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1 Introduction

To meet the growing energy demands, considerable efforts are being made to develop high-performance energy conversion and storage devices (*e.g.*, supercapacitors and batteries) to power our future society.^{1–3} Among the best energy materials, nanostructured carbons have attracted intensive attention due to their unusual size-/surface-dependent (*e.g.*, morphological, electrical, optical, and mechanical) properties useful in enhancing energy conversion and storage performance.^{4–8} In particular, 1D porous carbon nanofibers have been demonstrated to be one of the most promising candidates for creating advanced energy storage systems.^{9–14}

Porous carbons with 1D geometry would allow a fast and long-distance electron transport, and possess largely exposed surface area and good electrical conductivity because of the high length-to-diameter ratio. Recently, various carbon nanofibers with desirable porosities have been utilized in supercapacitors or lithium ion batteries and have shown excellent electrochemical performance.^{15–22} To date, many studies have focused on the preparation of 1D porous carbon nanofibers

Synthesis of superior carbon nanofibers with large aspect ratio and tunable porosity for electrochemical energy storage

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Porous carbon nanofibers (CNFs) are regarded as essential components of high-performance energy storage devices in the development of renewable and sustainable resources, due to their high surface areas, tunable structures, and good conductivities. Herein, we report new synthesis methods and applications of two types of porous carbon nanofibers, *i.e.*, colloidal mesoporous carbon nanofibers as electrode materials for supercapacitors, and microporous carbon nanofibers as substrate media for lithium–sulfur (Li-S) batteries. These carbon nanofibers can be synthesized either by confined nanospace pyrolysis or conventional pyrolysis of their polymeric precursors. The supercapacitor electrodes which are fabricated *via* a simple dipping and rinsing approach exhibit a reversible specific capacitance of 206 F g^{-1} at the current density of 5 A g^{-1} in 6.0 mol L^{-1} aqueous KOH electrolyte. Meanwhile, the Li-S batteries composed of microporous carbon nanofiber-encapsulated sulfur structures exhibit unprecedented electrochemical performance with high specific capacity and good cycling stability, *i.e.*, 950 mA h g^{-1} after 50 cycles of charge–discharge. The excellent electrochemical performance of CNFs is attributed to their high-quality fiber morphology, controlled porous structure, large surface area, and good electrical conductivity. The results show that the carbon nanofibers represent an alternative promising candidate for an efficient electrode material for energy storage and conversion.

with tailored architectures,23-27 mainly depending on strategies like electrospinning, chemical vapor deposition, and direct carbonization of 1D polymers through addition of porogens and/or further activation processes. However, it has come to light that those approaches always result in an inextricable problem of severe conglutination of the synthesized nanofibers that would cause difficulty in fabricating uniform and high quality fiber-based electrodes. Moreover, the obtained carbon nanofibers often possess small pore sizes and low surface areas.²⁸⁻³² Hence, to realize the applications of 1D nanocarbons in electrochemical fields, it is still a great challenge, but of great significance to explore a flexible and efficient synthesis to conveniently synthesize porous carbon nanofibers which have tailored pore size, high surface area, easy accessibility to assemble and reconstruct. Thus, the research on precise and simultaneous manipulation of carbon nanofibers with tunable porosity and accessible large surface area may have a major impact on the continuous advance of high performance energy materials.

Herein, we propose a controlled synthesis for porous carbon nanofibers with large aspect ratio and tunable porosity through a hydrothermal approach combined with our recently developed technique (namely, confined nanospace pyrolysis) or conventional pyrolysis. In other words, we can tune the fine

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structures of the final carbon nanofibers by selecting the appropriate pyrolysis process. In the case of using conventional pyrolysis of the polymer nanofibers (PNFs), carbon nanofibers with abundant micropores can be fabricated, while *via* confined nanospace pyrolysis, discrete and colloidally dispersible carbon nanofibers with well-defined mesopores and large surface area can be achieved. Importantly, the obtained two types of carbon nanofibers have shown excellent performance as energy storage materials in supercapacitors and lithium batteries. To the best of our knowledge, such carbon nanofibers with large aspect ratio and tunable porosity as high performance energy materials are reported here for the first time.

