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A conductive polymer derived N-doped carbon nanofiber supported Li₂S coating layer for Li–S batteries with high mass loading

Abstract

© 2020 Elsevier B.V. The commercialization of Li₂S as a potential candidate for lithium-sulfur cathode material is hampered due to its low electronic conductivity, the “shuttle effect” and the initial energy barrier. In this work, nanosized Li₂S particles coated carbon nanofibers are prepared via a solution-based chemical method. Benefiting from this synthetic method, a uniform Li₂S layer can be obtained without any agglomeration. Due to the small size of Li₂S particles, a smaller energy barrier is observed in the first charging process, which means it is easier to activate the Li₂S with a smaller cut-off voltage. In addition, the carbon nanofibers as matrixes could enhance the conductivity of cathode. Moreover, to verify the potential practical application of prepared materials, Li₂S cathodes with high loading amount of active materials (~3 mg cm⁻²) are prepared, which show excellent cycling and rate performance, delivering an initial specific capacity of 916.2 mA h g⁻¹ at 0.1C, and 321 mA h g⁻¹ capacity still can be reached at 2 C. This good performance can be attributed to the unique solution-based synthesis method, resulting in small and uniform Li₂S particles coated on carbon nanofibers.

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1 **A Conductive Polymer Derived N-doped Carbon Nanofiber Supported Li₂S Coating**
2 **Layer for Li-S Batteries with High Mass Loading**

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1 **Abstract**

2 The commercialization of Li_2S as a potential candidate for lithium-sulfur cathode material is
3 hampered due to its low electronic conductivity, the “shuttle effect” and the initial energy
4 barrier. In this work, nanosized Li_2S particles coated carbon nanofibers are prepared *via* a
5 solution-based chemical method. Benefiting from this synthetic method, a uniform Li_2S layer
6 can be obtained without any agglomeration. Due to the small size of Li_2S particles, a smaller
7 energy barrier is observed in the first charging process, which means it is easier to activate the
8 Li_2S with a smaller cut-off voltage. In addition, the carbon nanofibers as matrixes could
9 enhance the conductivity of cathode. Moreover, to verify the potential practical application of
10 prepared materials, Li_2S cathodes with high loading amount of active materials ($\sim 3 \text{ mg cm}^{-2}$)
11 are prepared, which show excellent cycling and rate performance, delivering an initial specific
12 capacity of $916.2 \text{ mA h g}^{-1}$ at 0.1 C , and 321 mA h g^{-1} capacity still can be reached at 2 C . This
13 good performance can be attributed to the unique solution-based synthesis method, resulting in
14 small and uniform Li_2S particles coated on carbon nanofibers.

15

16 **Keywords:** nitrogen-doped carbon nanofiber, Li_2S cathode, high mass loading, uniform
17 distribution, Li-S batteries.

1 **1. Introduction**

2 Lithium-sulfur (Li-S) batteries are promising power sources for portable devices and electric
3 vehicles owing to their high specific capacity (1675 mAh g⁻¹) and energy density (2600 Wh
4 kg⁻¹), as well as the low-cost of sulfur element.¹⁻⁴ However, the commercialization of Li-S
5 batteries has been hampered by their innate nature, such as the insulating property of sulfur and
6 Li₂S, the dissolved intermediate products and the large volume changes (80%) during cycling,
7 which could lead to low utilization rate of active material and fast capacity fading.⁵⁻⁷ Compared
8 with sulfur, when lithium sulfide (Li₂S) was applied as cathode, the anode materials can use
9 lithium-free materials,^{8,9} such as silicon, tin, carbon, etc., relieving the safety problems related
10 to lithium anode. Moreover, the Li₂S undergoes volume shrinkage in the initial charge
11 process,¹⁰⁻¹² which could release some voids to buffer the volume expansion, endowing the
12 cathode materials with structural integrity during cycling.

13 Like S cathode, the Li₂S also has been facing many difficulties during its commercialization
14 process,¹³⁻¹⁵ such as insulating nature and the dissolved polysulfides, leading to low capacity
15 and poor cycling stability. In addition, there is an activation energy barrier that needs to be
16 overcome in the first charge process for the Li₂S cathode.¹⁴ To deal with these obstacles,
17 electrolyte modification, including exploring solid-state electrolyte¹⁶⁻¹⁸ and introducing
18 additives¹⁹⁻²¹ (lithium nitrate, lithium iodide, transition-metal salts, etc.), has successfully
19 relieved the shuttle effect, thus improving the long-term cycle performance of Li₂S cathode. In
20 addition, great attention has been paid to synthesize nanosized Li₂S,²²⁻²⁵ because the nanosized
21 Li₂S usually possess a smaller activation energy barrier and faster reaction kinetics with higher
22 specific capacity than the usual commercial Li₂S.²⁶

23 At present, there are two commonly used methods to synthesize Li₂S nanoparticles due to its
24 moisture sensitivity. One method is to ball mill large particles of Li₂S, which are commercially

