Multifunctional Co$_3$S$_4$@sulfur nanotubes for enhanced lithium-sulfur battery performance

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ABSTRACT

Lithium sulfur batteries attract the increasing attentions because of the high energy density. However, sulfur cathodes suffer from several scientific and technical issues which are related to polysulfide ion migration, low conductivity, and volume changes. Many strategies such as porous hosts, polysulfide adsorbsents, catalyst, and conductive fillers and so on have been proposed to address these issues, separately. In this study, novel Co$_3$S$_4$ nanotubes are developed to efficiently host sulfur, adsorb polysulfides, and catalyze their conversion. Because of these multifunctional advantages in one structure, the resulting Co$_3$S$_4$@S nanotube electrodes demonstrate superior electrochemical properties for high performance lithium sulfur batteries.

1. Introduction

Lithium-sulfur (Li-S) batteries are receiving great attentions because of their high theoretical energy density (~2600 Wh kg$^{-1}$) [1,2], low cost, environmental friendliness, and natural abundance of sulfur resources [3–6]. Although Li-S batteries have many advantages, they suffer from several scientific and technical issues, which impede the practical implementation [7]. First, sulfur is an insulator with a very low conductivity of only 5×10$^{-8}$ S m$^{-1}$ [8], which limits the sulfur utilization and reduces the rate capability of Li-S batteries [9]. Second, the “shuttle effect” caused by polysulfides dissolution and diffusion decreases the specific capacity and Coulombic efficiency [10–15]. Third, the volume changes during sulfur lithiation/delithiation may damage the cathode structure and lower cycling performance of Li-S batteries [16].

Recently, nanostructured carbons, such as meso/micro-porous carbons [17,18], hollow carbon spheres [19,20], graphene [21–23], carbon nanotubes [24–26], and nanofibers [27,28], have been proposed to host sulfur materials. Because carbon is able to provide a rapid electron pathway and hollow structures physically trap polysulfides, the resulting carbon/sulfur composites prolong the cycle lives and increase the deliverable capacities [29]. However, carbon matrix is repellent to the polysulfides. During long-term cycling, sulfur species detach from the carbon matrix [30,31]. The weak interaction between polysulfide species and carbon matrix raises the charge transfer resistance and reduces the redox kinetics of polysulfides [32–34]. Recently, it was reported that heteroatom doped carbon provides the abundant adsorption sites and strong chemisorption of polysulfides to address the issues [35]. Ti$_4$O$_7$ [30], NiFe$_2$O$_4$ [36], TiO$_2$ [37], MnO$_2$ [38], Ti$_x$O$_{2n-1}$ and some other metal oxides [39,40], demonstrated the strong affinity to polysulfides and the high capacity retention when used in the cathodes of Li-S batteries. However, these metal oxides usually have relatively low electronic conductivity which reduces the electrode kinetics. To explore more conductive polysulfide adsorbsents, the research attentions have been turned to transition metal sulfides because some of them usually have the relatively high electronic conductivity. As the absorbent and conducting phase, the sulfides must first have high bulk conductivity to facilitate charge transports through the interfaces and electrodes. More importantly, a continuous electronic network is necessary to improve the overall electrode conductivity. Fiber or whisker-like morphology has a low percolation threshold to form a continuous conducting network. Thus, the conductive absorbents with high aspect ratios and hollow structures are highly desired for sulfur cathodes.

Since the charged and discharged products of sulfur are insoluble in the non-aqueous electrolytes and only the soluble polysulfide intermediates are mobile between cathodes and anodes, a rapid and catalytic conversion of sulfur species may have the same consequence as suppressing the shuttle effects and confining the sulfides inside cathodes by using hollow hosts. Nickel sulfide prepared by ball milling

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nickel and sulfur were first found to be catalytic for Li-S redox reactions [41]. Pt, Al, Ni, metal oxides, and heteratom-doped carbon have been explored to catalyze the Li-S redox reactions [42–47]. To further enhance the conversion kinetics of redox shuttles by electrocatalysts, the polysulfide anions must at best be chemically entrapped by the functional groups of catalyst materials and physically confined by structured hosts.