2 Experimental

2.1 Chemicals

Resorcinol (R, 99.5%), hexamethylene tetramine (HMT), cetyltrimethyl-ammonium bromide (CTAB) (99%), tetraethyl orthosilicate (TEOS), NaOH and ammonia solution (25%) were obtained from Sinopharm Chemical Reagent Co., Ltd. Pluronic F127 was purchased from Fluka. Sulfur (>99.99%) was purchased from Aldrich. All chemicals were used as received.

2.2 Synthesis of polymer nanofibers (PNFs)

Polymer nanofibers were prepared by the hydrothermal synthesis of R (2.5 mmol) and HMT (1.5 mmol) with surfactant F127 at 110 $^{\circ}$ C for 4 h. The polymer product (PNFs) was then washed with water three times.

2.3 Synthesis of mesoporous carbon nanofibers

The obtained PNFs were first treated in an acidic H₂SO₄ solution and then mixed with an aqueous ammonia solution after washing with deionized water several times. Subsequently, the CTAB solution was added into the mixture with vigorous stirring for 30 minutes. TEOS was added with further stirring for 16 h at room temperature. Thus, colloidal PNFs@SiO2 dispersion was obtained. PNFs@mSiO₂ was prepared by removing the CTAB from the silica shell with a hydrochloric acid alcohol solution (pH \sim 2) at 60 °C. CNFs-I@mSiO_2 was obtained by pyrolysis of the PNFs@mSiO₂ at 600 °C for 2 h under a nitrogen atmosphere. Immediately following carbonization, CNFs-I-A@mSiO2 were obtained by heating CNFs-I@mSiO2 to 750 °C in a steam stream for 120 min. CNFs-I and CNFs-I-A products were obtained after eliminating the SiO2 shell of CNFs-I@mSiO2 and CNFs-I-A @mSiO2 using NaOH alcohol-water solution at 50 °C for 24 h.

2.4 Preparation of CNFs-I-A/nickel foam electrodes for supercapacitors

The working electrodes were prepared by immersing the nickel foams (NFs) with area of 1 cm \times 1 cm and thickness of 1 mm into the CNFs-I-A aqueous dispersion (5 mg mL⁻¹) for 5 min under ultrasound and then dried in a 50 °C oven overnight. No other conductive agent was used. Finally the CNFs/NF was pressed under a pressure of 4 MPa for 5 min to fabricate an electrode. Then, the CNFs/NFs were washed with ethanol three

times and then placed into an oven at 50 $^\circ$ C for 4 h. The mean mass loading of the active material was *ca.* 3.0 mg cm⁻².

2.5 Synthesis of microporous carbon nanofibers and microporous CNF-encapsulated sulfur (CNF-S) composite

Microporous carbon nanofibers (CNFs-II) were obtained by pyrolysis of the PNFs at 600 °C for 2 h under a nitrogen atmosphere. Activated CNFs-II-A were synthesized by subsequent heating CNFs-II to 750 °C in a steam stream for 150 min. Sulfur and CNFs were thoroughly mixed according to a mass ratio of $m_{\rm S}: m_{\rm C} = 40: 60$ in a quartz mortar for 1 h to yield a black mixture. The mixture was then sealed in a glass container and heated at 155 °C for 20 h. The obtained C/S composite was denoted as CNF-S.

