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Simultaneous Immobilization and Conversion of Polysulfides on Co₃O₄–CoN Heterostructured Mediators Toward High-Performance Lithium–Sulfur Batteries

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ABSTRACT: Lithium–sulfur batteries exhibit great promise as a next-generation rechargeable battery system due to their high energy density, natural abundance and nontoxicity. Nevertheless, the insulated property of sulfur and lithium sulfides, and the electrochemical instability of intermediate polysulfides obstruct the commercialization of Li–S technologies. Herein, a hetero–phase Co_3O_4 –CoN sulfur host with the merits of efficient polysulfide anchoring (Co_3O_4) and high conductivity (CoN) is reported to enhance Li-S battery performance. Such porous Co_3O_4 –CoN heterostructures endow the intermediated lithium polysulfides with highly–efficient immobilization–diffusion–conversion process, thus enabling the accelerated redox kinetics and alleviating the polysulfide shuttling. The assembled cathode based on Co_3O_4 –CoN/CC electrode exhibits a high initial capacity of 1225 mAh g^{−1} at 0.5C with excellent rate capability (887 mAh g^{−1} at 3C), and the specific capacity can be well-maintained to 627 mAh g^{−1} at 3C even after 500 cycles. Our work provides an in–depth insight into the rational design of comprehensive host materials which realizes synchronous LiPS adsorption and conversion, and will greatly promote the practical use of Li–S batteries.

1. INTRODUCTION

The rising demand for advanced energy storage devices with high energy density, high power, and long cycle life, has triggered the urgent exploration of new battery systems beyond the currently dominant lithium-ion batteries (LIBs). Among the alternative battery chemistries, lithium-sulfur (Li-S) batteries have drawn extensive interest due to the high theoretical energy density of 2567 W h kg^{-1} , low cost, environmental friendliness, and natural abundance.¹⁻⁴ The energy density of the practical Li-S battery pack can reach as high as $500\text{--}600 \text{ Wh kg}^{-1}$, endowing their great promise in high-energy applications such as electric vehicles and intensive renewable energy storage.

While Li-S batteries have attractive properties, there are still numerous challenges obstructing the practical application of Li-S batteries.⁵⁻⁷ One of the major issues is the sluggish reaction kinetics originated from the insulation nature of sulfur and intermediate lithium polysulfides (LiPS). In addition, the large volumetric variation of sulfur cathode during cycling results in the mechanical failure of active materials, resulting in poor contact with current collectors to further capacity fading. The notorious issue is the shuttling of soluble LiPS between cathode and Li anode, which results in low utilization of active materials, low Coulombic efficiency, and poor reversibility.⁸

To restrain the shuttle effect, strenuous efforts have been made such as encapsulating cathodes with delicate designs of carbonaceous matrixes⁹⁻¹¹, developing functional interlayers and binders^{12, 13}, and employing novel electrolytes and additives^{14, 15}, as

summarized in review articles. Carbon materials are intensively selected as sulfur hosts due to their high conductivity and regulable porosity, while nonpolar carbon materials always exhibit weak interactions with polar sulfur species, which are not favorable to the immobilization of sulfur and polysulfides in the long range. Heteroatom doped carbons (N, O, S, N/S, N/P) have been demonstrated to trap polysulfides with strong chemical interactions.¹⁶⁻²³ Unfortunately, the heteroatom content is still low and unstable with the cycling. This causes the anchoring effect for polysulfides is still limited. Thus, the achievement of efficient sulfur hosts with strong trapping and high adsorption for polysulfides remains a big challenge.

Actually, the shuttle effect can be mainly derived from the two following reasons: (1) the LiPS dissolution in electrolyte; (2) the slow conversion of these LiPS to insoluble $\text{Li}_2\text{S}_2/\text{Li}_2\text{S}$.^{24, 25} In most cases, the LiPS dissolution is hard to be fully avoided due to the existence of contact area between sulfur and electrolyte. Especially, it becomes even severe in most cases with porous structures. Thus, the promising strategy for restraining the shuttle effect requires not only the strong polysulfide adsorption, but also the fast conversion of LiPS to insoluble $\text{Li}_2\text{S}_2/\text{Li}_2\text{S}$ for decreasing their dissolution in electrolyte. Very recently, several polar materials, such as metal oxides (TiO_2 , Fe_3O_4 , MnO_2)²⁶⁻²⁹, metal sulfides (CoS_2 and MoS_2)^{26, 30, 31}, metal nitrides (VN and Co_4N)³²⁻³⁵, and some metal free materials^{17, 36}, have been reported to alleviate the LiPS shuttling by strong polysulfide affinity and favorable catalytic conversion effects. However, non-conductive metal oxides and sulfides always possess high adsorption ability for LiPS but unfavorable conversion efficiency. Nevertheless, some conductive hosts with

