 and 169.9 eV corresponding to the sulfate formed on the surface of CoS_2 , are mainly related to the strong interactions with oxygen and water in the air. The two peak energies at 165.1 and 163.8 eV are attributed to the formation of disulfide S_2^{2-} in the CoS_2 , while the peaks centered at 164.0, 163.0, 162.8, and 161.8 eV suggest the presence of S^{2-} , which are due to the partial oxidation of CoS_2 . (Fig. 3b) [38]. As shown in Fig. 3c, the C 1s spec-

trum can be deconvoluted into three peaks located at 288.0, 285.8, and 284.8 eV, corresponding to C=O, C–N, and C–C bonds, respectively [20]. C–N bonds can provide more defects and active sites to adsorb Li ions and adjust the surface energy barrier of the carbon substrates [39]. The high-resolution N 1s spectrum reveals the existence of graphite N (405.1 eV), pyrrole N (401.4 eV), and pyridine N (398.9 eV) (Fig. 3d) [40]. The area percentages of pyridine N, pyrrole N, and graphite N are 23%, 70%, and 7%, respectively. As shown in the Raman spectra (Fig. S9), the peak intensity ratios ($I_{\text{D-band}}/I_{\text{G-band}}$) of $\text{Co}/\text{NC-CNTs-700}$ and $\text{CoS}_2/\text{NC-CNTs-700}$ are 1.008 and 1.009, respectively, manifesting no change in the carbon substrate before and after sulfurization. Combined with the XPS analysis, it is proved that no doped S form in the carbon substrate at moderate temperature.

Based on the above discussion, the electrochemical performance of $\text{CoS}_2/\text{NC-CNTs-p}$ was investigated using coin-type cells with metal Li as the counter electrode and EC/DEC/DMC with 1.0 mol L^{-1} LiPF_6 solution as the electrolyte. The carbonization temperature slightly influences the specific capacity of $\text{CoS}_2/\text{NC-CNTs-p}$. The cycle

Figure 3 XPS spectra of $\text{CoS}_2/\text{NC-CNTs-700}$. (a) Co 2p, (b) S 2p, (c) C 1s, (d) N 1s. Inset is the area percentages of pyridine N, pyrrole N, and graphite N.

and rate capabilities of CoS₂/NC-CNTs-600, CoS₂/NC-CNTs-700, and CoS₂/NC-CNTs-800 were tested and compared, and the results indicate that CoS₂/NC-CNTs-700 possesses the best electrochemical performance (Fig. S10a, b). It may be due to the differences in N species, N content, and particle size. Hence, CoS₂/NC-CNTs-700 was used for further electrochemical analysis. CV tests were conducted at 0.1 mV s⁻¹ between 0.01 and 3.00 V at the first four cycles to further investigate the lithium storage mechanism of CoS₂/NC-CNTs-700 (Fig. 4a). During the first cathodic scan, four peaks located at 1.57, 1.16, 1.04, and 0.65 V were observed, and then disappeared in the following cycles, resulting from the formation of a solid electrolyte interface (SEI) film and electrolyte decomposition [41,42]. In the second cycle, the positions of the oxidation peaks did not change, while the reduction peaks moved to 1.36, 1.76 and 2.06 V from the first cycle, which was caused by the enhanced reaction kinetics of the electrode. Over subsequent cycles, the CV curves in the 2nd, 3rd, and 4th cycles overlap well, suggesting high reversibility of the CoS₂/NC-CNTs-700 electrode. According to the analysis, these peaks are consistent with the reversible reaction between CoS₂ and Co⁰Li₂S. In the cathodic process, three peaks located at 1.36, 1.76, and 2.06 V obey the following

Equations (1, 2):

In the anodic process, two peaks at 2.03 and 2.56 V are related to the following Equations (3, 4) [11]:

Therefore, a reversible redox reaction mechanism can be derived, as shown in Equation (5): [43]

Fig. 4b shows the charge-discharge voltage profiles of CoS₂/NC-CNTs-700 at a current density of 100 mA g⁻¹ with a potential range of 0.01–3.00 V (vs. Li/Li⁺). The unobvious charge/discharge plateaus are consistent with the CV curves. In the first cycle, the charge and discharge specific capacities are 695 and 1160 mA h g⁻¹, respectively. The high initial coulombic efficiency (CE) is 65.1%, suggesting less capacity loss. After five activation cycles, the CE quickly increased to around 100%, indicating good reversibility. More importantly, in the slow charge-discharge process (a current density of 100 mA g⁻¹), the charge and discharge specific capacities and the voltage profiles in the 50th and 100th cycles are almost identical