Recent reports about sulfides absorbents found that cobalt sulfides (CoS2 and Co9S8) have the strong affinity to sulfur species [48,49]. Especially, CoS2 exhibits the good catalytic properties for the sulfur species conversion [48,50,51]. There are five intermediate phases (Co4S3±y, Co1−yS, Co3S4, and CoS2) in the Co-S binary systems [52]. Co4S3±y and Co1−yS are stable only at high temperatures. CoS2 (6.7×105 S m−1) [53] and Co3S4 (3.3×105 S m−1) [54] have much higher conductivity than Co9S8 (1.36 S m−1) [55]. Earlier research reported that Co3S4 has 2–3 times the electrocatalytic capability of CoS2 for oxygen reduction reactions [56]. Co3S4 has not been studied for catalyzing the conversion of sulfur species which is in the same group as oxygen in the periodic table. It intrigues us to tentatively explore what influences the catalytic, morphologic, and conducting properties of spinel Co3S4 have on Li-S batteries.

In this contribution, we developed a facile route to produce Co3S4@S nanotubes for high-performance Li-S batteries. As shown in Fig. 1a, the catalytic, morphologic, and conducting properties of polysulfide adsorbents/hosts are considered together to enhance the electrochemical properties of Li-S batteries. Nanostructured Co3S4 aims to absorb and catalyze the sulfur species by the relatively large surface area. The nanotube morphology helps to host sulfur species. The metallic conductivity of Co3S4 accelerates the kinetics. Due to these designs, the Co3S4@S nanotubes cathode is able to deliver a capacity of 1267 mA h g−1 AS (active sulfur basis) at 0.05 C. It shows a slow capacity decay rate of 0.041% per cycle through 1000 cycles, which significantly improves the electrochemical properties of Li-S batteries.

2. Experimental section

2.1. Synthesis of Co3S4 nanotubes

All the chemicals were purchased from Sinopharm Chemical Reagent Corporation and used without further purification. About 4 mmol of CoCl2·6H2O and 20 mmol of CO(NH2)2 were dissolved in 50 mL deionized water. The solution obtained was transferred to a Teflon-lined stainless-steel autoclave and heated at 95 °C for 8 h. After cooling down to room temperature, the precursor precipitates were filtered, rinsed, and dried in vacuum. The dry powder (~0.072 g) obtained was added into 1 M thioacetamide solution (40 mL). After hydrothermally treated at 200 °C for 12 h, the black precipitates in the autoclave were filtered, washed, and dried under vacuum at 50 °C for 2 h.

2.2. Synthesis of Co3S4 nanotubes and sulfur composite

The Co3S4@S nanotube composite was prepared via a simple melt-diffusion method. The mixture of sulfur and Co3S4 nanotubes was heated at 155 °C for 10 h in a sealed vessel. The composite electrodes with the varied mass ratios of sulfur and Co3S4 nanotubes were prepared and characterized for comparison.

2.3. Synthesis of Co3S4 nanoparticles

In a typical synthesis, 20 mmol Co(NO3)2·6H2O and 6 mmol NaOH were slowly dissolved in 60 mL deionized water under stirring. After the suspension was formed, about 4 mmol thioacetamide was dissolved into the solution under vigorous stirring for 30 min. The turbid solution obtained was transferred to a Teflon-lined stainless-steel autoclave and heated at 200 °C for 12 h. After cooling down naturally to room temperature, the precipitates were filtered, washed, and dried.

2.4. Materials characterization

X-ray diffraction (XRD) patterns of all samples were collected by a Rigaku D/Max III with Cu Kα radiation. The morphology observation was conducted within a Zeiss Ultra 55 field-emission scanning electron microscope (SEM). X-ray photoelectron spectra (XPS) were recorded on an ESCALab MKII X-ray photoelectron spectrometer with Mg Kα X-ray as the excitation source. The binding energies in XPS analysis were calibrated by C 1 s at 284.6 eV. Transmission electron microscope (TEM), high-resolution TEM (HRTEM) images, and energy dispersive

Fig. 1. Schematic illustration of (a) a Li-S battery with “shuttle effect” and a Co3S4@S nanotube composite to minimize the issues of polysulfides; (b) the fabrication procedure of Co3S4@S nanotubes.
X-ray (EDX) spectra were recorded on an FEI Tecnai F20 microscope at 200 kV. The amount of sulfur in the cathode was determined by a thermogravimetric analyzer (TGA, NETZSCH 209 F1 Libra) from room temperature to 600 °C in a nitrogen flow at a heating rate of 10 °C min⁻¹. N₂ adsorption measurements were performed on a Quantachrome Autosorb-iQ-2C-TCD-VP analyzer at 77 K using Barrett-Emmett-Teller (BET) calculations for surface area.

