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1. Introduction

In recent years, because of their lighter weight, longer life, and higher capacity compared to other rechargeable batteries, lithium-ion batteries have been extensively used as the primary electrical energy storage device in various portable electronics.¹ However, the present energy densities of such batteries are reaching their limit, making it difficult to meet the everincreasing demand of key markets, such as electric vehicles, in the long term. Therefore the search for the next generation batteries with a high energy density and lower cost is urgent. Because of the high theoretical energy density (2567 W h Kg⁻¹) and specific capacity (S: 1675 mA h g⁻¹), competitive cost and environmental benignity, lithium–sulfur (Li–S) batteries have been widely considered as an appealing candidate for the next



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The current investigation of lithium-sulfur (Li-S) batteries faces three practical problems: (1) the poor conductivity of sulfur; (2) the notorious shuttle mechanism; and (3) the volume variation of the sulfur cathode. In principle, carbon nanotubes (CNTs) have a strong potential for improving sulfur usage because of their high electrical conductivity. Furthermore, opening holes in CNTs or creating pores on the walls is also a useful approach to not only enhance the diffusion of Li ions, but also enable more sulfur to fill the interior of the CNTs, which would be beneficial in retaining the soluble poly-sulfide intermediates and accommodate volume variations. Herein, we designed a mild one-step oxidation approach to create porous CNTs (PCNTs) through a chemical reaction between CNTs and rare oxygen sourced from a nebulized water stream at high temperatures. The higher specific surface area and pore volume values confirmed that PCNTs had significant porosity, compared with raw CNTs. When the PCNTs-S composites were tested as cathode materials in Li-S batteries, the cathode with 78 wt% S content exhibited an initial reversible capacity of 1382 mA h q^{-1} at 0.2 C. Furthermore, a reversible capacity of 150 mA h g⁻¹ can be preserved, even at a very high current rate of 15 C. More importantly, it is also confirmed that a cathode with 89 wt% S content unexpectedly delivered a reversible capacity as high as 1165 mA h g^{-1}_{sulfur} /830 mA h $g^{-1}_{electrode}$ at the initial cycle, and 792 mA h g^{-1}_{sulfur} /564 mA h $g^{-1}_{electrode}$ after 200 cycles at a current rate of 0.2 C. To the best of our knowledge, such a high rate performance (15 C) and S loading (89 wt%) in cathodes of advanced Li-S batteries have been infrequently reported in previous research.

generation of large-scale and high-energy storage devices.^{2,3} However, the current investigation of Li–S batteries still faces three practical problems: (1) the intrinsic poor electronic conductivity of sulfur; (2) the high solubility of the poly-sulfide reaction intermediates (Li₂S_n, 4 < n < 8) and their notorious shuttle mechanism in organic electrolytes; and (3) the volume variation of the sulfur cathode during cycling.^{4,5}

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To overcome these critical issues, one popular approach is to confine the sulfur in a multifunctional carbon matrix, which would improve the electrical conductivity of the S cathode, trap the soluble poly-sulfide intermediates, and accommodate the volume variation of the S cathode. Recently, many types of carbon materials, such as ordered mesoporous carbon,6 hierarchical porous carbon,7 hollow carbon spheres,4,5,8 and graphene⁹ have been developed as the confining/conductive medium and have produced improved performances in Li-S battery applications. However, the synthesis of these carbon materials or carbon-sulfur composites typically involves a high cost and extensive procedures involving multiple surface coatings followed by the partial dissolution of S,⁷ or the use of corrosive acids to remove templates.5 Obviously, these complex designs and fabrication processes are ill-suited for the largescale practical applications of Li-S batteries. With the rapid