favorable conversion efficiency are limited by poor affinity to LiPSs. Inspiring of this, the construction of non-conductive with conductive sulfur hosts can synergize strong LiPS chemisorptivity and desirable conversion efficiency, and gives rise to the enhanced electrochemical performance of Li-S batteries. In this regard, two vivid examples recently were reported along these lines. For example, TiO_2 - TiN based interlayer and VO_2 - VN binary host are designed for advanced Li-S batteries. Cobalt oxide (Co_3O_4) has attracted intensive interest because of its fast ionic diffusion ability and attractive catalytic activities.^{37,38} Wang *et al.* reported Co_3O_4 showed strong affinity for binding LiPS, thus achieving extraordinary electrochemistry performance.^{39,40} However, Co_3O_4 always exhibits undesirable catalytic conversion of LiPS due to its low electrical conductivity. As a congener of Co_3O_4 by substituting O with N, cobalt nitride (CoN and Co_4N) with favorable electrical conductivity has gained intensive attention for advanced sulfur hosts. Dong *et al.* reported Co_4N spheres presented strong affinity and fast trapping for LiPSs, and efficient catalytic activities for redox processes, thus achieving extraordinary electrochemistry performance.³² However, to date, there are rare reports of hetero-phase Co_3O_4 - CoN sulfur host to realize synchronous anchoring and conversion of LiPSs, thus consequently rendering the enhanced performance of Li-S batteries.

In this contribution, a Co_3O_4 - CoN binary sulfur host with the merits of efficient polysulfide anchoring (Co_3O_4) and high conductivity (CoN) is reported to boost the overall performance of Li-S batteries. Through this design, a binary sulfur host synergizing strongly anchored Co_3O_4 and highly conductive CoN aims at realizing

highly-efficient immobilization–diffusion–conversion process of LiPSs. As a result, sulfur cathode based on Co_3O_4 –CoN/CC composites accommodating Li_2S_6 catholyte exhibits enhanced capacities, long-term cycling stability, and superior rate capability. The proposed strategy represents a significant advance in the design of sulfur host via construction of non-conductive with conductive sulfur hosts to synergize strong LiPS chemisorptivity and desirable conversion efficiency, and contributes to the research community for the fundamental electrode design criterion study of Li-S batteries.

2. EXPERIMENTAL SECTION

2.1 Material Synthesis. Co_3O_4 –CoN/CC was synthesized by a simple hydrothermal method assisted plasma process. Firstly, as previously reported, the $\text{Co}_2(\text{OH})_2\text{CO}_3$ nanowire arrays supported on CC were prepared by a hydrothermal method.⁴¹ Before the hydrothermal process, CC was acidized with 35% HNO_3 at 80 °C for 12 h to increase its hydrophilic nature. One piece of CC with an area of 8 cm² was fixed on one piece of a glass slide using Kapton tape and immersed into the hydrothermal solution containing 0.2571 g $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 0.0643 g NH_4F , 0.2571 g urea and 30 mL de-ionized (DI) water. The liner was sealed in a 50 mL stainless steel autoclave and maintained at 110 °C for 5 h. The obtained samples were washed with DI water, dried in oven at 60 °C and then annealed in furnace at 300 °C under Ar atmosphere for 1.5 h leading to the formation of Co_3O_4 . The average mass loading was about 1.5~1.8 mg cm⁻². The obtained electrode is labelled as Co_3O_4 /CC. For the synthesis of Co_3O_4 –CoN@CC, the obtained $\text{Co}(\text{OH})\text{F}$ nanowires were directly undergone a N_2 RF plasma

treatment at 300 W and 13.56 MHz for 1 min to obtain the target product.

2.2 Characterization. The morphology and structure characterization of the samples were carried out by transmission electron microscope (TEM, JOEL JEM 2100F), scanning electron microscopy (FESEM, Model JSM–7600F, JEOL Ltd., Tokyo, Japan), and X-ray diffraction (XRD, Bruke D8). Raman spectroscopy was recorded by Renishaw Raman Microscopy with 2.33 eV (532 nm) excitation laser. The XPS measurements were performed with a VG ESCALAB 220i–XL system using a monochromatic Al K α 1 source (1486.6 eV). All XPS spectra were obtained in the constant pass energy (CPA) mode. The pass energy of analyser was set to be 10 eV to have high measurement accuracy. The binding energy scale was calibrated with pure Au, Ag and Cu by setting the Au 4f_{7/2}, Ag 3d_{5/2}, and Cu 2p_{3/2} at binding energy of 84.0, 368.3, and 932.7 eV, respectively.

2.3 Preparation of electrolyte and polysulphide catholyte. The blank electrolyte was prepared by dissolving an appropriate amount of lithium trifluoromethanesulfonate (LiCF₃SO₃, Sigma, 1M) and LiNO₃ (0.2M) in 1,2-dimethoxyethane (DME, Sigma) and 1,3–dioxolane (DOL, Sigma) (1:1 by volume). The polysulphide catholyte was prepared by chemically reacting sublimed sulphur and an appropriate amount of Li₂S in the blank electrolyte to form Li₂S₆ (1.0 M) in the solution. The solution was then stirred at 50 °C in an Ar–filled glove box overnight to produce a brownish–red catholyte solution.