For the visualized adsorption characterization, a LiS₄ solution was synthesized by adding Li₂S and sulfur with a molar ratio of 1:3 in dimethyl ether (DME) under stirring according to literature [38]. The obtained solution containing about 1.4 mg mL⁻¹ LiS₄ was used for the sulfide adsorption test. CoS₄ and acetylene black (AB) were added into 10.0 mL of LiS₄/DME solutions, respectively. The mixtures were adequately stirred for 0.5 h for adsorption test.

2.5. Electrochemical measurements

The sulfur cathodes were fabricated by slurry casting a mixture of 80 wt% active materials, 10 wt% AB, and 10 wt% polyvinylidene fluoride (PVDF) binder on Al foil. The sulfur loading was around 2–4 mg cm⁻². The obtained laminate was dried in vacuum at 50 °C. The CoS₄@S cathode was assembled with lithium into coin cells in an Ar-filled glove box. The electrolyte used was 1.0 M bis(trifluoromethane)sulfonimide lithium (LiTFSI) and 0.1 M LiNO₃ with the 1:1 vol ratio of 1,3-dioxolane (DOL) and DME. About 40 μL electrolyte was added for each coin cell. Galvanostatic charge/discharge was carried out between 1.6 and 2.6 V using a Land Battery Tester. Cyclic voltammograms (CVs) were measured by a VSP potentiostat (Bio-Logic Corp).

For symmetrical cells, the electrodes used contain no elemental sulfur. AB or CoS₄ were dispersed together with PVDF in N-methyl pyrrolidone (NMP) with a weight ratio of 8:2. The slurry was cast on Al foil and dried in vacuum at 50 °C. The obtained laminates were used as the identical working and counter electrodes. The electrolyte contained 1.6 and 2.6 V using a Land Battery Tester. Cyclic voltammograms (CVs) were measured by a VSP potentiostat (Bio-Logic Corp).

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The EDX spectrum exhibits the element distribution of Co and S along the nanotube walls. The Co:S ratios for these three samples are 1:3, 1:1, and 3:1, respectively. The areal loading of these three samples is around 2 mg cm⁻². The TGA plots in Fig. 2h indicate that CoS₄-S2, CoS₄-S3, and CoS₄-S4 have the elemental sulfur of 64.4, 74.2, and 79.3 wt%, respectively. Their XRD patterns (Fig. 2g) show the typical combination of elemental sulfur and CoS₄.

The interactions between CoS₄ and polysulfides (Li₂S₄, n=4, 6, 8, see in Fig. S1) are studied by the first-principle calculations based on the density functional theory (DFT). The calculation details are presented in the Supporting information (SI). The binding energy (Eₛ) of polysulfides on the substrate is defined as Eₛ=Eₛ₄+Eₚₑ₋Eₛ₄₋ₚₑ, where Eₛ₄, Eₚₑ, and Eₛ₄₋ₚₑ represent the ground-state energies of the substrate, polysulfides, and substrate-polysulfide (Fig. 3a) [30,48]. Fig. 3b and Table S1 show that the binding energies of Li₂S₄, Li₂S₆, and Li₂S₈ on CoS₄ are 1.61–2.76 eV, which are higher than those on graphitic carbon (0.42–0.58 eV). The first principle calculation explains the strong adsorption between polysulfides and CoS₄. To further evaluate the interaction between CoS₄ and polysulfides, the as-synthesized CoS₄ nanotubes were added into a 1,2-dimethoxyethane solution containing 1.4 mg mL⁻¹ LiS₄. In the optical photo of Fig. 3d, the original yellow-brown solution turned transparent, indicating the strong adsorption. By contrast, the solution with adding the same amount of acetylene black was still yellow-brown.