2.6 Characterization

Scanning electron microscopy (SEM) investigations were carried out with a FEI Nova NanoSEM 450 instrument. Transmission electron microscopy (TEM) analyses were carried out with a Tecnai G²20S-Twin equipment operating at 200 kV. The samples for TEM analysis were prepared by dropping an ethanol droplet of the products on carbon-coated copper grids and drying at room temperature. Nitrogen adsorption isotherms were measured with an ASAP 2020 sorption analyzer (Micromeritics). The Brunauer–Emmett–Teller (BET) method was utilized to calculate the specific surface areas (S_{BET}). Pore size distributions (PSDs) were determined from the adsorption branches of the isotherms using density functional theory (DFT). Total pore volumes (V_{total}) were calculated from the amount adsorbed at a relative pressure, P/P_0 , of 0.90. Micropore volumes (V_{micro}) were calculated using the *t*-plot method.

2.7 Electrochemical measurements

2.7.1 Electrochemical measurements for supercapacitors. The capacitive performance of the single electrode was carried out on an CHI660D electrochemical workstation (CH Instruments Inc., Shanghai, China) using a standard three-electrode test system composed of Hg/HgO as reference electrode and Pt plate as counter electrode in 6 M KOH electrolyte at 25 °C. Cyclic voltammetry (CV), alternating current impedance and galvano-static charge–discharge cycling (GC) measurements were employed in the evaluation of the electrode electrochemical performance. The capacitance of the supercapacitor cell of the carbon was calculated by using the following equation:

$$C_{\text{cell}}(\text{F g}^{-1}) = \frac{I\Delta t}{m\Delta V}$$

where I(A), $\Delta t(s)$, $\Delta V(V)$ and m(g) are the discharge current, the discharge time, the operation potential window from the end of the voltage drop to the end of the discharge process and the total mass of two electrodes, respectively.

2.7.2 Electrochemical measurements for Li-S batteries. Electrochemical experiments were performed *via* CR2025 cointype test cells assembled in an argon-filled glove box with lithium metal as the counter and reference electrodes at room temperature. The cathode for Li-S batteries was prepared by

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mixing 80 wt% composite materials, 10 wt% carbon black and 10 wt% polyvinylidene difluoride (PVDF) in *N*-methyl-2-pyrrolidone (NMP) to form a slurry. Subsequently, the slurry was pasted onto a carbon-coated aluminum foil and Celgard 2400 membrane was used as the separator to isolate electrons. The electrolyte was 1 M bis(trifluoromethane)sulfonimide lithium salt (LiTFSI) dissolved in a mixture of 1,3-dioxolane (DOL) and dimethoxyethane (DME) (1:1 by volume). The dischargecharge measurements were conducted at a voltage interval of 1.0 to 3.0 V using a Land CT2001A battery test system.

3 Results and discussion

3.1 Properties of colloidal mesoporous carbon nanofibers (CNFs-I) and microporous carbon nanofibers (CNFs-II)

The overall process for the synthesis of porous carbon nanofibers is illustrated in Scheme 1 (see Experimental section for details). As shown, the first step towards the synthesis of carbon nanofibers involves the fabrication of uniform polymer nanofibers (PNFs) *via* a controlled hydrothermal approach by using resorcinol and hexamethylene tetramine (HMT) as carbon precursor and Pluronic F127 as the morphology-directing agent.²⁰ Such solution-phase hydrothermal synthesis offers a remarkable opportunity for the molecular design of carbon morphologies and flexible control of the aspect ratio of final carbons, where the surfactant concentration determines the morphology of the self-assembled composite, driven by the hydrogen-bond interaction between RF resin and F127 micelles.

Under this consideration, we herein introduce surfactant Pluronic F127 to the reaction system to adjust the aspect ratio of PNFs and corresponding carbon nanofibers (denoted CNFs). The porous structure can be tuned by controlling the pyrolysis processes, which is beneficial for enhancing their electrochemical performance. By conducting a confined nanospace pyrolysis process (I),^{33,35} discrete and colloidal mesoporous carbon nanofibers can be achieved. That is, coaxial PNFs@mSiO₂ nanocables with mesoporous SiO₂ shell are first prepared and then pyrolyzed to form CNFs-I(@mSiO₂)



Scheme 1 Schematic illustration for the formation process of mesoporous carbon nanofibers (CNFs-I) and microporous carbon nanofibers (CNFs-II).