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progress in industrial mass production and commercialization of carbon nanotubes (CNTs),¹⁰ the incorporation of S into CNTs for advanced Li-S batteries may be one of the more promising options. Furthermore, in principle, CNTs have a strong potential for improving sulfur usage and restraining the solubility of lithium poly-sulfides because of their high degree of graphitization, electrical conductivity, and excellent mechanical properties.11 Recently, some researchers have attempted to fabricate CNTs-S cathodes that achieve high specific capacities exceeding 1200 mA h g^{-1} corresponding to the initial charging capacity.^{12,13} However, the relatively high decay rates and low sulfur loading and content in these CNTs-S cathodes remain tricky problems. These problems may originate from the relatively low specific surface area (SSA) (<250 m² g⁻¹) and specific pore volume (V_T) (<1 cm³ g⁻¹) of the common CNTs, as well as the weak interface bonding between S and the CNT matrix, thus limiting the capturing of sulfur and retaining of soluble polysulfides. Opening holes in CNTs or creating pores on the walls is an ideal approach to further increase the SSA and $V_{\rm T}$ of CNTs. Furthermore, porous walls will not only enhance the diffusion of Li⁺ in the electrolyte, but also enable more sulfur to fill the interior of the CNTs, which would be beneficial in retaining the soluble poly-sulfide intermediates and accommodate volume variations. Although some recent treatments involving chemical oxidation using strong acid or alkali, or electron irradiation, to create pores in CNTs have been confirmed,^{15,16} the structural integrity and high electrical conductivity of the nanotubes cannot be retained, owing to the harsh reaction conditions. Therefore, for advanced Li-S batteries, a milder oxidation treatment is highly desired to make CNTs porous, while retaining their structure and electrical conductivity.

It is well known that water is a natural green solvent. When water is heated to approximately 1000 °C, a small percentage is separated into oxygen and hydrogen. Inspired by this fact, we designed a mild one-step oxidation approach to create porous CNTs (PCNTs) through the chemical reaction between CNTs and the rare oxygen sourced from nebulized water stream at high temperatures. Higher SSA and $V_{\rm T}$ values confirmed that CNTs etched by water steam had significant porosity compared with raw CNTs. The milder method holds several advantages: (1) the pore size was easy to control, (2) the structural integrity and high electrical conductivity of the CNTs were retained, (3) no rudimental outgrowths were developed, and (4) oxygencontaining groups in PCNTs were introduced in abundance. When the etched PCNTs-S composites were tested as a cathode material in Li-S batteries, the cathode exhibited a high reversible capacity, excellent rate performance, and good cycle stability. The simplicity, greenness, and scalability of this method means a potential boost in the near future to produce PCNTs with high SSA and $V_{\rm T}$ for real applications in advanced Li-S batteries.

2. Results and discussion

The preparation of the etched PCNTs is illustrated in Fig. 1. In a typical procedure, water is first nebulized to create a mist of droplets. The droplets formed are then passed into a quartz



Fig. 1 Schematic of the synthesis process of the PCNTs.

tube of raw commercial CNTs using an Ar-carrying gas when the desired temperature of 850 °C is reached. The final product is then collected from the quartz tube. The morphological structures of the obtained PCNTs samples (Fig. 2a and S1⁺) were observed by transmission electron microscopy (TEM), which reveals that the 850PCNTs exhibit abundant lattice defects and the outer shell and surface appear irregular and rough compared with the raw CNTs. Fig. 2b shows the nitrogen sorption isotherm of the as-prepared PCNTs; the isotherm feature hysteresis between desorption and adsorption branches indicating the presence of mesopores.¹⁷ Along with SSA and $V_{\rm T}$, the mesopore volume (V_{Meso}) and micropore volume (V_{Micro}) of these PCNT samples etched at various temperatures are summarized in Table 1; the $V_{\rm T}$ and SSA values of these PCNTs have significantly increased compared with the raw CNT values. This result, coupled with the TEM observations, strongly confirmed that CNTs can be etched by water steam at high temperatures (750-950 °C). It is speculated that the increase of SSA and pore volume of these etched PCNTs may be due to opening some closed structure in the inner cavity of CNTs or creating some pores on the walls.



Fig. 2 (a) Typical TEM images of the 850PCNTs; (b) nitrogen sorption isotherms of various PCNTs and raw CNTs; (c and d) pore size distribution of various PCNTs and raw CNTs.