2.4 Cell Assembly and Electrochemical Measurements. The Li/dissolved

polysulphide cells (CR2032 coin cells) were assembled in an Ar-filled glove box. The $\text{Co}_3\text{O}_4\text{-CoN/CC}$, $\text{Co}_3\text{O}_4\text{/CC}$ and CC were dried at 60°C under vacuum overnight before using. These samples were cut and directly used as Li-S battery electrodes without a metal current collector, binder and conductive additive. Next, inside an Argon-filled glovebox, $30\ \mu\text{l}$ Li_2S_6 catholyte (1.0 M) was added into the $\text{Co}_3\text{O}_4\text{-CoN/CC}$, $\text{Co}_3\text{O}_4\text{/CC}$ and CC electrodes, corresponding to a sulphur loading of $3\ \text{mg cm}^{-2}$. The Celgard 2400 separator was then placed on top of the electrode, followed by adding 30 ml of the blank electrolyte. Finally, the lithium-metal foil anode was placed on the separator as the anode. Galvanostatic charging and discharging tests were conducted using a battery tester (NEWARE) at different current rates. All the specific capacities reported in this work were based on the mass of sulfur only. Cyclic voltammetry (CV) was performed using an electrochemical workstation (CHI 760D, Chenhua, Shanghai) from 1.7 to 2.8 V at a scan rate of $0.1\ \text{mV s}^{-1}$. Electrochemical impedance spectroscopy (EIS) was also carried out with an electrochemical workstation over a frequency range from $10^6\ \text{Hz}$ to 100 mHz at open circuit potential after two galvanostatic charging and discharging cycles at $100\ \text{mA g}^{-1}$. For the cycled samples, the cycled cells were disassembled inside an Argon-filled glove box, and the electrodes were rinsed with DME solvent to remove the lithium salt and dried inside the glove box at room temperature before analysis. For the ex situ adsorption measurement, 0.05M Li_2S_6 solution was prepared by chemically reacting sublimed sulphur and Li_2S in mixed DOL/DME (1:1 in volume).

2.5 In Situ Raman Spectroscopy. Li-S coin cells with a quartz window on negative shell were employed for in situ micro-Raman spectroscopy analysis. The same method

was used to prepare Co₃O₄-CoN/CC and Co₃O₄/CC cathodes as aforementioned. A hole was created on lithium metal foil to allow the laser shed on the separator. The cells were run at a charging rate of 0.5C. Raman signals were recorded simultaneously by a 532 nm laser with an $\approx 1 \mu\text{m}$ laser spot on the separators near the lithium ring.

2.6 Theoretical calculations. All of the calculations were performed using the Vienna ab initio simulation package (VASP).⁴² Projector-augmented-wave (PAW) potentials were used to consider the electron-ion interactions, whereas the electron exchange-correlation interactions were treated using the Perdew-Burke-Ernzerhof (PBE) exchange correlation functional in the scheme of generalized gradient approximation (GGA).⁴³ And we used the vdW-DF2 functional to include the physical van der Waals (vdW) interaction in the simulation⁴⁴, which is proved to be very important for calculation.^{45,46} A $4 \times 4 \times 1$ Monkhorst-Pack k grid was used for sampling the Brillouin zones at structure calculation, whereas a denser mesh of $8 \times 8 \times 1$ used to calculate the densities of the states (DOS), which is to use to insure our calculation accuracy. All the atomic positions and lattice vectors fully optimized using a conjugate gradient algorithm to obtain the unstrained configuration. The electron wavefunctions were expanded in a plane wave basis with kinetic energy cutoff of 500 eV. Atomic relaxation performed until the change in total energy was less than 1×10^{-5} eV, and maximum forces were smaller than $0.001 \text{ eV}/\text{\AA}$. The adsorption energies (E_b) are calculated to evaluate the binding strength between LiPS and sulfur host materials (CoN and Co₃O₄), which is defined by:

$$E_b = E_{s+host} - E_s - E_{host} \quad (1)$$

where E_{s+host} , E_s , and E_{host} are the energies of the polysulfides–host material, polysulfides, and host material, respectively. According to this definition, a more negative value of E_b indicates a more energetically favorable (exothermic) reaction. For each monolayer substrate, a vacuum space of 15 Å placed between adjacent layers to avoid periodic interactions.

3. RESULTS AND DISCUSSION

The fabrication of porous Co₃O₄–CoN composites involves two steps. Firstly, Co(OH)F nanowire arrays were directly grown on carbon cloth (see **Experimental Section**). Then, the obtained Co(OH)F nanowires were undergone a N₂ RF plasma at room temperature for 1 min, as illustrated in **Figure 1a**. The phase and morphology of Co(OH)F nanowires were characterized and shown in **Figure S1**. The final product can be cut into plates for directly accommodating Li₂S₆ catholyte, without any metallic current collector, conductive additives, or binder.