Fig. 3c presents the X-ray photoelectron spectroscopy (XPS) data of pure CoS₄ and the CoS₄/LiS₄ precipitates, which were separated from the adsorption experiments in Fig. 3d. The Co 2p₁/₂ spectrum of pure CoS₄ has a broad peak consisting of two components of 779.3 and 780.8 eV, which correspond to CoO²⁻ and Co²⁺ [57–59]. For the CoS₄/LiS₄ precipitates, the Co 2p₁/₂ peak shifts towards higher binding energy and pronounced satellite indicate that the electron transfer from LiS₄ molecules to Co [48,49,60]. Generally, both experimental and theoretical studies indicate that CoS₄ has the strong affinity to LiS₄ and as an effective sulphide host, may minimize the diffusion issues of polysulfide ions for Li-S batteries [61–63].

The electrochemical properties of CoS₄@S nanotube composites were characterized with lithium as the counter electrode in coin cells. Fig. 4a shows that the galvanostatic charge/discharge curves of CoS₄-S3 have two plateaus. The first plateau voltage range is 2.2–2.9 V, which is due to the reduction of long-order polysulfides to insoluble Li₂S₄ or Li₂S [64]. The second plateau voltage range is 2.5–2.8 V which is attributed to the oxidation of Li₂S₄ and Li₂S₆ phase to LiS₄ (x > 2). The second charging plateau at 2.35–2.4 V represents the oxidation from polysulfides to sulfur [65]. CoS₄-S3 in the first cycle delivers a specific capacity of 1158 mAh g⁻¹ AS (0.25 C) with a Coulombic efficiency of 96.0%, which gradually increases to 100% in next 10 cycles.

To determine what capacity CoS₄ could provide, a cell with CoS₄ as the cathode is characterized in Fig. 4b, which shows that CoS₄ has nearly no capacity between 1.9 and 2.6 V. Its specific capacity (< 80 mAh g⁻¹) below 1.9 V is almost negligible as compared to that of sulfur.

It is well known that CoS₄ has a particularly high conductivity [54], which may help to decrease the resistance of electron conduction and transfer. By contrast to the widely-used AB conductive agent, CoS₄ has the good affinity to polysulfides, yielding the close contact between polysulfides and conduction pathway. The good conductivity and affinity to polysulfides facilitate the electron conduction and transfer. Previous theoretical and experimental studies have demonstrated that the nanotube morphology is conducive to the formation of electron and ion transportation. The good conductivity and affinity to polysulfides and conduction pathway are established by the first principle calculation and experimental data.

Fig. 4b presents the charge/discharge curves of the sulfur electrode, which delivers an initial capacity of 1032 mAh g⁻¹ AS at 0.1 C. Its Coulombic efficiency is 89.1% in the first cycle. A rapid capacity decay occurs in next few cycles. The polarization (ΔE) of CoS₄-S3 at a half capacity is around 0.18 V, which is lower than that of sulfur (0.22 V).
Fig. 2. SEM and TEM images of (a–b) Co(CO$_3$)$_{0.35}$Cl$_{0.20}$(OH)$_{1.10}$ intermediate precipitates, (c–d) Co$_3$S$_4$ nanotubes, and (e–f) Co$_3$S$_4$/sulfur composite (Co$_3$S$_4$:S3). The inset in (d) is the HRTEM image of Co$_3$S$_4$ nanotube walls. The plots in (d–f) are EDX element Co and S distribution along the diameters of Co$_3$S$_4$. (g) XRD patterns of intermediate precipitates, Co$_3$S$_4$, elemental sulfur, and Co$_3$S$_4$@S composite. (h) TGA curves of three Co$_3$S$_4$@S samples.

Fig. 3. (a) Typical binding geometries and energies of three polysulfide molecules (Li$_2$S$_4$, Li$_2$S$_6$, Li$_2$S$_8$) on Co$_3$S$_4$ (111) surface. (b) Binding energies of polysulfides anchored on different Co$_3$S$_4$ surfaces. (c) High-resolution XPS spectra of Co 2p$_{3/2}$ of the pristine Co$_3$S$_4$ and the Co$_3$S$_4$ powder separated from the adsorption test. (d) Optical photo of Li$_2$S$_4$ adsorption on AB and pristine Co$_3$S$_4$. 
Fig. 4. Charge/discharge curves of (a) Co$_3$S$_4$-S3 and (b) sulfur electrodes. (c) CV curves of Co$_3$S$_4$-S3 and sulfur electrodes. (d) Charge/discharge curves of Co$_3$S$_4$-S3 at varied C rates (S loadings: 2 mg cm$^{-2}$).