1 available, with conductive additives; another method is to react Li_2SO_4 with carbon precursor
2 at high-temperature ($\sim 900\text{ }^\circ\text{C}$). Although the synthesized $\text{Li}_2\text{S-C}$ composites also showed
3 promising electrochemical performance, both these methods have their own drawbacks: the
4 ball-milling method directly uses commercial Li_2S particles combined with a conductive agent,
5 which is expensive for the large-scale commercialization of Li_2S cathode; and the high-
6 temperature method requires complicated facilities and procedures, which are not suited to
7 large-scale production. In addition, with the solid-state reaction methods, it is usually hard to
8 achieve a uniform Li_2S particle distribution on conductive agents. Given all these
9 considerations, solution-based synthetic methods usually can yield small size and uniform
10 particle distributions compared with the above-mentioned methods.²⁷ For example, Li_2S
11 spheres with a uniform size of $0.5\text{ }\mu\text{m}$ can be synthesized by the solution-based chemical
12 lithiation of S;²⁸ some other advanced Li_2S -carbon composites, including carbon nanotube
13 (CNT)- Li_2S , graphene- Li_2S , and C- Li_2S have been obtained by the simple infiltration of Li_2S -
14 ethanol solutions,^{29, 30} which all showed a uniform distribution of Li_2S nanoparticles in these
15 composites. Therefore, it is necessary to find a facile method to synthesize nanosized Li_2S and
16 realize the uniform distribution of Li_2S on conductive matrices simultaneously.

17 To improve the cycling performance of Li_2S cathode, the Li_2S particles should be combined
18 with some kinds of conductive materials (e.g. carbonaceous materials, polymer composites or
19 conductive metal-based materials) to physically or chemically trap the polysulfides.³¹⁻³⁷
20 Among them, heteroatom-doped carbon materials have been drawn much attention due to the
21 relative strong chemical bond between heteroatom functional groups and polysulfides, which
22 could effectively trap the dissolved polysulfides.³⁸⁻⁴⁰ For example, Yu's group designed a
23 nitrogen and phosphorus co-doped carbon framework to support Li_2S nanoparticles for Li-S
24 batteries,²⁵ which indicated that the doped nitrogen and phosphorus in the carbon could
25 mitigate the "shuttle effect" because the heteroatoms could chemically bonded with the

1 polysulfides, leading to stable cycling capability. Meanwhile, heteroatom maybe help to
2 catalyze the conversion of Li_2S into polysulfides and vice versa, improving the reaction kinetics
3 and rate capability. Therefore, using chemical adsorbents to trap dissolved polysulfides is
4 essential to obtain advanced Li_2S cathodes.

5 In this paper, a facile and solution-based synthetic method was designed to prepare Li_2S
6 nanoparticles, which coated on the N-doped carbon nanofibers derived from polypyrrole. Due
7 to the solution-based procedures, the Li_2S layer was uniformly coated on the carbon framework
8 without any aggregation. The small-sized Li_2S possesses relatively lower activation barriers
9 and could shorten the lithium-ion diffusion distance, resulting in fast kinetics for the reactions
10 and high specific capacity. In addition, using the N-doped carbon nanofiber as the matrix could
11 efficiently enhance the conductivity of cathode and trap soluble polysulfides, thus improving
12 the utilization of Li_2S . Moreover, Li_2S electrode with $\sim 3 \text{ mg cm}^{-2}$ loading amount was also
13 obtained, which deliver high capacity (705 mA h g^{-1} at 0.2 C) and good cycling stability (479.3
14 mA h g^{-1} can be achieved after 200 cycles at 0.2 C).

15 **2. Experimental sections**

16 2.1 Preparation of N-doped carbon (N-C) nanofibers

17 The N-C nanofibers were synthesized by thermal treatment of polypyrrole (PPy) nanofibers,
18 which was prepared *via* a chemical oxidative polymerization process, which is detailed
19 discussed in our previous paper.⁴¹ The prepared PPy nanofibers were heated at $600 \text{ }^\circ\text{C}$ for 2 h
20 under Ar atmosphere with a heating rate of $5 \text{ }^\circ\text{C min}^{-1}$ to get the N-C nanofibers.

21 2.2 Synthesis of sulfur coated N-C nanofibers (S@N-C)

22 15 mg N-C nanofiber was added into 1 mL toluene solution containing 30 mg sulfur at $60 \text{ }^\circ\text{C}$,
23 and then the raw S/N-C nanofiber was obtained after evaporating the toluene at $80 \text{ }^\circ\text{C}$ for 10

1 hours. To realize the uniform dispersion of S on the N-doped carbon nanofibers, the raw S/N-
2 C nanofibers were sealed and reacted at 155 °C for 10 hours in an autoclave.

3 2.3 Synthesis of lithium sulfide coated N-C nanofibers (Li₂S@N-C)

4 50 mg of the obtained S@N-C nanofibers and a certain amount of n-Butyllithium was put into
5 a small vial with a cap and then heated to 110 °C for 4 h. After that, the obtained black powders
6 were the Li₂S coated N-C nanofibers (denoted as Li₂S@N-C). Since the Li₂S was very sensitive
7 to moisture, the whole process was conducted in a glovebox filled with argon and the content
8 of H₂O and O₂ both < 0.1 ppm.