composites. Eliminating the SiO₂ shell would release discrete and colloidal carbon nanofibers (CNFs-I) which showed welldesigned mesopores, high surface area, and good dispersibility in water and ethanol. Alternatively, after conventional pyrolysis (II) of PNFs, high-quality microporous carbon nanofibers (CNFs-II) can be obtained. Furthermore, to enable reliable performance in electrochemical applications, simple steam activation for both CNFs-I and CNFs-II was conducted subsequently so as to create desired pores and large surface area. The porous parameters of these materials are summarized in Table 1, including the specific surface area (S_{BET}), total pore volume (V_{total}), and micropore volume (V_{micro}).

The as-prepared polymer nanofibers and carbon nanofibers were characterized by SEM and TEM. As seen in Fig. 1a, PNFs were composed of high-quality fibrous polymer nanofibers with diameters of 50 ± 5 nm and lengths up to several microns. After extraction of F12734 and consecutive silica coating by a modified Stöber process, well-defined PNFs@mSiO2 nanocables were achieved via the surfactant-templating sol-gel process by the hydrolysis and condensation of tetraethyl orthosilicate (TEOS) in the presence of surfactant cetyltrimethyl-ammonium bromide (CTAB) to prevent polymer/carbon conglutination during high temperature treatment.33 Subsequently, confined nanospace pyrolysis of the PNFs@mSiO2 led to the production of CNFs-I@mSiO2 with visible and nicely coated core-shell nanocable structure (Fig. 1b). To the best of our knowledge, synthesis of well-defined CNFs-I@mSiO2 nanocables with high aspect ratio carbon fibers as the core component and a mesoporous shell has not been achieved so far. Removal of the silica shell resulted in CNFs-I with fine fibrous morphology and diameter of about 40 \pm 5 nm (Fig. 1c). Interestingly, as shown in the TEM image and N₂ adsorption-desorption isotherm, CNFs-I exhibited obvious mesoporous structure, which was achieved by self-activation from the confinement effect in situ during the confined nanospace pyrolysis.35 The sample showed a BET surface area of 1050 $\text{m}^2 \text{g}^{-1}$ and a total pore volume of 1.015 cm³ g⁻¹ (Table 1).

As is well known, an ideal electrical energy material should have large accessible surface area, appropriate pore size distribution (PSD), and shortened transportation channels.^{17,36} Thus, we used the common and simple steam activation to tune the porous texture of the carbon nanofibers product (denoted as CNFs-I-A). As seen in Fig. 2a, the mesoporous CNFs retained the originally fibrous morphology with diameters of ~40 nm. The

Table 1	Structural and textura	parameters of the obtain	ed carbon nanofibers
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Sample	$S_{\rm BET}^{a}$ (m ² g ⁻¹)	$V_{\rm mic}^{b} \left({\rm cm}^3 {\rm g}^{-1} \right)$	$V_{\text{total}}^{c} (\text{cm}^3 \text{g}^{-1})$
CNFs-I	1050	0.118	1.015
CNFs-II	529	0.195	0.296
CNFs-I-A	1218	0.698	1.075
CNFs-II-A	1144	0.551	0.666

^{*a*} S_{BET} : the specific surface areas calculated from the adsorption data in the relative pressure range of 0.05 to 0.3 using the Brunauer–Emmett–Teller (BET) method. ^{*b*} V_{mic} : micropore volume calculated by the *t*-plot method. ^{*c*} V_{total} : total pore volume at $P/P_0 = 0.90$.



Fig. 1 $\,$ (a) SEM image of PNFs. (b) TEM image of CNFs-I@mSiO_2. (c) TEM and (d) N_2 adsorption–desorption isotherm of CNFs-I.