Table 1 Textural properties of the raw CNT and PCNT samples

Samples	Temperature (°C)	Time (min)	$\frac{\text{SSA}^a}{(\text{m}^2 \text{ g}^{-1})}$	$V_{\rm T}^{\ b} ({ m cm}^3 { m g}^{-1})$	$\frac{\mathrm{V_{Meso}}^{c}}{\mathrm{(cm^{3}g^{-1})}}$	${\operatorname{V_{Micro}}^{d}}{\left(\operatorname{cm}^{3}\operatorname{g}^{-1} ight)}$	Average pore ^e (width per nm)
RAW CNTs			255.3	0.81	0.799	0.011	12.7
750PCNTs	750	10	315.7	1.28	1.273	0.007	16.3
800PCNTs	800	10	349.1	1.56	1.559	0.011	18.3
850PCNTs-1	850	3	320.5	1.31	1.369	0.009	16.7
850PCNTs-2	850	5	341.5	1.52	1.51	0.010	18.0
850PCNTs	850	10	367.2	1.68	1.669	0.011	18.6
850PCNTs-3	850	20	401.9	1.97	1.961	0.009	18.9
A-850PCNTs	850	10^{f}	367.0	1.62	1.614	0.006	18.2
900PCNTs	900	10	421.1	2.10	2.092	0.011	19.2
950PCNTs	950	10	431.2	2.16	2.159	0.011	19.5

^{*a*} Specific surface area. ^{*b*} Total pore volume. ^{*c*} Mesopore volume. ^{*d*} Micropore volume. ^{*e*} Average pore size (estimated from the equation of $4V_{T/}$ SBET). ^{*f*} Etched for 10min and annealed for 1 h in argon.

A clear understanding of the porosity can be deduced through the pore size distribution (PSD) analysis derived from the Barrett-Joyner-Halenda method. The typical PSD curves in Fig. 2c and d clearly show the variation in mesopore size (2-10 nm) for these CNTs before and after water etching, whereas Table 1 shows that there is little variation in the micropore volume in $V_{\rm T}$, and the variation in $V_{\rm Meso}$ is dominant in these PCNTs. This data indicates that the mild etching reaction on CNTs mainly occurred at the mesopore (2-10 nm) scale. Furthermore, from Table 1, SSA and $V_{\rm T}$ are found to gradually increase as the etching temperature changes from 750 to 950 °C. For the 950PCNTs, the SSA and $V_{\rm T}$ are 431.2 m² g⁻¹ and 2.16 cm³ g^{-1} , which are much larger than that of the raw CNTs with 255 $m^2\ g^{-1}$ and 0.81 $cm^3\ g^{-1}.$ With the temperature fixed at 850 °C, the SSA and $V_{\rm T}$ also increase with extending the etching times. These results suggest that both the etching temperature and time should be critical factors in this mild oxidation reaction. It is believed that the SSA, $V_{\rm T}$, and pore-size distribution for these PCNTs can be controlled by changing these factors.

To clarify whether the PCNTs maintain their intrinsic tubular structures during water etching, measurements from wide-angle-powder X-ray diffractometry (XRD) (Fig. S2a[†]) and Raman spectroscopy (Fig. S2b[†]) were obtained. From Fig. S2a,[†] all of the PCNTs display two similar peaks (43.4° and 26.2° corresponding to the (100) and (002) planes, respectively) as for the CNTs. In Fig. S2b,[†] the intensity ratio I_D/I_G is increased stepwise with increasing the etching temperature. However, this variation occurred in a small scale (*i.e.*, varying from 1.27 to 1.49), which suggests that the water etching only produces a small amount of damage and the intrinsic structure of the CNTs is largely reserved.

In principle, the large SSA and $V_{\rm T}$ are acceptable in maintaining excellent electrical properties for these PCNTs, thereby rendering them as a promising electrode material for energy storage. The performance of the PCNTs was evaluated as a sulfur host for Li–S batteries. Typically, the 850PCNT–S nanocomposites (850PCNT–S) are prepared using a melt-diffusion process at 160 °C. After loading with 78 wt% S (Fig. 3a), no bulk S particles can be found from the scanning electron microscope (SEM) and TEM images (Fig. 3b and c, and S3a–d†). The corresponding elemental maps (Fig. S3e–g†) and the line-scan analysis of the hybrids (Fig. 3e) demonstrate a uniform distribution of S onto the PCNTs. Furthermore, from the high-resolution TEM images in Fig. 3d, S can be observed to have permeated into the interior of the 850PCNTs. In Fig. 3f, no characteristic XRD peaks of the pure S phase can be detected in