9 2.4 Physical Characterizations

10 X-ray diffraction (XRD, GBC MMA 017) were conducted to know the crystalline structure of
11 prepared samples with a 2θ range from 10° to 80°. The field emission scanning electron
12 microscopy (JEOL: FESEM-7500) and transmission electron microscopy (TEM, JEM-
13 2100UHR, JEOL) were used to investigate the morphologies of the prepared composites. Due
14 to the sensitive nature of Li₂S, the loading amount of Li₂S on N-doped carbon nanofibers was
15 calculated by the amount of sulfur on N-C nanofibers. The loading amount of sulfur on the N-
16 C nanofibers can be measured by Thermogravimetric analysis (TGA) using a SETARAM
17 instrument in argon atmosphere.

18 2.5 Electrochemical measurements

19 The electrochemical performance of the Li₂S@N-C composite was investigated using 2032
20 coin cells, which were assembled in a glovebox with the contents of H₂O and O₂ < 0.1 ppm.
21 For preparing the Li₂S@N-C electrode, 80 wt% Li₂S@N-C hybrid, 10 wt% carbon black and
22 10 wt% poly(vinylidene fluoride) (PVDF) binder were mixed in N-methyl-2-pyrrolidinone
23 (NMP) solvent to get a slurry, which was spread on the Al foil disks using a doctor blade. The

1 obtained electrodes were dried in glovebox for overnight at 60 °C. The pure Li₂S electrode was
2 also prepared using the same method, which contains 55 % commercial Li₂S, 35 % carbon
3 black and 10 % PVDF. The commercial Li₂S and carbon black were purchased from Sigma-
4 Aldrich with purity both > 99.95 %. The SEM images of Li₂S and carbon black are shown in
5 Figure S2. The mass loading of Li₂S on the electrodes could be adjusted from 1 to 3 mg cm⁻²
6 by repeating the spread method. 1 M lithium bis(trifluoromethane sulfonyl)imide (LiTFSI) in
7 1,3-dioxolane (DOL)/1,2-dimethoxyethane (DME) (1:1 by volume) with 0.1 M LiNO₃ as
8 additive was used as electrolyte. The cyclic voltammetry (CV) profiles were conducted using
9 a Biologic VMP3 electrochemical workstation between 1.7 V and 2.8 V with a scan rate of
10 0.05 mV s⁻¹. The cycling and rate performance were obtained in a LAND battery test system
11 at different C rates (1 C = 1166 mA g⁻¹) between 1.7 V and 2.8 V.

12 **3. Results and Discussion**

13 The preparation illustration for the Li₂S@N-C nanofibers is shown in **Figure 1**. First, the PPy
14 nanofibers were prepared via a polymerization method.⁴¹ Then, the N-doped carbon nanofibers
15 were obtained by a thermal treatment of PPy nanofibers at 600 °C for 2 h. After that, the sulfur
16 layer was coated on the N-doped carbon nanofibers by simple evaporation of S-toluene solution
17 followed by vacuum redistribution. Finally, the S@N-C nanofiber was lithiated by n-
18 Butyllithium at 110 °C for 4 h in a glove box to obtain Li₂S@N-C nanofibers.