Figure 1. (a) Schematic illustration of synthesis process of $\text{Co}_3\text{O}_4\text{-CoN/CC}$ composite. Morphology and structural characterization of $\text{Co}_3\text{O}_4\text{/CC}$ and $\text{Co}_3\text{O}_4\text{-CoN/CC}$ composites. SEM images of (b) $\text{Co}_3\text{O}_4\text{/CC}$, and (e) $\text{Co}_3\text{O}_4\text{-CoN/CC}$. TEM and HRTEM images of (c)–(d) $\text{Co}_3\text{O}_4\text{/CC}$. TEM image of (f) $\text{Co}_3\text{O}_4\text{-CoN/CC}$, and HRTEM images of (g) Co_3O_4 in section I and (h) CoN in section II, inset showing the fast Fourier

transform (FFT) pattern. (i) The dark field image of Co₃O₄–CoN nanowires. Elemental mapping images of Co₃O₄–CoN: (j) Co, (k) O and (l) N.

The morphology and microstructure of Co₃O₄/CC and Co₃O₄–CoN/CC composites were characterized by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). SEM images show the obtained nanowires with a diameter of around 50–100 nm (**Figure 1b** and **Figure S2a–b**). TEM image also reveals the nanowire morphology (**Figure 1c**). HRTEM image shows two interplanar spacings of 0.466 nm, corresponding to (111) lattice planes of Co₃O₄, respectively (**Figure 1d**). After N₂ RF plasma treatment for 1 min, the sample still maintains the nanowire morphology, but reveal obvious roughness on the surface of nanowires (**Figure 1e** and **Figure S2c–d**). TEM image also clearly shows the rough interface along the nanowire after N₂ plasma treatment (section II in **Figure 1f**). HRTEM image in the core part of the nanowire (section I) shows (111) plane with an interlayer spacing of 0.466 nm, corresponding to lattice plane of Co₃O₄ (**Figure 1g**). Meanwhile, HRTEM image in shell area (section II) shows a distinct lattice fringe of 0.21 nm, corresponding to the (200) planes of CoN (**Figure 1h**). The dark field image and elemental mapping analysis confirm the core–shell Co₃O₄–CoN heterostructure. It is clearly observed that the coexistence and homogenous dispersion of Co, O and N elements within the nanowire framework (**Figure 1i–l**).

X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), and Raman measurements were performed to determine the phase and composition of the products.

Typical XRD patterns of $\text{Co}_3\text{O}_4/\text{CC}$ and $\text{Co}_3\text{O}_4\text{--CoN}/\text{CC}$ are shown in **Figure 2a**. The diffraction peak at 26.5° and the weak peak at 43.2° in three samples are indexed well to (002) and (004) planes of graphitic carbon, ascribing to graphitic carbon from CC. After the N_2 plasma treatment for 1 min, XRD patterns clearly show the formation of the $\text{Co}_3\text{O}_4\text{--CoN}$ heterostructures with the typical patterns of the two components appearing simultaneously, indicating that Co_3O_4 phase is partly converted into CoN phase. Meanwhile, Co_3O_4 has stronger peaks than CoN. Raman spectra in **Figure 2b** indicates three characteristic peaks of graphitic carbon, observed at 1350, 1580, and 2720 cm^{-1} and corresponding to the D, G, and 2D bands, respectively. After the growth of Co_3O_4 and $\text{Co}_3\text{O}_4\text{--CoN}$, I_D/I_G ratios of $\text{Co}_3\text{O}_4/\text{CC}$ and $\text{Co}_3\text{O}_4\text{--CoN}/\text{CC}$ increase to 1.04 and 1.05, compared to 0.6 of the bare CC, which indicating the strong coupling between CoN (or Co_3O_4) and CC substrate. The Raman signals at 189, 471, 513 and 676 cm^{-1} can be assigned to Co_3O_4 . In the Raman spectrum of $\text{Co}_3\text{O}_4\text{--CoN}/\text{CC}$, blue shift ($\sim 5\text{ cm}^{-1}$) of characteristic peaks compared to those of Co_3O_4 can be observed, indicating the structural change after N_2 plasma. The surface chemical compositions of $\text{Co}_3\text{O}_4/\text{CC}$ and $\text{Co}_3\text{O}_4\text{--CoN}/\text{CC}$ were further investigated by XPS. The Co spectra shows Co $2p_{3/2}$ and Co $2p_{1/2}$ peaks at 797.5 and 781.5 eV with satellite peaks (803.4 and 786.6 eV), which are in good agreement with those reported for Co_3O_4 (**Figure 2c**). The well-defined satellite peaks at 786.5 and about 803.4 eV are still observed in $\text{Co}_3\text{O}_4\text{--CoN}/\text{CC}$, suggesting the breakdown of the spinel structure after N_2 plasma exposure and the presence of Co^{2+} .³⁹ Both Co $2p_{3/2}$ and Co $2p_{1/2}$ peaks of $\text{Co}_3\text{O}_4\text{--CoN}/\text{CC}$ show a positive chemical shift of 0.5 eV compared with that of $\text{Co}_3\text{O}_4/\text{CC}$,

indicating a modulation of the surface electronic band bending after N₂ plasma. For the N1s spectrum of Co₃O₄-CoN/CC, the existence of pyridinic N (398.4 eV) and pyrrolic N (400 eV) demonstrates there are natively doped N atoms in CC (**Figure 2d**). In addition, one dominant peak at 397 eV corresponding to N in metal nitride, confirms the Co-N bond in Co₃O₄-CoN/CC.