Fig. 3 (a) TGA curve of the 850PCNT–S composites. Typical SEM (b), TEM (c), HRTEM (d) and line scan analysis (e, the black and red lines in the inset are C and S, respectively) images for the 850PCNT–S composite. (f) X-ray diffraction curves of S, 850PCNTs and 850PCNTs–S composite.

the 850PCNT–S nanocomposites, which also indicates a uniform distribution of S particles with a small size in the composite cathode. Furthermore, from Fig. S4a and b,† the 850PCNTs were found to possess a high SSA of 367.2 m² g⁻¹ and large $V_{\rm T}$ of 1.68 cm³ g⁻¹, which reduced to 5.4 m² g⁻¹ and 0.017 cm³ g⁻¹, respectively, after the incorporation of S, indicating that S filled into most of the pores.

To study the electrochemical properties of the as-made PCNT-S nanocomposites, CR2025 coin cells with metallic lithium anode were fabricated and evaluated. Note that all capacity values stated are given in mA h g⁻¹ per sulfur mass if not mentioned specifically. The kinetic processes of sulfur reduction and sulphide oxidation of the 850PCNT-S composites were studied using cyclic voltammetry. From the results shown in Fig. 4a, there are two peaks in the first cathodic reduction process. The peak at 2.32 V (vs. Li⁺/Li⁰) corresponds to the reduction of elemental sulphur (S_8) to polysulphide anions $(S_x^{2-}; 2 < x < 8)$. A strong cathodic peak at 2.05 V (vs. Li⁺/Li⁰) suggests a strong reduction of soluble polysulphide anions to an insoluble low-order Li₂S₂/Li₂S deposit. In the first anodic process, the oxide peak at about 2.35 V is associated with the formation of $\text{Li}_2 S_n$ (n > 2).^{2,7} From the second to the fourth cycles, the potentials of the two reductive peaks exhibit a slight positive shift, whereas the oxide peak gradually shifts to a lower potential, implying that the cell obtains a better reversibility and a more reliable stability for the extended cycles.18 Moreover, the variation of oxidation peaks between the first and second cycles may be ascribed to the rearrangement of active sulfur from its original position to more energetically stable sites. A similar phenomenon can also be found in previous reports.5,18 The charge-discharge curves under various current rates are depicted in Fig. S5.† Consistent with the cyclic voltammetry results, the typical two-plateau behavior of the sulfur cathode is observed, corresponding to the formation of long-chain polysulfides (Li₂S_x, $4 \le x \le 8$) and short-chain Li₂S₂ and Li₂S. Similar to study elsewhere,8 inevitable polarization of the cathode materials is also observed due to fast electron transfer



Fig. 4 (a) CV profiles of the 850PCNTs–S composites; (b) rate performance and (c) cycling stability of raw CNTs–S hybrids and 850PCNTs–S hybrids; (d) the cycling stability of 850PCNTs–S composites at various current rates.

with the increasing current rates. The rate capability of the 850PCNT-S composite at various current densities from 0.5-15 C is shown in Fig. 4b. Compared with the raw CNTs-S composite, the 850PCNTs-S composite exhibits a much higher capacity at various rates, with specific capacities of 1308, 985, 922 mA h g^{-1} at 0.5, 1, and 2 C, respectively. Furthermore, a reversible capacity of 150 mA h g⁻¹ can be preserved, even at a very high current rate of 15 C. More importantly, a reversible capacity of 1035 mA h g^{-1} can still be reversed when the current is switched back to 0.5 C, which is close to the initial capacity $(1052 \text{ mA h g}^{-1})$, indicating a highly reversible and excellent rate performance for the 850PCNT-S nanocomposites. To the best of our knowledge, to date such a high rate performance (especially higher than 10 C) for the Li-S battery with 78 wt% S content has only appeared spasmodically, possibly because of the intrinsic poor electronic conductivity of sulfur.8 The cycling stability of the 850PCNT-S nanocomposite is illustrated in Fig. 4c. An initial reversible capacity of 1382 mA h g^{-1} is achieved at the current rate of 0.2 C, which is about 82.5% of sulfur usage based on the theoretical value (1675 mA h g^{-1}) for sulfur. A rapid capacity drop is seen in the next three cycles followed by good stability on subsequent cycling, which has been explained by an activation step, whereby the S in the hybrids is not initially fully accessible to the electrolyte because the pores are filled.5 After the first few cycles, about 950 mA h g^{-1} is achieved over 250 cycles with a steady Coulombic efficiency of 93%. In stark contrast, the raw CNT–S composites only retain 171 mA h g^{-1} after 250 cycles and exhibit a low Coulombic efficiency, which shows poor cycling stability. Fig. 4d shows the cycling stability of the 850PCNTs-S nanocomposite at relatively high rates. With a high current rate of 5 C, the capacity remains at 455 mA h g^{-1} after 250 cycles vs. 652 mA h g^{-1} after the first cycle with a capacity fading rate of 0.8 mA h g^{-1} per cycle. Furthermore, from Fig. S6a,† no obvious changes can be observed for both the anodic/cathodic peaks in the voltammetric profiles, and there is no evident increase in combination resistance from electrochemical impedance spectroscopy after 200 cycles (Fig. S6b⁺), indicating good electrochemical stability for the 850PCNTs-S cathode.