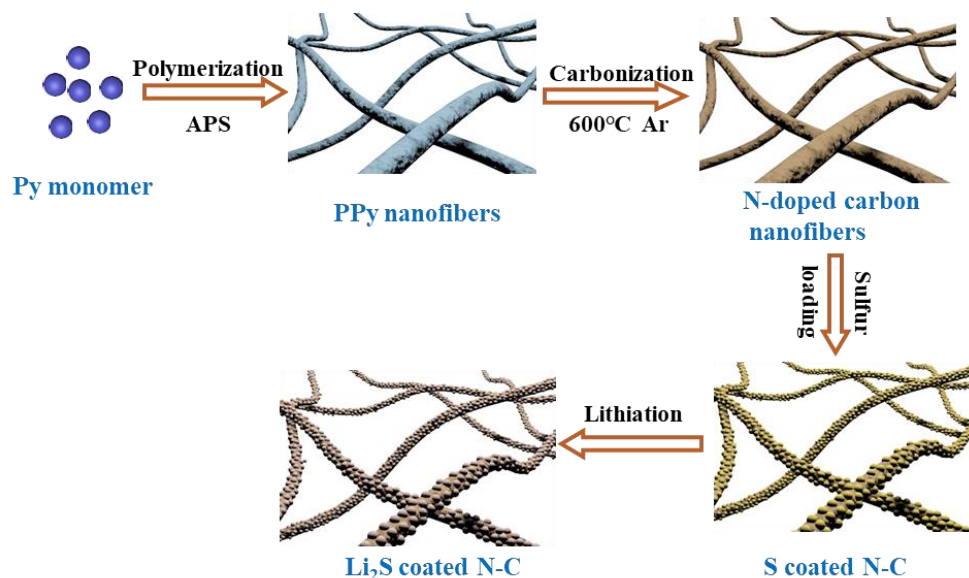
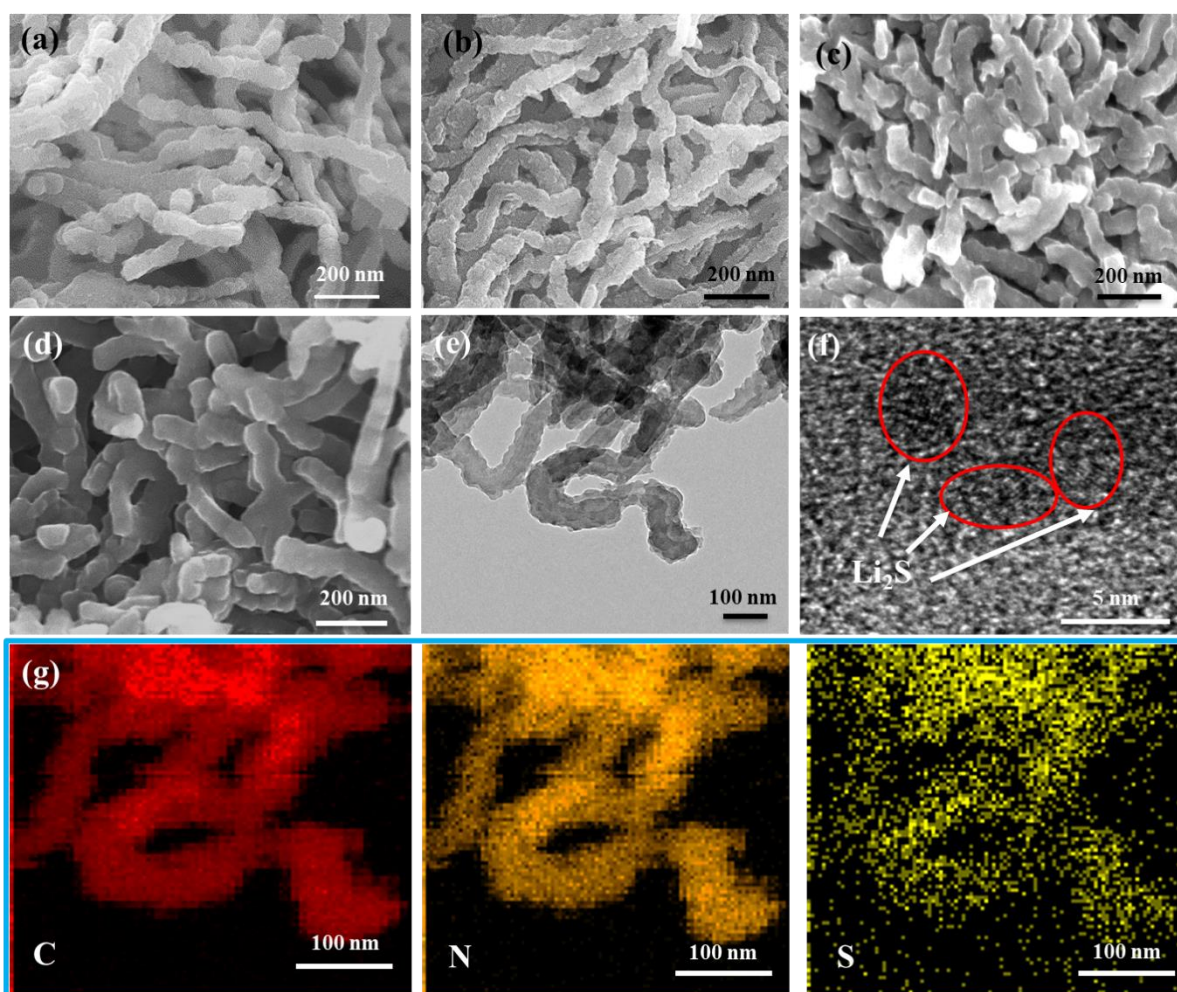


Figure 1. Schematic illustration of the preparation of the $\text{Li}_2\text{S}@\text{N-C}$ nanofibers.

1
2
3
4 Field emission scanning electron microscope (FESEM) images were used to investigate the
5 morphologies of the synthesized composites. **Figure 2a** shows the SEM images of the obtained
6 PPy nanofibers with a diameter of about 70 nm. After the thermal treatment, the N-doped
7 carbon nanofibers preserve the original morphology of the PPy nanofibers, but the surfaces of
8 the N-doped carbon nanofibers become rougher, because during the high-temperature process,
9 the PPy nanofiber could release lots of gas and generate many pores, obtaining a porous
10 structure (Figure 2b), which can be able to increase the surface area to load sulfur feasibly. The
11 $\text{S}@\text{N-C}$ nanofiber composite still maintains this original nanofiber morphology after S loading,
12 but a smooth surface instead of the rough one was observed, indicating an S layer coated on
13 the N-C nanofibers (Figure 2c). Figure 2d shows SEM images of $\text{Li}_2\text{S}@\text{N-C}$ nanofibers, which
14 show the same morphology as the $\text{S}@\text{N-C}$ nanofibers, and there is no obvious agglomeration
15 of nanoparticles, indicating the uniform distribution of Li_2S on the surfaces of the N-C
16 nanofibers. The structural characterization of the $\text{Li}_2\text{S}@\text{N-C}$ nanofibers was also determined
17 by the Transmission electron microscopy (TEM) images. As shown in Figure 2e, the $\text{Li}_2\text{S}@\text{N-}$

1 C nanofibers maintain the fibrous structure of the S@N-C nanofibers, which is consistent with
2 the SEM image (Figure 2d). High-Resolution TEM (HRTEM) reveals that Li_2S nanoparticles
3 show a very small size (less than 5 nm), which are tightly embedded in the N-doped porous
4 carbon nanofibers. The corresponding elemental maps further confirm the carbon, nitrogen,
5 and sulfur elements were homogeneous distribution in the Li_2S @N-C nanofibers (Figure 2g),
6 indicating the uniform distribution of Li_2S on the N-C nanofibers.