Fig. 2 (a) SEM image, (b) TEM image, (c) N_2 adsorption–desorption isotherm and (d) Tyndall phenomenon of CNFs-I-A in water.

high-resolution TEM (HRTEM) image clearly revealed the homogeneous presence of mesoporous channels through the whole nanofibers with pore diameters of *ca.* 2–10 nm which were parallel to the axis of the CNFs-I-A (Fig. 2b).

The porosity of the sample was investigated by N_2 adsorption–desorption measurement. The isotherm (Fig. 2c) of CNFs-I-A revealed the details of the low-pressure region where micropore filling occurs, as well as a type H2 hysteresis at the relative pressure of 0.42–0.80, indicating a mesopore characteristic. A sharp increase of the uptake at a relative pressure near to 1.0 was due to the filling of the spaces from the dried and packed carbon nanofibers. The activated CNFs-I-A had a high BET surface area of 1218 m² g⁻¹, which is a key feature for adapting electrical double layer capacitors (EDLCs) for energy storage (Table 1). The PSD in Fig. 2c demonstrated CNFs-I-A had a well-defined micro-mesopore size distribution with sharp peaks at

0.5 nm, 1.3 nm, 3.5 nm and 9.2 nm, indicating the coexistence of hierarchical micropores, mesopores, and macropores in the final samples. The micropores were created during steam activation and the latter mesopores were obtained via confined nanospace pyrolysis, which was in good agreement with the TEM observation. Such suitably developed interconnected meso-/micropores are of great importance for electrochemical performance, which can be effectively covered by electrolyte ions, thus facilitating their penetration and providing a minimized inner-pore resistance, leading to a high ion-accessible surface area.^{17,30,31} Noticeably, a stable colloidal suspension of carbon nanofibers was obtained, demonstrated from the Tyndall phenomenon in Fig. 2d, which is of significance for carbon nanofibers used as building blocks or assembly component in constructing devices. To our knowledge, this is the first report that discrete and colloidally dispersible carbon nanofibers have been successfully prepared, which resulted from the special technique, *i.e.*, confined nanospace pyrolysis.

3.2 Colloidal mesoporous carbon nanofibers (CNFs-I-A) as superior supercapacitor electrodes

The colloidal mesoporous carbon nanofibers CNFs-I-A were adopted as an active material to form a uniform film on a framework of nickel foam (NF) by means of a simple dipping and rinsing process (Fig. 3a). Distinctively, such a process leaves out the need for grinding and mixing steps. Here, discrete and dispersible carbon nanofibers with excellent colloidal behavior are of critical importance for constructing the CNFs/NF



Fig. 3 (a) Schematic illustration of the preparation of a CNFs-I-A/NF electrode. (b–e) SEM images of the as-formed CNFs-I-A/NF electrode at different magnifications. (f–h) Electrochemical performances measured in a three-electrode system in 6.0 M KOH solution. (f) Cyclic voltammmograms at different scan rates. (g) Galvanostatic charge–discharge curves at different current densities. (h) Electrochemical impedance spectra (inset: magnified 0.44–0.60 Ω region) at an opencircuit voltage, an ac amplitude of 5 mV, and frequencies of 10 mHz to 100 kHz.

electrodes. The SEM images with different resolutions of the resulting CNFs/NF composite clearly showed that CNFs had been deposited and coated on the framework of the nickel foam (Fig. 3b–e). Thus, the distances of ion/electron transportation in the electrodes were shortened resulting from the unique open pore system and unique structure of such CNFs/NF. Such highly conductive electrodes with optimized nanoarchitectures for facile ion/electron transport are indispensable for fabricating ideal electrochemical capacitors (ECs).