Figure 2. Phase and chemical composition characterization of Co₃O₄/CC and Co₃O₄-CoN/CC composites. (a) XRD patterns of CC, Co₃O₄/CC and Co₃O₄-CoN/CC. (b) Raman spectra of CC, Co₃O₄/CC and Co₃O₄-CoN/CC. XPS spectra of Co₃O₄-CoN/CC: (c) Co 2p and (d) N 1s peaks.

To investigate the potential feasibility of Co₃O₄-CoN/CC as cathode of Li-S batteries, Li-S coin cells are assembled using Li₂S₆ as catholyte, which is directly adding to Co₃O₄-CoN/CC and forming a free-standing cathode. The average areal sulfur loading

of the electrode was $\sim 3 \text{ mg cm}^{-2}$. The electrochemical performance of the as-derived $\text{Co}_3\text{O}_4\text{-CoN/CC}$ and $\text{Co}_3\text{O}_4\text{/CC}$ cathodes was compared to specify the synergizing advantages of $\text{Co}_3\text{O}_4\text{-CoN}$ binary hosts for mitigating polysulfide shuttle, facilitating the redox kinetics, and buffering volume expansion.

Figure 3. Electrochemical performances of $\text{Co}_3\text{O}_4\text{-CoN/CC}$ and $\text{Co}_3\text{O}_4\text{/CC}$ cathodes. (a) The typical CV curves of $\text{Co}_3\text{O}_4\text{-CoN/CC}$ and $\text{Co}_3\text{O}_4\text{/CC}$ electrodes at a scan rate of 0.2 mV s^{-1} . (b) Galvanostatic charge-discharge voltage profiles of $\text{Co}_3\text{O}_4\text{-CoN/CC}$ and $\text{Co}_3\text{O}_4\text{/CC}$ electrodes at 0.2C . (c) Rate capabilities of the $\text{Co}_3\text{O}_4\text{-CoN/CC}$ and $\text{Co}_3\text{O}_4\text{/CC}$ cathodes. (d) Cycling performances and Coulombic efficiency of $\text{Co}_3\text{O}_4\text{-CoN/CC}$ and $\text{Co}_3\text{O}_4\text{/CC}$ cathodes at 0.5C for 100 cycles. (e) Cycling stability of the $\text{Co}_3\text{O}_4\text{-CoN/CC}$ and $\text{Co}_3\text{O}_4\text{/CC}$ electrodes at a high rate of 3C for 500 cycles.

Figure 3a shows the typical CV curves of the $\text{Co}_3\text{O}_4\text{-CoN/CC}$ and $\text{Co}_3\text{O}_4\text{/CC}$ cathodes in the voltage range from 1.7 to 2.8 V at a scan rate of 0.2 mV s^{-1} . Both cathodes show two representative cathodic peaks, which can be attributed to the reduction of sulfur to long-chain lithium polysulfides (Li_2S_x , $3 \leq x \leq 8$) at the higher potential, and the formation of insoluble shortchain $\text{Li}_2\text{S}_2/\text{Li}_2\text{S}$ at the lower potential. When scanning back, the anodic peaks corresponded to the oxidation of $\text{Li}_2\text{S}/\text{Li}_2\text{S}_2$ to polysulfides and then to sulfur. Interestingly, the peaks of $\text{Co}_3\text{O}_4\text{-CoN/CC}$ cathode present distinguishable positive shift in the reduction process and negative shift in the oxidation process, indicating that the $\text{Co}_3\text{O}_4\text{-CoN}$ heterostructure can enhance the reaction kinetics for LiPS redox (**Figure S3**). Moreover, the electrocatalytic effect of the $\text{Co}_3\text{O}_4\text{-CoN}$ heterostructure is validated by the changes in onset potentials for both cathodes. Here, the onset potential is defined at a current density of $10 \mu\text{A cm}^{-2}$ beyond the baseline current, following a common definition employed in electrocatalysis. It is interesting to note that the onset potentials of cathodic (anodic) peaks with the $\text{Co}_3\text{O}_4\text{-CoN}$ heterostructure appeared at higher (lower) potentials than those with the $\text{Co}_3\text{O}_4\text{/CC}$ cathode, verifying the incorporation of CoN into Co_3O_4 indeed accelerates the redox processes in Li-S battery system (**Figure S4**). The comparison of electrochemical kinetics is further verified by galvanostatic charge/discharge tests at a constant current rate of 0.2C (**Figure 3b**). Both cathodes show typical discharge/charge plateaus of Li-S batteries, in agreement with the CV results. Impressively, the $\text{Co}_3\text{O}_4\text{-CoN/CC}$ cathode shows lower polarization with the smaller voltage gap of only 170 mV, much lower than that of $\text{Co}_3\text{O}_4\text{/CC}$ cathode (230 mV). The voltage gap difference