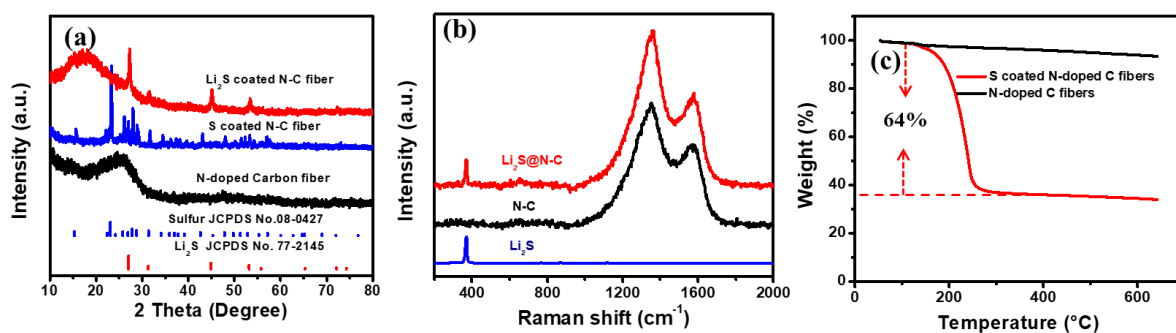
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8 **Figure 2.** SEM images of (a) PPy nanofibers, (b) N-doped carbon nanofibers, (c) S@N-C
9 nanofibers, and (d) Li_2S @N-C nanofibers, (e) TEM and (f) HRTEM images of Li_2S @N-C
10 nanofibers, and (g) corresponding element mapping.

11

1 X-ray diffraction (XRD) patterns were used to confirm the crystalline structures of the prepared
 2 composites, as shown in **Figure 3a**. The N-doped carbon nanofibers possess an amorphous
 3 structure by showing a broad peak between 20-30°. And the pronounced peaks in the S@N-C
 4 sample belongs to the orthorhombic sulfur (JCPDS card No: 08-0427). After reaction with n-
 5 Butyllithium, sulfur is converted into cubic phase Li₂S (JCPDS card No. 77-2145). No sulfur
 6 residual and other crystal impurity were observed, indicating the complete conversion of sulfur
 7 to Li₂S. Raman spectroscopy was applied to further prove the successful synthesis of Li₂S in
 8 the composite, as shown in Figure 3b. For pure Li₂S, the peak located at 372 cm⁻¹ is related to
 9 the T_{2g} phonon mode of Li₂S, representing the Li-S bond vibrations.^{33, 42} The N-C nanofibers
 10 show two peaks at around 1355 cm⁻¹ and 1597 cm⁻¹, which is related to the D band and the G
 11 band, respectively.⁴³ The Raman spectrum of the Li₂S@N-C nanofibers shows the
 12 characteristic peaks of both Li₂S and N-doped carbon, indicating the successful loading of Li₂S
 13 on N-C nanofibers, which is consistent with the results of element mapping (Figure 2g). The
 14 amount of sulfur coated on the S@N-C composite was investigated by the Thermogravimetric
 15 analysis (TGA) in pure argon atmospheres. Because the Li₂S was obtained from the lithiation
 16 of sulfur, the content of Li₂S coated on the N-C nanofibers can be calculated from the content
 17 of sulfur. As shown in Figure 3c, the sulfur in the S@N-C composites is 64%, which means
 18 that the Li₂S amount coated on the surface of N-C nanofibers is 68%.

19



20

1 Figure 3. (a) XRD patterns of prepared N-doped carbon nanofibers, S@N-C nanofibers, and
2 Li₂S@N-C nanofibers; (b) Raman spectra of commercial Li₂S, N-doped carbon nanofibers,
3 and Li₂S@N-C nanofibers; (c) TGA curves of N-doped carbon nanofibers, S@N-C nanofibers
4 in Ar atmosphere.