The electrochemical capacitive performance of the CNFs-I-A/ NF electrodes was evaluated by cyclic voltammetry (CV) measurement at different sweep rates from 5 to 100 mV s⁻¹ (Fig. 3f). The CV curves displayed relatively good rectangular profiles, showing a typical characteristic of double-layer capacitance. We also observed that the CV curve of the final electrode still kept the rectangular shape even at a potential scan rate of 100 mV s⁻¹. The specific capacitance (C_s) is up to 390 F g⁻¹ at a scan rate of 5 mV s⁻¹ and 276 F g⁻¹ even at 100 mV s⁻¹. Further, galvanostatic charge-discharge experiments were performed at various current densities in a three-electrode system. As shown in Fig. 3g, all charge-discharge curves showed isosceles triangular shapes at current densities ranging from 0.5 to 5 A g^{-1} and only a slight change in the specific capacitance was observed here. CNFs-I-A/NF electrode presents a high specific capacitance of 276 F g^{-1} at 0.5 A g^{-1} , and retains a capacitance of 206 F g^{-1} at 5 A g^{-1} , indicating a good capacitance retention capability of such an electrode. Comparing our results with published data, it is clear that the C_s value of the mesoporous CNFs is much higher than those of porous carbon fiber materials^{15,17,37,38} (Table 2). The superior performance should be attributed to the unique architecture of the CNFs, where the 1D nanostructure provides a shortened path for electron transport and electrolyte penetration; meanwhile, the interconnected pore texture combined with the large surface area offers a good charge accommodation and ability to handle high current loads.

Electrochemical impedance spectroscopy (EIS) is also employed to monitor the electrochemical behavior of the electrodes. Nyquist plots collected in the frequency range of 100 kHz to 10 mHz are shown in Fig. 3h. In the low frequency region, a nearly vertical line demonstrates the domination of capacitive behavior at the electrolyte–electrode material interface. The high frequency loop was small, demonstrating low charge transfer resistance associated with good electrolyte pore accessibility. The equivalent series resistance was observed to be \sim 0.45 Ohms. Such low resistance is crucial for enhancing the rate capability or the power density of electrochemical capacitors.³⁹ On the basis of the results described above, it is reasonable to conclude that the excellent performances of CNFs electrode material can be attributed to the combination effect of good conductivity, large surface area, well-designed pore texture, and the short distances of charge transfer from carbon fibers to the nickel foam. Furthermore, the CNFs were exposed to the electrolyte for the access of ions to form electrochemical double-layers, ensuring complete utilization of the exposed surface for charge storage and the nickel framework shortened the distances of charge transfer.

3.3 Microporous carbon nanofiber (CNFs-II-A)-encapsulated sulfur cathodes for high specific capacity rechargeable lithium–sulfur batteries

Alternatively, microporous carbon nanofibers are also considered as one of the most intriguing energy materials, which are attracting more and more attention as host substrates for enhancing Li-S cell performance.14,21 Encapsulating the sulfur in microporous carbon can improve its utilization as an active mass and avoid the diffusion of the Li_2S_n species to the electrolyte solution.⁴⁰⁻⁴² As shown in Scheme 1, after conventional pyrolysis (II) of PNFs, high-quality microporous carbon nanofibers (CNFs-II) can be obtained, but with a relatively low surface area of 529 m² g⁻¹. Here, to permit a high load of sulfur and a reliable performance in Li-S batteries, simple steam activation was conducted subsequently so as to create effective pores and large surface area. As seen from the N₂ adsorption-desorption isotherm in Fig. 4a, the BET specific surface area of CNFs-II-A calculated from adsorption isotherms increases significantly due to steam activation from the initial value of 529 $m^2 g^{-1}$ to 1144 m² g⁻¹. The pore size distribution (PSD) curve of 0.5-100 nm gives a wealth of information regarding the distribution of different size pores. The CNFs-II-A mainly had sharp peaks at \sim 0.54 nm and 1.27 nm, indicating the microporous structure.