Figure 4 (a) CV curves of the CoS₂/NC-CNTs-700 electrode at 0.1 mV s⁻¹ and (b) charge-discharge curves of CoS₂/NC-CNTs-700 at 100 mA g⁻¹ in the 1st, 2nd, 3rd, 50th, and 100th cycles; (c) cycle stability and CE of CoS₂/NC-CNTs-700, CoS₂/NC, and CNTs at 0.2 A g⁻¹; (d) rate capability comparison of CoS₂/NC-CNTs-700, CoS₂/NC, and CNTs.

with that of the 3rd, suggesting excellent stability of the CoS₂/NC-CNTs-700 electrode and the effectiveness of our strategy in improving the electrochemical performance.

Fig. 4c shows the cycle performance comparison of CoS₂/NC-CNTs-700, CoS₂/NC, and CNTs at 200 mA g⁻¹. CoS₂/NC-CNTs-700 displays the highest discharge specific capacity of 719 mA h g⁻¹ compared with CoS₂/NC (458 mA h g⁻¹) and CNTs (360 mA h g⁻¹) and retains its cycle stability without fading after 100 cycles. To further illuminate the intrinsic mechanism of such improvement, electrochemical impedance spectroscopy (EIS) measurements and SEM images were performed before and after cycling. Notably, the charge-transfer resistance (R_{ct}) of the fresh CoS₂/NC-CNTs-700 electrode is close to that of the fresh CoS₂/NC electrode. After 5 cycles, the R_{ct} gradually decreases. It can be attributed to the chemical activation process of dissolution and redistribution of the active material. After activation, the cycled CoS₂/NC-CNTs-700 electrode delivers smaller R_{ct} and diffusive resistance compared with the cycled CoS₂/NC electrode (Fig. S11). In addition, CoS₂/NC-CNTs-700 can maintain its original morphology at 0.2 A g⁻¹ after 100 cycles, suggesting high structural stability (Fig. S12). The rate capabilities of CoS₂/NC-CNTs-700, CoS₂/NC, and CNTs were evaluated at various current densities ranging from 0.1 to 5.0 A g⁻¹. As shown in Fig. 4d, the discharge specific capacities of CoS₂/NC-CNTs-700 can reach 768, 687, 573, 486 and 418 mA h g⁻¹ at the current densities of 0.1, 0.2, 0.5, 1.0, and 2.0 A g⁻¹, respectively. Specifically, when tested at a superhigh current density of 5.0 A g⁻¹, the CoS₂/NC-CNTs-700 electrode can retain 335 mA h g⁻¹, which is higher than that of CoS₂/NC and CNTs (Fig. 4d). After that, the CoS₂/NC-CNTs-700 electrode can resume a reversible capacity of 870 mA h g⁻¹ when the current density reverts to 0.1 A g⁻¹.

To further illuminate the Li-storage mechanism of CoS₂/NC-CNTs-700, kinetic analysis was conducted using CV curves. As shown in Fig. 5a, with increasing scan rates, the CV curves maintain a similar shape, and the peak current gradually increases. According to the relationship between peak current (i) and scanning rate (v), the contribution ratio of pseudocapacitance can be determined by the following Equations (6, 7):[44,45]

$$i = av^b, \quad (6)$$

$$\log(i) = b\log(v) + \log(a), \quad (7)$$

where a is a constant and b is determined by the slope of the linear plot of $\log(i)$ vs. $\log(v)$. As the b -value increases to 1.0, this indicates that surface capacitive behavior

dominates, while a b -value equal to 0.5 indicates that the charge storage mechanism is completely controlled by the diffusion process. If the b -value is between 0.5 and 1.0, it suggests that both surface capacitance and charge storage are contributing. As shown in Fig. 5b, the b -value calculated by peak 1 is 0.63 in the cathodic scanning process, and the b -values calculated by peaks 2 and 3 are 0.64 and 0.68 in the anodic scanning process, respectively (Fig. 5b). The results indicate the Li-storage mechanism of the CoS₂/NC-CNTs-700 electrode includes both diffusion- and capacitive-controlled behaviors. The current at a fixed voltage can be divided into a capacitive effect (k_1v) and diffusion-controlled process ($k_2v^{1/2}$) using Equation (8) [45]:

$$i(V) = k_1v + k_2v^{1/2}, \quad (8)$$

where $i(V)$ represents the current at a fixed voltage, and both k_1 and k_2 are constants at the given voltage. The corresponding k_1 can be obtained at a specific voltage by calculating the ratio of $i(V)/v^{1/2}$ to $v^{1/2}$, and the intercept is the value of k_2 . As shown in Fig. 5c, the contribution of pseudocapacitance (the red part) accounts for about 71% total capacity at a sweep rate of 0.8 mV s⁻¹. With an increasing sweep rate, the pseudocapacitance contribution gradually increases. Specifically, the capacitive contribution can reach 77% at 1.0 mV s⁻¹ (Fig. 5d). This high capacitive contribution is an important factor for excellent rate capacity.

The outstanding lithium storage properties of CoS₂/NC-CNTs-700 can be attributed to the higher theoretical capacity of CoS₂ and the 3D hierarchical, high-conductivity network design (Fig. 5e). In particular, the as-prepared CoS₂/NC-CNTs composites possess ultra-small dispersed CoS₂ nanoparticles embedded in N-doped carbon, ensuring a stable electrode structure for fast reaction kinetics and high specific capacity and the N-doped carbon shell coating on CoS₂ accommodates the large volume expansion of small-size CoS₂ nanoparticles at the lithium reaction, thus effectively mitigating the issue of fading capacity. The conductive CNTs assemble an interconnected 3D network against the aggregation of CoS₂ nanoparticles, providing a full electrolyte/electrode contact and short diffusion path for ions and electrons, which further improves the sodium reaction rate and alleviates the structural degradation.

CONCLUSIONS

In summary, an interconnected CoS₂/NC-CNT network was successfully synthesized using ZIF-67-CNTs as a precursor by a two-step thermal treatment. The CoS₂

Figure 5 (a) CV curves of CoS₂/NC-CNTs-700 at various scan rates; (b) the ratios of log(*i*) to log(*v*) at different oxidation/reduction peaks; (c) the proportions of capacitance in the total charge contribution at a scan rate of 0.8 mV s⁻¹; (d) the contribution of capacitance and diffusion control capacity at different scan rates; (e) schematic illustration of the electron/ion transport channels of CoS₂/NC-CNTs-700.

nanoparticles covered by thin-layered carbon were uniformly distributed on the CNTs, thus accommodating the large volume change and improving the charge transfer. Due to the synergistic effect of CoS₂, N-doped carbon, and CNTs, when evaluated as an anode material in LIBs, the optimized CoS₂/NC-CNTs-700 electrode exhibited superior rate capability (768 mA h g⁻¹ at 0.1 A g⁻¹, 418 mA h g⁻¹ at 2.0 A g⁻¹, 335 mA h g⁻¹ at 5.0 A g⁻¹) and excellent cycle performance (719 mA h g⁻¹ after 100 cy-

cles at 0.2 A g⁻¹). These results may provide access to the preparation and rational engineering of MOF-derived electrode materials, in addition to lithium storage systems.

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Supplementary information Supporting data are available in the online version of the paper.

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交联状CoS₂/NC-CNTs网络作为高性能负极在锂离子电池中的应用

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摘要 二硫化钴(CoS_2)因具有较高的理论容量(870 mA h g^{-1}), 被认为是一种很有前途的锂离子电池负极材料. 然而, 其在充放电过程中会发生体积变化和电导率极化, 严重阻碍了其实际应用. 针对上述问题, 在本文中, 我们设计制备了一种具有三维网络结构的 CoS_2 /氮掺杂碳/碳纳米管($\text{CoS}_2/\text{NC-CNTs-700}$)复合材料来改善 CoS_2 的电化学储锂性能. 小尺寸的 CoS_2 纳米粒子镶嵌在氮掺杂碳中, 并均匀地分散在碳纳米管表面. 氮掺杂碳可以有效地抑制 CoS_2 纳米粒子的体积膨胀, 同时碳纳米管构建的三维导电网络提供了足够的电子/质量传输距离. 得益于此, $\text{CoS}_2/\text{NC-CNTs-700}$ 作为锂离子电池负极展现出较高的稳定性(0.2 A g^{-1} 下100次循环后, 剩余比容量为 719 mA h g^{-1})和优异的倍率性能(5.0 A g^{-1} 大倍率下, 容量依然高达 335 mA h g^{-1}). 这项工作不仅拓展了 CoS_2 基材料新的设计思路, 也推动了新型电池负极材料的研究和发展.