5

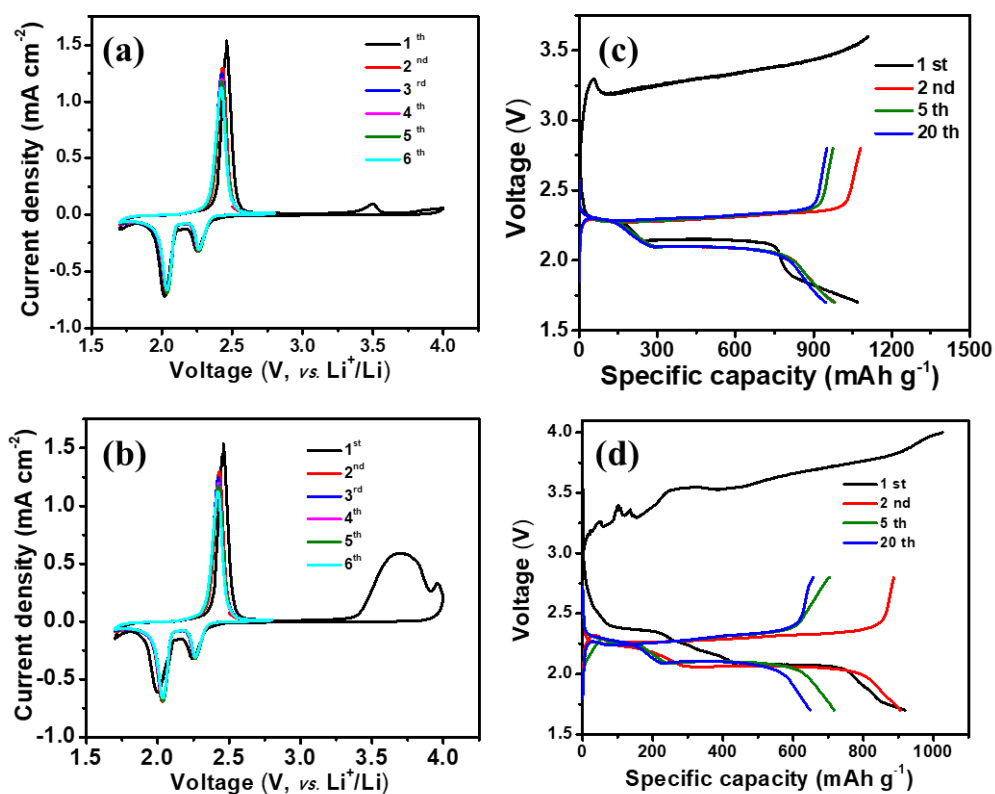
6 The electrochemical performances of the synthesized Li₂S@N-C hybrid and commercial Li₂S
7 particles were first investigated by cyclic voltammetry (CV) measurements, which were shown
8 in **Figure 4a** and b. Due to the energy barrier in the first charging process, the electrodes were
9 first activated by charging to 4 V.¹⁵ From Figure 4a and b, the Li₂S@N-C and pure Li₂S
10 electrodes both show one typical anodic peak and two typical cathodic peaks. The first
11 reduction peak located at ~ 2.3 V can be ascribed to the conversion of sulfur to long-chain
12 polysulfides (Li₂S_n, 2 < n ≤ 8), which is soluble in the electrolyte and results in “shuttle” effect.
13 Then the long-chain polysulfides will be further reduced to lithium sulfides (Li₂S₂/Li₂S), which
14 is revealed by the second cathodic peak located at around 2.0 V. The peak at around 2.5 V in
15 the oxidation process represents the conversion of Li₂S to Li₂S_n (2 < n ≤ 8), and finally to S.⁴⁴
16 The Li₂S@N-C electrode shows an additional small oxidation peak at ~ 3.5 V in the initial
17 charging process, however, which is related to the energy barrier needed to activate the Li₂S
18 cathode. The pure Li₂S electrode also shows a broad peak at 3.7 V in the initial charging process,
19 as shown in Figure 4b, which is located at higher voltage position than that of the Li₂S@N-C
20 electrode, indicating that the potential barrier of Li₂S@N-C electrode is lower than that of pure
21 Li₂S electrode, owing to the small size and uniform distribution of the prepared Li₂S particles
22 on the N-C nanofibers.^{15, 45} After the first activation, these electrodes both can normally work
23 in the following cycles just like sulfur cathode, which means that the Li₂S electrode was
24 successfully activated by the high cut-off voltage.

25 The charge-discharge profiles of Li₂S@N-C and pure Li₂S electrodes are also shown in Figure
26 4c and d. For the Li₂S@N-C electrode, the cut-off voltage was set to 3.6 V, while for the pure

1 Li₂S electrode, the cut-off voltage was set to 4 V. As we can see, in the first charging process,
2 the voltage rapidly increased and then decreased, followed by a gradual increase to the cut-off
3 voltage. The voltage increase at the beginning is known as the energy barrier of Li₂S.⁴⁶ The
4 energy barrier of Li₂S@N-C electrode is slightly lower than that of the pure Li₂S electrode.
5 After activation, the charge-discharge profiles of Li₂S@N-C and pure Li₂S electrode both show
6 two discharge plateaus, relating to the reduction of sulfur to long-chain lithium polysulfides,
7 and then to the lithium sulfides (Li₂S₂/Li₂S). The discharge plateaus are long and flat, indicating
8 a stable out-put power can be achieved. In the charging process, there is one plateau, which
9 was related to the reversible reaction from Li₂S to sulfur. These results are all consistent with
10 the CV results. The above results indicate that a cut-off voltage of 3.6 V is enough for Li₂S@N-
11 C electrode to activate Li₂S due to the small size and uniform distribution of the as-prepared
12 Li₂S. The activation voltage of this work compared with some related papers, which is listed
13 at Table S1. The activation voltage of 3.6 V is smaller than most of that of published works.