For such an excellent rate performance and high capacity in the 850PCNTs-S cathode, the porous structure in 850PCNTs may be one of the important factors because of their intrinsic capability to trap soluble intermediate polysulfides, and to accommodate volume variations of the S cathode. Moreover, the porous structure can also help to convey Li⁺ ions in the electrolyte as a consequence of the large number of pores.¹⁴ In addition, from the IR spectroscopy of the 850PCNTs in Fig. S7a,[†] the presence of the oxygen-containing groups (indicated by the strong peak at 3434 cm⁻¹)¹⁹ is particularly noteworthy. The XPS curve in Fig. S7b† also supports this result. For the 850PCNT-S composites, a strong interaction between the PCNTs and S is demonstrated by the fact that the S in the PCNT-S nanocomposites exhibits a better thermal stability compared with the pure S powder (Fig. 3a). Strong C=S stretching and weak C-S stretching are also detected from FT-IR spectrometry at 1220 and 1098 cm⁻¹, respectively, together with S-O-C stretching at 825 cm⁻¹ (Fig. S7a[†]).^{19,20} In the high-resolution the

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O_{1s} spectra of 850CNTs-S (Fig. S7d[†]), an obvious up-shift can be observed compared with that of 850CNTs, which suggests the presence of S-O bonding in the 850CNTs-S. All these results imply that S has been chemically bonded to the PCNTs. We believe that the strong chemical bonding between S and the CNT matrix benefits the absorption of more S and traps soluble intermediate polysulfides. To further verify the influence of the oxygen-containing groups, the 850PCNTs were annealed at 850 °C in argon for an hour (the obtained material labeled A-850PCNTs), as expected, the peak of the hydroxyl groups disappeared (Fig. S8[†]). From Fig. S9,[†] the as-made A-850PCNT-S cathode is found to exhibit inferior electrochemical performance compared with the 850PCNT-S cathode. Consistent with the voltage profiles (Fig. S10[†]), for the A-850PCNT-S composites, the shift in the declining peaks with cycling clearly indicates electrochemical instability. In contrast, the 850PCNT-S composites exhibit narrower peaks with slight shifts with cycling, indicating excellent electrochemical stability. Moreover, for the 850PCNTs-S composites, the difference between the first reduction peak at \sim 2.32 V and the oxidation peak at 2.35 V is less than that for the A-850PCNT-S composites, suggesting an effective retention of capacity and prevention of the shuttle mechanism. We speculate that the S in the 850PCNT-S composites and the polysulfides formed in the redox reaction are not free, but are bonded to the PCNTs via C-S or S-O-C bonds. The chemically bonded S is slowly converted to free, but highly dispersed, reactive material upon cycling. All these results also strongly confirm that the introduced oxygen-containing groups for the 850PCNTs after water etching should be another important feature for advanced Li-S batteries.