becomes more obvious with increased current densities (**Figure S5**). For example, at a high current rate of 1C, the voltage gap between oxidation and reduction plateaus for the $\text{Co}_3\text{O}_4\text{-CoN/CC}$ cathode is 260 mV, while the $\text{Co}_3\text{O}_4\text{/CC}$ cathode exhibit larger voltage polarization (330 mV), suggesting the excellent kinetic reaction process of the $\text{Co}_3\text{O}_4\text{-CoN/CC}$ cathode. Electrochemical impedance spectroscopy (EIS) measurements also corroborate the above results (**Figure S6**). The $\text{Co}_3\text{O}_4\text{-CoN/CC}$ cathode exhibits relatively lower ohmic resistance between the electrode and electrolyte and charge-transfer resistance than the $\text{Co}_3\text{O}_4\text{/CC}$ cathode. The above results reveal that the enhanced electrical conductivity and efficient electrocatalytic activity of the $\text{Co}_3\text{O}_4\text{-CoN/CC}$ heterostructure result in faster redox reaction kinetics due to the incorporation of CoN into Co_3O_4 nanowires.

Figure 3c draws a comparison of the rate capability based on $\text{Co}_3\text{O}_4\text{-CoN/CC}$ and $\text{Co}_3\text{O}_4\text{/CC}$ cathodes. When cycled at 0.2C, 0.5C, 1C, 3C and 5C, the $\text{Co}_3\text{O}_4\text{-CoN/CC}$ cathode can deliver impressive reversible capacities of 1379, 1225, 1015, 887 and 731 mAh g^{-1} , respectively. When the current rate is abruptly adjusted back to 0.2C again, the $\text{Co}_3\text{O}_4\text{-CoN/CC}$ cathode could still maintain a specific capacity of 1309 mAh g^{-1} , indicating the excellent high-rate tolerance ability of the $\text{Co}_3\text{O}_4\text{-CoN/CC}$ cathode. In contrast, the $\text{Co}_3\text{O}_4\text{/CC}$ cathode exhibited lower discharge capacity and poorer stability under the identical test conditions. **Figure 3d** compares the cycling performance of the $\text{Co}_3\text{O}_4\text{-CoN/CC}$ and $\text{Co}_3\text{O}_4\text{/CC}$ cathodes over 100 cycles at 0.5C. The $\text{Co}_3\text{O}_4\text{-CoN/CC}$ cathode exhibits stable cycling ability with a reversible capacity of 1165 mAh g^{-1} after 100 cycles at 0.5C, indicating the efficient suppressing of polysulfide dissolution into

the organic electrolyte in the $\text{Co}_3\text{O}_4\text{-CoN/CC}$ electrode. It is noted that there is almost no capacity contributed from the $\text{Co}_3\text{O}_4\text{-CoN/CC}$ electrode (**Figure S7**). In comparison, the $\text{Co}_3\text{O}_4\text{/CC}$ cathode exhibits relatively poor cycling stability, an initial discharge capacity of 1085 mAh g^{-1} fades quickly to 906 mAh g^{-1} after 100 cycles at 0.5C . In order to further examine the potential of the cathode for high power storage, $\text{Co}_3\text{O}_4\text{-CoN/CC}$ and $\text{Co}_3\text{O}_4\text{/CC}$ cathodes endure long-term cycling and high-rate at 3C for over 500 cycles, as shown in **Figure 3e**. The $\text{Co}_3\text{O}_4\text{-CoN/CC}$ cathode displays remarkably cycling stability with a reversible capacity of 627 mAh g^{-1} after 500 cycles at 3C . The capacity fading rate is 0.058% per cycle. However, the $\text{Co}_3\text{O}_4\text{/CC}$ cathode fades from 667 to 271 mAh g^{-1} after 500 cycles at the same current rate. Compared to the reported performance of Li-S batteries, our $\text{Co}_3\text{O}_4\text{-CoN/CC}$ electrode exhibits more attractive performance, including high discharge capacities, superior rate capability, and very stable cycling performance (as shown in **Tables S1** and **S2**). The superior electrochemical performance of the $\text{Co}_3\text{O}_4\text{-CoN/CC}$ cathode can be ascribed to the following merits. First, Co_3O_4 has a strong chemical binding for LiPSs, rendering fast trapping and high adsorption for polysulfides, which is accorded with the fundamental calculation results given below. Second, CoN with high conductivity as a polar host can instantaneously realize the fast LiPS nucleation and conversion, thus accelerating the redox reaction kinetics. Third, CoN has similar catalytic activity to that of the precious metals, which improves the redox reaction kinetics. It was reported that one electron lone pair of N atom can serve as a conductive Lewis base “catalyst” matrix to strengthen the adsorption energy of Li in Li_2S_n ($3 \leq n \leq 8$).⁴⁷ What is more, porous and

conductive $\text{Co}_3\text{O}_4\text{--CoN}$ nanowire arrays are directly supported on CC to form a freestanding binder-free 3D conductive network throughout the insulated sulfur without any additives or mechanical supporter, and hence leads to a high overall capacity for Li-S batteries. As a result, speedy LiPSs nucleation/conversion can be realized in an ideal way at the interface, thus effectively restraining the LiPS shuttling and enhancing sulfur utilization.