Fig. 5. (a) Nyquist plots of sulfur and Co$_3$S$_4$@S nanotube electrodes at open circuit voltage. (b) Rate capability and (c) cycling properties (0.5 C) of sulfur and Co$_3$S$_4$@S electrodes. (d) The capacity comparison of different samples on different bases. (e) Cycling properties of the Co$_3$S$_4$-S3 electrode at 5 C.
their spec.

By contrast, the sulfur electrode could only retain a capacity of ~239 mA h g−1 AS at 4 C. These results indicate the good rate capability of Co3S4-S composites. More importantly, when the C rate returns to 0.1 C, the Co3S4@S nanotube electrodes are able to recover more deliverable capacities than the sulfur electrode. The large capacity gap at 0.1 C is observed between the cycled Co3S4@S composites and sulfur electrodes. The specific capacities of the four electrodes do not return to the initial values of 0.1 C. There are more irreversible processes inside the sulfur electrode than the Co3S4@S composites. These irreversible processes may reduce the long term cycling stability of the sulfur electrode without Co3S4. During the galvanostatic cycling, the sulfur and Co3S4@S nanotube electrodes show relatively high initial capacities at 0.5 C and slight capacity decays in the first 10 cycles as shown in Fig. 5c. Their Coulombic efficiencies gradually increase to ~100% in the first 10 cycles. After 20 cycles, the Co3S4@S composites deliver relatively stable capacities. In contrast, the sulfur electrode still exhibits the obvious capacity decay.

The battery characterization requires the studies on the materials, electrode, cell, and battery levels [76]. The specific capacity based on the sulfur mass partly reveals the utilization ratio of active sulfur. It does not include the mass of conductive agents and binders. For a practical sulfur cathode, the electrode-based capacity is usually important to compare the real performance of different electrode configurations. Fig. 5d summarizes the specific capacities of the four electrodes at the initial and 100th cycles on active sulfur and total electrode bases (the electrode basis includes the mass of active sulfur, Co3S4 nanotubes, conductive agents, and binders), respectively. It can be seen that Co3S4 nanotubes are able to concurrently improve the electrode-based capacity and cyclability.

The long-term cycling performance in Fig. 5e demonstrates that the Co3S4@S composite has a superior cyclability with an initial capacity of 517 mA h g−1 AS at 5 C and a low capacity fading rate of 0.041% per cycle. After 1000 cycles, it remains a specific capacity of 305 mA h g−1 AS, which corresponds to 59% of its initial value. When the areal loading of sulfur increases to ~4 mg cm−2, the Co3S4@S composite also exhibits high capacity and cyclability as shown in Fig. S4. The good cyclability may be attributed to the Co3S4 nanotubes because they are able to effectively conduct electrons and adsorb polysulfides.
Meanwhile, the high affinity of sulfur species to Co$_3$S$_4$ enables uniform distribution on the inner and outer surface of Co$_3$S$_4$ nanotubes. The uniform coating decreases kinetic resistances of Li-ion diffusion and improves the cycling properties of Co$_3$S$_4$@S composite electrodes. Table S3 shows the comparison of performance with other polar materials in Li-S batteries.

The polysulfides adsorption is proportional to the surface area of Co$_3$S$_4$ nanotubes. The BET measurements reveal that Co$_3$S$_4$ nanotubes have only a surface area of 31 m$^2$ g$^{-1}$ (Fig. S5), which is not enough to adsorb all sulfur species. To explore what factors further enhance the electrochemical properties of Co$_3$S$_4$@S nanotube electrodes, a symmetric cell (Fig. 6a) using Co$_3$S$_4$ nanotube electrodes is constructed with or without adding Li$_2$S$_6$ in the electrolyte, respectively. Fig. 6b presents the chronoamperometry curves of Co$_3$S$_4$ and AB symmetrical cells. With adding Li$_2$S$_6$ in the electrolyte, both the Co$_3$S$_4$ and AB cells show much higher current response than cells without Li$_2$S$_6$. It implies that the lithiation/delithiation reactions dominate the current responses instead of double-layer capacitance. The EIS spectra in Fig. 6c show that the reaction semicircle of the Co$_3$S$_4$ cell has a much smaller diameter than that of the AB cell. According to Zhang and Li's reports [48,72,77], the reduced charge transfer resistance (R$_{ct}$) of symmetric Co$_3$S$_4$ cell represents the enhanced electrode reaction kinetics [78]. Similarly, the CV curves in Fig. 6d show that the Co$_3$S$_4$ cell has the high current responses as compared to the AB cell in Li$_2$S$_6$-containing electrolyte. It indicates that Co$_3$S$_4$ not only absorbs sulfur species, but also accelerates the electrochemical conversion of polysulfides.[48,72]. The results obtained from the symmetric cells lead us to conclude that the Co$_3$S$_4$ nanotubes enhance the kinetics of the lithiation/delithiation reaction of polysulfides. In conjunction with the polysulfide affinity and conductivity enhancement of Co$_3$S$_4$, the catalytic effect further explains why the Co$_3$S$_4$ nanotubes electrodes have the high specific capacity and good rate and cycling properties.