Activated microporous carbon nanofibers CNFs-II-A were used to prepare a porous carbon nanofiber–sulfur (CNF-S) composite electrode material for rechargeable Li-S cells with a loading of 27 wt% sulfur through a melt-diffusion method. As a result, the porous S/CNFs-II-A nanocomposites exhibit a smooth outer surface (Fig. 4b). The typical discharge–charge profiles for the initial two cycles at the 0.1 C rate (1 C = 1675 mA g⁻¹) between 1.0 and 3.0 V are presented in Fig. 4c. The discharge curves shows the typical two-plateau behavior of a sulfur cathode, corresponding to the formation of long-chain polysulfides (Li₂S_x, 4 ≤ $x \le 8$) at 2.3 V and short-chain Li₂S₂ and

Table 2 A comparison of the electrochemical performance of carbon materials from literature

Materials	$C_{\rm s}^{\ a} \left({ m F g}^{-1} ight)$	Ref.
Mesoporous carbon nanofibers	276 (0.5 A g^{-1}), 390 (5 mV s^{-1})	This work
Self-sustained thin webs consisting of porous CNFs	$140(5 \text{ mV s}^{-1})$	37
Nitrogen-doped porous CNFs	$202(1.0 \text{ A g}^{-1})$	15
Mesoporous CNFs	$280 (0.5 \text{ A g}^{-1})$	17
PANI-based activated carbon	$220(0.5 \text{ A g}^{-1})$	38

^a Measurement conditions: three-electrode system, 6 M KOH solution.



Fig. 4 (a) N₂ adsorption–desorption isotherm and pore size distribution of CNFs-II-A. (b) SEM image of S/CNFs-II-A. Electrochemical properties of S/CNFs-II-A electrode at 0.1 C: (c) initial galvanostatic discharge–charge profiles and (d) cycling performance and coulombic efficiency.

Li₂S at 2.1 V.^{21,42} Moreover, the second plateau is flat, suggesting a uniform deposition of Li₂S with little kinetic barriers. This could be attributed to the pore system and unique 1D nanometer-scale of carbon nanofibers, which significantly improved electronic and ionic transport at the cathode. Cycling performance and coulombic efficiency at 0.1 C are presented in Fig. 4d, the reversible capacity remains at about 950 mA h g^{-1} after 50 cycles of charge-discharge, showing improved performance in specific capacity as compared to the previous study on carbon nanofiber-encapsulated sulfur composites.14,40,42 The suitably developed micropores and large external surfaces after steam activation directly contributed to the good capacitive behavior of the high performance Li-S batteries. In addition, those 1D porous CNFs provide an effective electronic conduction path and their network-like structure forms a stable structure of the S electrode to restrict polysulfides and reduce their dissolution into the electrolyte. Our preliminary results show that sulfur-impregnated CNFs can serve as a promising cathode for Li-S cells. We are going to tune the pore size and volume of CNFs in a precise manner to increase the sulfur content and simultaneously restrain the escape of Li_2S_n from the carbon pore space to obtain valuable Li-S batteries.

4 Conclusions

We have prepared two types of porous carbon nanofibers with large aspect ratio and tunable porosity, *i.e.*, colloidal mesoporous carbon nanofibers and microporous carbon nanofibers, which were respectively synthesized by confined nanospace pyrolysis and conventional pyrolysis of the polymer nanofibers. Depending on the pore structures, the carbon nanofibers can be used as electrode materials for supercapacitors and lithiumsulfur batteries. The supercapacitor electrode which was composed of activated mesoporous CNFs and fabricated *via* the simple dipping and rinsing approach exhibited a reversible specific capacitance of 206 F g⁻¹ at the current density of 5 A g⁻¹ in 6.0 mol L⁻¹ aqueous KOH electrolyte. Meanwhile, the Li-S

batteries composed of microporous carbon nanofiber-encapsulated sulfur structures demonstrated unprecedented electrochemical behavior with high specific capacity and good cycling stability, *i.e.*, 950 mA h g⁻¹ after 50 cycles of charge–discharge. The excellent electrochemical performance of CNFs was attributed to their 1D nanostructure, porous texture, large surface area, and good electrical conductivity of nanometer-scale carbon nanofibers. The results show that the carbon nanofibers represent an alternative promising candidate for an efficient electrode material for energy storage and conversion.

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