In order to validate the origins of the above electrochemical results of the cells using $\text{Co}_3\text{O}_4\text{--CoN/CC}$, and $\text{Co}_3\text{O}_4\text{/CC}$ cathodes, we carried out a series of characterizations via Raman, XPS, SEM and TEM. To gain insight into the shuttling mechanism of LiPSs, *in situ* micro-Raman spectroscopy is performed by characterizing the chemical state of sulfur on the separator adjacent to the lithium anode during the discharge/charge processes, which is illustrated in **Figure 4a**. **Figure 4b** shows the voltage profile of the cell in the voltage range of 1.7–2.8 V at 1C. During the discharge process, it is clearly revealed that various long-chain and mid-chain polysulfides are found for the cell using the $\text{Co}_3\text{O}_4\text{/CC}$ cathode (**Figure 4c**). At the first plateau, the peak intensity of S_8^{2-} anion is strongly highlighted by a characteristic peak at 396 cm^{-1} . With the continuous discharge, the signal of S_8^{2-} anion gradually disappears. Meanwhile, the peak at 242 cm^{-1} corresponding to Li_2S_4 appears when the voltage decreases to the ending of the first plateau. Observably, serious shuttle effect occurs for the cell using the $\text{Co}_3\text{O}_4\text{/CC}$ cathode. In contrast, *in situ* Raman spectra of the cell using the $\text{Co}_3\text{O}_4\text{--CoN/CC}$ cathode are shown in **Figure 4d**. We could clearly observe that no Raman signals of any LiPS (Li_2S_n , $3 \leq n \leq 8$) are highlighted on the time-resolved Raman image. Apparently, the

introduction of CoN into Co_3O_4 host enables effective suppression of LiPS shuttling.

The contrasting Raman spectra of the cells with the $\text{Co}_3\text{O}_4\text{-CoN/CC}$ and $\text{Co}_3\text{O}_4\text{/CC}$ cathodes indicates that the $\text{Co}_3\text{O}_4\text{-CoN/CC}$ composite host combines the merits of highly adsorptive Co_3O_4 with conducting CoN, where LiPSs are strongly trapped by Co_3O_4 and then smoothly diffused across the smooth $\text{Co}_3\text{O}_4\text{/CoN}$ interface to CoN that promotes LiPS nucleation and fast conversion into insoluble products.

Figure 4. *In situ* micro-Raman measurements of $\text{Co}_3\text{O}_4\text{-CoN/CC}$ and $\text{Co}_3\text{O}_4\text{/CC}$ electrodes during discharging: (a) Schematic illustration of Li-S configurations

with a sealed glass window for *in situ* Raman experiments. (b) Galvanostatic charge–discharge voltage profiles of Li–S cell at 1C. Raman spectra of the Li–S cell with (c) Co₃O₄/CC and (d) Co₃O₄–CoN/CC electrodes at different discharge voltages as indicated in (b). (e) Elemental XPS Co 2P spectrum of Co₃O₄–CoN/CC electrode before and after cycling.

XPS was applied to investigate the mechanism of the interaction between the Co₃O₄–CoN/CC electrode and polysulfides. The Co₃O₄–CoN/CC electrode is disassembled from Li–S batteries after discharging for two cycles at 0.2C, which is then washed with dimethyl ether (DME) to remove any residual LiTFSI. Figure 4e shows the Co 2p XPS spectra in the Co₃O₄–CoN/CC electrode before and after cycling. Before cycling, the Co spectrum shows one Co 2p_{3/2} peak at 782 eV, which is assigned to the Co–N bond. After cycling, Co 2p_{3/2} spectrum has an additional peak at 780.6 eV, indicating the presence of Co–S bond. Meanwhile, the intensity of the former peak at 782.1 eV recedes. This result corroborates the advanced anchoring capability of Co₃O₄–CoN with respect to sulfur species.

To further evaluate the electrode materials, it is essential to understand their electronic properties. Co₃O₄ has a relatively large band gap (1.0 eV) (Figure 5a), which agrees well with the previous theoretical study.^{48–50} In comparison, CoN exhibits a direct–band–gap (0.6 eV), which significantly enhancing the electronic conductivity and leading to an improved electrode reaction kinetics (Figure 5b). To demonstrate the strong affinity between different components and sulfur species, theoretical simulation based on density functional theory (DFT) method was also conducted to evaluate the binding energies between these components. The binding energies between the (111)

plane of Co_3O_4 with Li_2S_4 , Li_2S_6 , and Li_2S_8 species are calculated to be -7.81 , -7.99 and -7.67 eV, respectively (**Figure 5c**). In comparison, the binding energies between the (111) plane of CoN with Li_2S_4 , Li_2S_6 , and Li_2S_8 species are calculated to be -7.55 , -5.29 , and -6.58 eV, respectively. These values are much higher than those of Co_3O_4 , suggesting the strong interactions between Co_3O_4 and sulfur species. The most stable chemisorption model structures of sulfur species with (111) plane of CoN and Co_3O_4 are shown in **Figure 5d** and **Figure S8**, respectively.