14 The cycling performance of Li₂S@N-C and pure Li₂S electrode with Li₂S mass loading of 1
15 mg cm⁻² are also compared in **Figure 6a**. The electrode was firstly cycled for 10 cycles at 0.1
16 C to fully activate the Li₂S, and then cycled at 0.2 C. The Li₂S@N-C electrode shows a much
17 higher specific capacity than that of pure Li₂S electrode in the whole cycling process. The pure
18 Li₂S electrode delivered an initial discharge capacity of 1017.3 mA h g⁻¹ at 0.1 C and decreased
19 to 550.5 mA h g⁻¹ after 20 cycles at 0.2 C, showing a fast capacity fading. Compared to pure
20 Li₂S electrode, the Li₂S@N-C electrode experiences a more stable cycling capability,
21 delivering an initial specific capacity of 1036.6 mA h g⁻¹ at 0.1 C and maintaining at a capacity
22 of 704.2 mA h g⁻¹ after 200 cycles. The results of this work compared with some reported
23 literatures, which is listed in Table S2. The prepared Li₂S@N-C materials show better
24 electrochemical performance than many related Li₂S composites. From the above results, the
25 cycling capability of Li₂S@N-C electrode is visibly enhanced compared with the pure Li₂S

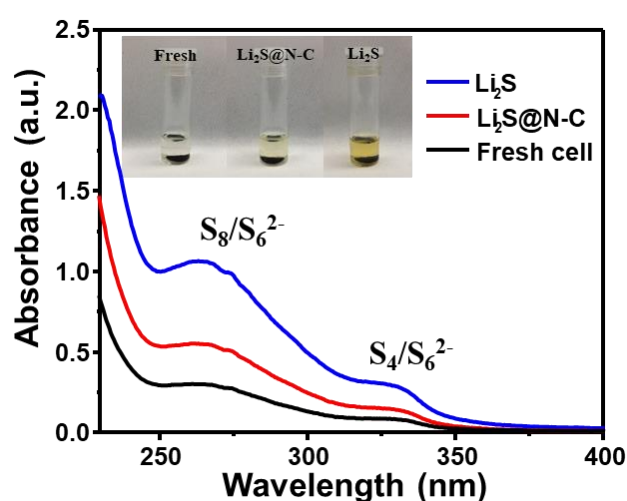
1 electrode, suggesting that the N-C nanofibers could efficiently adsorb lithium polysulfides,
2 mitigating the shuttle effect of intermediate products. In addition, the small size and uniform
3 distribution of Li_2S particles could improve the utilization of Li_2S .



4
5 **Figure 4.** CV profiles of (a) $\text{Li}_2\text{S}@N\text{-C}$ and (b) pure Li_2S at 0.05 mV s^{-1} ; Charge-discharge
6 profiles of (c) $\text{Li}_2\text{S}@N\text{-C}$ and (d) pure Li_2S electrodes at different current densities.

7
8 To investigate the effect of prepared electrode on trapping polysulfides during the cycling
9 process, the cycled $\text{Li}_2\text{S}@N\text{-C}$ and pure Li_2S electrodes at a fully charged stage were
10 disassembled after 50 cycles. The cycled electrodes were put into a dioxolane/dimethoxyethane
11 (DOL/DME) ($v/v = 1:1$) solvent for 12 h. Then, ultraviolet-visible (UV-vis) spectroscopy is
12 conducted to measure the amount of soluble polysulfides dissolved in the electrodes. After 12
13 h soak, the colour of DOL/DME solutions with different cycled electrodes were shown in the
14 inset of **Figure 5** using digital photographs. The colour of DOL/DME solutions with cycled

1 Li₂S@N-C electrode is lighter yellow, while the colour of DOL/DME solutions with cycled
 2 pure Li₂S electrode is dark yellow, indicating less polysulfides were dissolved into electrolyte
 3 in the Li₂S@N-C electrode. The UV-vis absorption spectra of the above-mentioned solutions
 4 were shown in Figure 5. The adsorption peak of Li₂S@N-C electrode is lower than that of the
 5 pure Li₂S electrode, indicating the Li₂S@N-C electrode could efficiently anchor the
 6 polysulfides and reduce their dissolution compared with that of pure Li₂S electrode, resulting
 7 a high utilization rate of active materials and stable cycling performance.

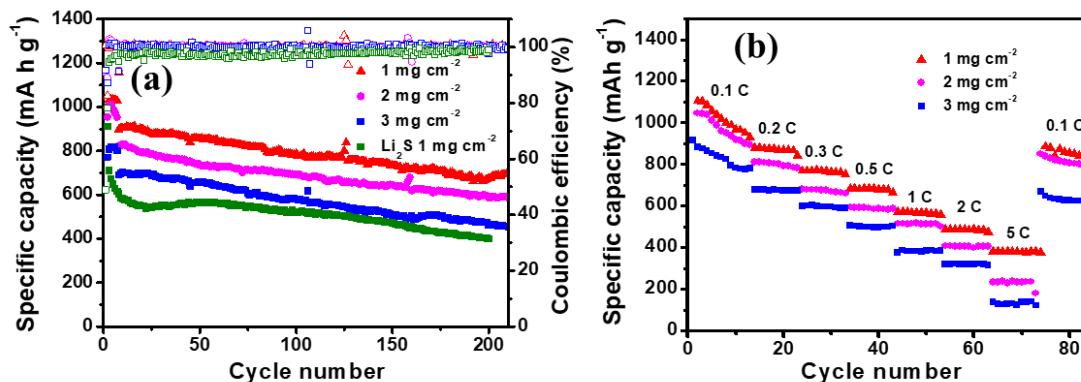


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9 **Figure 5.** UV/vis absorption spectra of DOL/DME solutions exposed to cycled Li₂S@N-C and
 10 pure Li₂S electrodes after 50 cycles, with the inset showing the colour of the solutions exposed
 11 to different electrodes.