Recent advances involving CNT-S cathodes have demonstrated enhancement in the capacity and stability of Li-S batteries. Although in the literature the capacity is reported as very high when calculated only by the weight of S, the specific capacity based on the total electrode mass is generally lower than 500 mA h g^{-1} ,²¹ which is mainly attributed to the low content of S (generally lower than 80 wt%). Therefore, to raise the specific capacity of cell-levels in Li-S batteries, the S content in each cell must be increased. Surprisingly, when loaded with 89 wt% of S (Fig. S11[†]), the as-prepared 850PCNT-S composite (active material : conductive agent : PVDF = 90 : 5 : 5, *i.e.*, the total content of S in the electrode is 80.1 wt%, dubbed as S80.1) unexpectedly delivered a reversible capacity as high as 895 mA h ${
m g}^{-1}_{
m sulfur}$ /717 mA h ${
m g}^{-1}_{
m electrode}$ after the initial cycle and 625 mA h $g^{-1}_{sulfur}/500$ mA h $g^{-1}_{electrode}$ after 100 cycles with a stable Coulombic efficiency of 95% at a low current rate of 0.1 C (Fig. 5a). Moreover, when increasing the amount of conductive agent (active material : conductive agent : PVDF = 80 : 10 : 10, i.e., the total content of S in the electrode is 71.2%, dubbed as S71.2), an initial reversible capacity of 1165 mA h g^{-1}_{sulfur} 830 mA h $g^{-1}_{electrode}$ could be obtained at a current rate of 0.2 C. More importantly, 564 mA h $g^{-1}_{electrode}$ could also be retained after 200 cycles, with Coulombic efficiencies averaging 95% (Fig. 5c). The voltage profiles of the first, 50th, 100th, 150th, and 200th cycles are depicted in Fig. S12.[†] It can be found that the hysteresis between the charge and discharge cycles increases slightly after 200 cycles, which indicates a good electrochemical



Fig. 5 Cycling stabilities and Coulombic efficiencies of the S80.1 cathode at a current rate of 0.1 C (a), and the S71.2 cathode at a current rate of 0.2 C (c); a comparison between our work (the S80.1 (b) and S71.2 (d) cathode) and some other typical reports on the specific capacity per cathode mass.

stability. Furthermore, even at a current rate of 1 C, a satisfactory capacity of 672 mA h $g^{-1}_{sulfur}/478$ mA h $g^{-1}_{electrode}$ was achieved, and the recovery of a reversible capacity of 930 mA h $g^{-1}_{sulfur}/662$ mA h $g^{-1}_{electrode}$ was achieved at 0.2 C following the charge/discharge process at a current rate of 1 C (Fig. S13†). To the best of our knowledge, these reversible capacity values in our experiments are comparable with those of Li–S batteries given in some recent reports (Fig. 5b and d).^{3,4,7,11,22–27}

3. Conclusions

In summary, we have developed a simple, green, and scalable one-step approach to obtain PCNTs with high SSA and $V_{\rm T}$, using a mild chemical reaction between CNTs and rare oxygen sourced from nebulized water vapor at high temperatures. We obtained SSA and VT values for PCNTs after water etching as high as 431.2 m² g⁻¹ and 2.16 cm³ g⁻¹, which are much larger than those for raw CNTs of 255 $m^2 g^{-1}$ and 0.81 $cm^3 g^{-1}$. When the etched PCNTs-S composites were tested as a cathode material in Li-S batteries, a cathode containing 78 wt% S delivered a high initial capacity of 1382 mA h g^{-1} and maintained a reversible capacity of 950 mA h g^{-1} after 250 cycles at a current rate of 0.2 C. Furthermore, the etched CNTs-S cathode also exhibited a good rate performance, and a reversible capacity of 150 mA h g⁻¹ can be preserved at the very high current rate of 15 C. More importantly, we also developed a Li-S battery with higher sulfur content. A cathode with 89 wt% S content unexpectedly delivered a reversible capacity as high as 1165 mA h $g^{-1}_{sulfur}/830$ mA h $g^{-1}_{electrode}$ at the initial cycle, and 792 mA h g^{-1}_{sulfur} /564 mA h $g^{-1}_{electrode}$ after 200 cycles at a current rate of 0.2 C. To the best of our knowledge, such a high rate performance (15 C) and S loading (89 wt%) in cathodes of

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advanced Li–S batteries have been infrequently reported in previous research. PCNTs etched with nebulized water hold great potential for real applications in advanced Li–S batteries. We believe that the mild oxidation treatment can also be applied to prepare other porous graphite materials for catalytic, electronic, and even optical applications.