Figure 5. Theoretical simulation of the polysulfide adsorption ability of CoN and Co_3O_4 . Band structures of (a) Co_3O_4 and (b) CoN. (c) The high binding energies indicate the stronger adsorption of Co_3O_4 with sulfur species. (d) Binding geometric configurations and binding energies of Li_2S_6 with the (111) plane of CoN.

Moreover, to experimentally confirm the strong absorption of different electrodes with sulfur species, a visual observation was conducted by immersing the Co_3O_4 -CoN/CC

and $\text{Co}_3\text{O}_4/\text{CC}$ electrode with a dimension of $2 \times 4 \text{ cm}^2$ into a solution of $0.05 \text{ M Li}_2\text{S}_6$ solution. After 12 h, the Li_2S_6 solutions containing the $\text{Co}_3\text{O}_4\text{-CoN}/\text{CC}$ electrode became colorless, similar to a solution containing $\text{Co}_3\text{O}_4/\text{CC}$ electrode (**Figure 6a**). This clearly shows the strong adsorption abilities of $\text{Co}_3\text{O}_4\text{-CoN}/\text{CC}$ and $\text{Co}_3\text{O}_4/\text{CC}$ electrodes. After cycling test, the nanowire morphology and the intact microstructure of the $\text{Co}_3\text{O}_4\text{-CoN}/\text{CC}$ electrode are well preserved after intensive cycling (**Figure 6b–c** and **Figure S9**). STEM elemental mapping was performed to track the sulfur distribution in $\text{Co}_3\text{O}_4\text{-CoN}$ nanowires after cycling. The high-angle annular dark-field STEM image and corresponding elemental maps of cobalt, oxygen, nitrogen and sulfur show that the sulfur species are uniformly distributed and strongly adsorbed on the surface of $\text{Co}_3\text{O}_4\text{-CoN}$ nanowires (**Figure 6d–h**). This result verifies the experimental observations and corresponding theoretical calculations, corroborating the advanced anchoring capability of $\text{Co}_3\text{O}_4\text{-CoN}$ with respect to sulfur species.

Figure 6. (a) Ex situ adsorption measurements (Top: from the left to right, left: pure Li_2S_6 , right: Li_2S_6 and $\text{Co}_3\text{O}_4\text{-CoN}/\text{CC}$ composites, down: from the left to right, left:

pure Li_2S_6 , right: Li_2S_6 and $\text{Co}_3\text{O}_4/\text{CC}$ composites). (b)–(c) SEM images of $\text{Co}_3\text{O}_4\text{--CoN/CC}$ electrode after 100 cycles, indicating the good integrity of the electrode after long-term cycling. (d) STEM image of one $\text{Co}_3\text{O}_4\text{--CoN}$ nanowire after cycling with the corresponding elemental maps of (e) cobalt, (f) oxygen, (g) nitrogen and (h) sulfur.

4. CONCLUSIONS

In summary, we have developed a facile and efficient method to *in situ* construct a hetero-phase $\text{Co}_3\text{O}_4\text{--CoN}$ sulfur host that boosts the overall performance of sulfur cathodes. Such a binary host combines the merits of ultrafast anchoring (Co_3O_4) with high conducting (CoN) to accomplish highly-efficient immobilization–diffusion–conversion of LiPSs, thereby greatly suppressing the polysulfide shuttling, promoting the redox kinetics, and hence boosting the electrochemical performance of Li–S batteries. The assembled cathode based on $\text{Co}_3\text{O}_4\text{--CoN/CC}$ electrode exhibits a high initial capacity of 1225 mAh g^{-1} at 0.5C with excellent rate capability (887 mAh g^{-1} at 3C), and the specific capacity can be well-maintained to 627 mAh g^{-1} at 3C even after 500 cycles, much better than other counterparts ($\text{Co}_3\text{O}_4/\text{CC}$ and CC). This *in situ* construction strategy of hetero-phased functional materials provides conceptually novel opportunities for Li–S cathode designs. Considering versatile sulfur hosts, it is undoubtful that optimized interface engineering to regulate charge transfer and LiPS conversion would further improve the electrochemical performance of Li–S batteries. We believe that our work not only can shed more light into the rational design of comprehensive host materials for high performance Li–S batteries, but also would hold great application potential in portable electronics and implantable devices.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

Structures and morphologies of Co(OH)F nanowire arrays precursor and Co₃O₄-CoN nanowire arrays, CV curves, peak voltages, onset potentials, galvanostatic charge-discharge voltage profiles and nyquist plots of Co₃O₄-CoN/CC and Co₃O₄/CC electrodes, electrochemical performances of the Co₃O₄-CoN/CC composite without Li₂S₆ catholyte, morphology of Co₃O₄-CoN/CC and Co₃O₄/CC electrodes after cycling.

Notes

The authors declare no competing financial interest.

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Conflict of Interest

The authors declare no conflict of interest.

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Table of Contents Graphic

We present an *in situ* plasma construction of hetero-phase $\text{Co}_3\text{O}_4\text{-CoN}$ sulfur host combining the merits of efficient polysulfide anchoring (Co_3O_4) with high conductivity (CoN) to realize simultaneous immobilization–diffusion–conversion of lithium polysulfides.