Both the polysulfide adsorption and catalytic kinetic enhancement are related to the surface area of Co$_3$S$_4$. To improve the electrochemical properties of sulfur cathodes, nanostructuring Co$_3$S$_4$ is an easy approach to obtaining the high surface area. However, nanostructured Co$_3$S$_4$ may have the varied morphologies which influence the electron conductivity of sulfur/Co$_3$S$_4$ composite cathodes. It is well known that the conductivity of composite electrodes can be described by $\sigma = \sigma_a * (f-f_c)^{\tau}$, where $\sigma_a$ is the conductivity of conductive agents (Co$_3$S$_4$ or AB), $\tau$ is the critical exponent for conductivity, $f$ is the ratio of conductive agents, and $f_c$ is the percolation threshold [79]. Fig. 7a and b show that Co$_3$S$_4$ nanotubes have the relatively lower percolation threshold than Co$_3$S$_4$ nanoparticles (Fig. S6) on the bases of either weight or volume fractions because the large aspect ratio of nanotubes readily forms a conducting network (as shown in Fig. S7). Fig. 7a shows that AB has the lowest percolation threshold on the weight basis. However, AB requires the higher volume fraction to form the percolation network because of its particulate morphology and much lower density than Co$_3$S$_4$ as shown in Fig. 7b. In view of the high catalytic capability of Co$_3$S$_4$ and low density of AB, it is suggested that the combination of Co$_3$S$_4$ nanotubes and AB may serve to enhance the electrochemical properties of sulfur composite cathodes as illustrated in Fig. S8.

The overall performance of Li-S batteries is sensitive to the ratio of sulfur to inactive components. High S loading is always desired for practical applications. As for three issues which Li-S batteries face (S insulator, shuttle effects, and volume changes), the concepts of using hollow hosts, catalysis, conductive agents, and adsorbents have been proposed to address each issue respectively in previous reports [23,49,80,81]. Our tentative study shows that it is advantageous to combine these approaches into one structure of Co$_3$S$_4$ nanotubes, which realized the S ratio of 79.3 wt% and the S loading of up to 4 mg cm$^{-2}$. The approach of making multifunctional nanotube catalysts with the conducting and absorbing capabilities provides more opportunities to further improve the high-performance Li-S batteries.

4. Conclusions

We have proposed the use of multifunctional Co$_3$S$_4$ nanotubes as sulfur host with a high sulfur loading and good electrochemical properties. Due to the high electron conductivity and polysulfide affinity of Co$_3$S$_4$, the specific capacity and rate capabilities of Co$_3$S$_4$@S nanotube electrodes are significantly improved. The high affinity between Co$_3$S$_4$ and polysulfides minimize the polysulfide ions dissolution and increase the cyclability of the sulfur composite electrodes. In addition, Co$_3$S$_4$ nanotubes can also enhance the redox kinetics of polysulfides. More importantly, the multifunctional nanotubes help to form effective conductive networks. An optimized Co$_3$S$_4$@S nanotube electrode is able to deliver a capacity of 1267 mA h g$^{-1}$ AS at 0.05 C and show a low capacity decay rate of 0.041% per cycle at 5 C. Even after 1000 cycles, it still remains a specific capacity of 305 mA h g$^{-1}$ AS. Generally, we demonstrate a multifunctional Co$_3$S$_4$@S nanotubes composite which enables a Li-S battery with high capacity, good rate capabilities, and cycling properties.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.nanoen.2017.05.009.