12 For practical application, the large loading mass of active materials is very important. The
 13 Li₂S@N-C cathodes with different loading mass of 1, 2, and 3 mg cm⁻² were evaluated, as
 14 shown in **Figure 6a**. The electrodes were first fully activated for 10 cycles at 0.1 C, and then
 15 cycled for 200 cycles at 0.2 C. As we can see, the specific capacities are decreasing with
 16 increasing Li₂S loading. The Li₂S@N-C composite with a mass loading of 1 mg cm⁻² delivers
 17 the highest initial specific discharge capacity of 1036.6 mA h g⁻¹ at 0.2 C, and after 200 cycles
 18 a high capacity of 704.2 mA h g⁻¹ is still maintained. The Li₂S@N-C composites with a mass
 19 loading of 2 mg cm⁻² and 3 mg cm⁻² also show a discharge capacity of 602.5 mA h g⁻¹ and

1 479.3 mA h g⁻¹, respectively, after 200 cycles. These results indicate that the thick electrode
2 could prevent the rapid transfer of electrons into/from the active materials and reduce the
3 utilization of Li₂S (**Figure S1**). Nevertheless, the Li₂S@N-C electrode with 3 mg cm⁻² active
4 materials still shows higher specific capacity than the pure Li₂S with 1 mg cm⁻² active materials,
5 which can be ascribed to the small size and uniform distribution of our prepared Li₂S particles
6 and the conductive N-C nanofibers, which both are beneficial to the fast electrons transport and
7 enhance the use ratio of Li₂S. The rate capability of the Li₂S@N-C composites with different
8 mass loading is shown in Figure 6b. The Li₂S@N-C composite with 1 mg cm⁻² mass loading
9 shows the highest capacities at all current density, which delivers a specific discharge capacity
10 of 1106.4, 880.3, 769.6, 683.9, 571.4, and 489.3 mA h g⁻¹ at 0.1 C, 0.2 C, 0.3 C, 0.5 C, 1 C, and
11 2 C, respectively. Even at a high current density of 5 C, the specific capacity still can reach
12 380.4 mA h g⁻¹. And when the current density was suddenly recovered back to 0.1 C, a
13 discharge capacity of 887.5 mA h g⁻¹ still obtained. In comparison, the Li₂S@N-C composite
14 with 2 mg cm⁻² mass loading can deliver a specific discharge capacity of 233 mA h g⁻¹ at 5 C.
15 And the Li₂S@N-C composite with 3 mg cm⁻² mass loading shows capacities of 916.2, 677,
16 598.1, 505.4, 376.8, 321 and 139 mA h g⁻¹ at 0.1 C, 0.2 C, 0.3 C, 0.5 C, 1 C, 2 C, and 5 C,
17 respectively. The Li₂S@N-C electrode with high mass loading shows excellent cycling and
18 rate performance, which can be ascribed to the following reasons: First, the small size of Li₂S
19 prepared by the solution-based method could possess a small energy barrier in the first charging
20 process, which is easier to activate and improves the utilization; Second, the N-doped carbon
21 could improve the conductivity of electrode and enhance the utilization of active materials.



1

2 **Figure 6.** (a) Cycling performance and (b) rate capability of different electrodes with different
 3 mass loading of active materials.

4 **4. Conclusion**

5 In summary, a facile solution-based chemical method has been reported for the preparation of
 6 $\text{Li}_2\text{S}@N\text{-C}$ composites. Compared with the solid-based method and thermal treatment method,
 7 the solution-based method could yield small-sized Li_2S particles and a uniform distribution of
 8 them on the matrix without agglomeration, which could enhance the contact between the N-C
 9 nanofibers and the Li_2S particles. The N-doped carbon nanofiber matrix derived from PPy
 10 nanofibers could enhance the electrical conductivity of electrode and improve the utilization of
 11 Li_2S . In addition, a $\text{Li}_2\text{S}@N\text{-C}$ electrode with a 3 mg cm^{-2} loading amount was prepared to
 12 show the potential for practical application of our prepared samples, and it delivered high
 13 specific capacity of $916.2 \text{ mA h g}^{-1}$ and 321 mA h g^{-1} at 0.1 and 2 C, which is both higher than
 14 that of pure Li_2S electrode with a 1 mg cm^{-2} loading amount. The excellent cycling stability
 15 and rate capability can be ascribed to small size and uniform distribution of Li_2S particles on
 16 the N-doped carbon nanofibers. This work is likely to be helpful and offer new insight into the
 17 preparation of nanosized Li_2S composites as a high-performing Li-S cathode material with high
 18 active material loading.

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