4. Experimental section

Synthesis of porous carbon nanotubes (PCNTs)

The raw carbon nanotubes (dubbed as raw CNTs) for the study were purchased from a commercial corporation. In a typical procedure, water was first nebulized to create a mist of droplets. The droplets formed were then passed into a quartz tube of raw commercial CNTs using an Ar-carrying gas when the desired temperature of 850 °C is reached. After the water etching, the water steams were turned off, and the furnace was cooled to room temperature under argon flow. As a control experiment, other carbon materials obtained under various conditions, such as the etching temperature and time, were synthesized in the same way. The resulting materials were denoted accordingly as 850PCNTs, 900PCNTs, 850PCNTs-1, 850PCNTs-2, 850PCNTs-3, and so on.

Synthesis of CNTs-sulfur composites

The CNTs–S composites were prepared following a melt-diffusion strategy. In a typical procedure, the PCNTs and sulfur (high purity sulfur, 99.99% metal basis, Aladdin) were mixed. Then the powder was ground and heated in an oven at 160 °C for 12 h, followed by another 12 h at 180 °C. For comparison, the raw CNTs–S composite were prepared *via* the same method.

Structure characterization

X-ray photoelectron spectroscopy (XPS) measurements were carried out with an ultrahigh vacuum setup, equipped with a monochromatic Al KR X-ray source and a high resolution Gammadata-Scienta SES 2002 analyzer. X-ray diffraction patterns (XRD) were obtained with a D/MAX-2400 diffractometer using Cu K_{α} radiation (40 kV, 100 mA, $\lambda = 1.54056$ Å). Raman spectra were taken under ambient conditions using a Renishaw (inVia) with an Ar-ion laser beam at an excitation wavelength of 532 nm. The nitrogen adsorption/desorption data was recorded at the liquid nitrogen temperature (77 K) using a Micromeritics ASAP 2020 M apparatus. The samples were degassed at 120 °C under vacuum for 3 h prior to the measurement. The pore size distribution (PSD) was derived from the adsorption branch of the isotherms using the Barrett-Joyner-Halenda (BJH) model. The total pore volumes were calculated from the amount adsorbed at a relative pressure (P/P_0) of 0.99. The specific surface area was calculated using the Brunauer-Emmett-Teller (BET) equation. The IR spectrum was collected on a Nicolet 6700 FTIR spectrometer. SEM images were obtained with a JSM-6700F field-emission scanning electron microscope. TEM analyses were carried out with a JEOL-3010 instrument operating at 200 kV. The samples for TEM analysis were prepared by dropping dehydrated alcohol droplets

of the products on copper grids and drying at 45 °C. Thermogravimetric analysis (TGA) was measured at a heating rate of 10 °C min⁻¹ under nitrogen flow, using a STA449 F3 Jupiter thermogravimetric analyzer (NETZSCH).

Electrochemical characterization

Electrochemical experiments were performed via CR2025 cointype test cells assembled in an argon-filled glovebox with lithium metal as the counter and reference electrodes at room temperature. The cathode for the Li-S batteries was prepared by mixing 90 wt% composite materials, 5 wt% conductive agent and 5 wt% polyvinylidene difluoride (PVDF) in N-methyl-2-pyrrolidone (NMP) to form a slurry. Subsequently, the slurry was pasted onto an aluminum foil after drying at 60 °C overnight and a Celgard 2400 membrane was used as the separator to isolate electrons. The electrolyte was 1 M bis(trifluoromethane) sulfonimide lithium salt (LiTFSI) with 1% LiNO3 dissolved in a mixture of 1,3-dioxolane (DOL) and dimethoxymethane (DME) (1:1 by volume). The discharge/charge measurements were conducted at a voltage interval of 1.0 to 3.0 V using a CT2001A battery test system (LAND Electronic Co.). Cyclic voltammetry (CV) measurements were performed on CHI6600 electrochemical workstation at a scan rate of 0.2 mV s^{-1} .

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