Shan *et al. Chin. J. Mech. Eng.* (2019) 32:60
https://doi.org/10.1186/s10033-019-0374-2

Chinese Journal of Mechanical Engineering

ORIGINAL ARTICLE Open Access

Mesoporous TiO_2 Nanofiber as Highly Efficient Sulfur Host for Advanced Lithium–Sulfur Batteries

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Abstract

Currently, lithium–sulfur batteries suffer from several critical limitations that hinder their practical application, such as the large volumetric expansion of electrode, poor conductivity and lower sulfur utilization. In this work, TiO_2 nanofibers with mesoporous structure have been synthesized by electrospinning and heat treating. As the host material of cathode for Li–S battery, the as prepared samples with novelty structure could enhance the conductivity of cathode composite, promote the utilization of sulfur, and relieve volume expansion for improving the electrochemical property. The initial discharge capacity of TiO_2/S composite cathode is 703 mAh/g and the capacity remained at 652 mAh/g after 200 cycles at 0.1 C, whose the capacity retention remains is at 92.7%, demonstrating great prospect for application in high-performance Li–S batteries.

Keywords: TiO_2 nanofibers, Mesoporous structure, Lithium–sulfur batteries, Cathode, Electrochemical property

1 Introduction

With the rapid development of portable equipment, handheld electronic products and hybrid electric vehicles, problems related to energy storage and conversion devices have attracted more and more attention. Because of low cost of sulfur, no harmful to the environment and higher theoretical energy density, lithium–sulfur batteries are being expected to become the most potential next generation of batteries in the world [1, 2]. However, currently most traditional lithium–sulfur batteries suffer from several critical limitations that hinder their practical application on account of the large volumetric expansion of elemental sulfur during lithiation, poor conductivity of both the final products, and so on. In addition to this, in the discharge process, the major obstacle is that intermediate polysulfides are highly dissolved in organic electrolyte, which the so-called "shuttle effect" causes an irreversible loss of active sulfur, poor cycle stability and low coulombic efficiency during charge/discharge cycling [3–5].

To overcome these impediments for the development of Li–S batteries, several strategies have been developed. For example, carbon acted as the sulfur matrix (graphene, carbon nanotubes and porous carbon [6–9], which mainly encapsulated the sulfur and polysulfide species into porous conductive materials through physical interaction. Meanwhile, more and more metal oxides as host materials for Li–S batteries has been put forward, owing to their strong chemisorption effect towards polysulfides (LiPSs), including SiO_2, MnO_2, TiO_x, Al_2O_3, etc [10–14]. Among them, titanium dioxide (TiO_2) has drawn much attention due to its low cost, environmental protection and structural stability [15]. An et al. [16] prepared TiO_2@NC interlayer to absorpt polysulfide in Li–S batteries. Because of good electronic conductivity, the reversible capacity reached 1460 mAh/g at 0.2 C. She et al. [17] designed a sulphur-TiO_2 yolk-shell nano-architecture to take in the large volumetric expansion of sulphur and minimize polysulphide dissolution, and the capacity decayed 0.033% every cycle after 1000 cycles. Li et al. [18] designed mesoporous hollow TiO_2 spheres (HTSs) to solve the

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above problems, and the capacity retention of 71% at 1 C (1 C = 1672 mA/g). The mesoporous morphologies of host is important for the improving the electrochemical property of Li–S batteries, because of the higher utilization of sulfur and chemisorption of lithium polysulfides. Moreover, it could afford large surface to infuse sulfur and accommodate volume changes during the charge/discharge reactions. Therefore, it is important to prepare the TiO_2 with the mesoporous structure by simple methods and research on charge and discharge mechanism of Li–S batteries deeply.

Herein, the mesoporous TiO_2 nanofibers were synthesized through an electrospinning method and subsequent thermal treatment. The mesoporous structure could encapsulate sulfur in their pores to trap soluble polysulfides (S_8 combining with the Li^+ in the anode), and accommodate large volumetric expansion of sulphur during lithiation/delithiation. In addition, the cathode conductivity is improved by TiO_2/S composite as electrodes. It results in excellent electrochemical performance and significantly improved cycle stability of the TiO_2/S composite cathode for Li–S batteries.

2 Experimental Section

2.1 Reparation of the Porous Nanofiber TiO_2 Membranes

The nanofiber TiO_2 was prepared by electrospinning, the details as follows: 0.8 g Polyvinylpyrrolidone (PVP) was directly dissolved in 6 mL ethanol, and stirred for 3 h. Meanwhile, to obtain a solution of TiO_2, 2.5 mL tetra-n-butyl titanate was dissolved in 2 mL acetic acid and 5 mL ethanol, and stirred for 3 h. After that above mixture was mixed with the PVP/ethanol solution together, and stirring for 12 h at room temperature. This solution was loaded into a perfusion tube equipped with pipette tip through syringe with silver-coated needle. The pipette tip was connected to a high-voltage power supply. The electric voltage was set as 15 kV. Gained nonwoven fabrics was consist of PVP/TiO_2 nanofibers. After peeled off, nonwoven fabrics was calcined at 500 °C with heat-up speed of 5 °C/min for 2 h in air flow, following by being calcined at 700 °C for 5 h to yield the final products.

2.2 Preparation of TiO_2/S Cathode

As-prepared Nanofiber TiO_2 and sulfur powder in a mass ratio of 3:7 were mixed and ground together for 30 min. Then the mixture of powder was converted to a sealed stainless steel vessel and calcined for 24 h at 155 °C. Finally, TiO_2/S cathode was obtained, corresponding to a sulfur loading of 3.0 mg/cm^2 and a sulfur content of 70 wt% in the whole cathode.

2.3 Materials Characterization

The microstructure of the samples were investigated by X-ray diffraction (XRD, D-MAX II A X-ray diffractometer). The micro morphological images were obtained by field emission scanning electron microscope (FE-SEM, S4800, Hitachi) and transmission electron microscopy (TEM, Tecnai F20). Energy-dispersive X-ray spectroscope (EDS) was measured to gain the elemental mapping results. Thermogravimetric (TG) analysis (Perkin-Elmer TGA 7 thermogravimetric analyzer) was used to evaluate the sulfur content of TiO_2/S cathode at a heating rate of 5 °C/min from 40 °C to 600 °C in flowing N_2. The pore size distributions and specific surface area of TiO_2/S cathode were measured by TriStar II 3020 3.02 (Micromeritics Instrument Corporation, USA).

2.4 Electrochemical Performance Measurements

CR2025 coin cells were prepared in a glove box, which is filled with argon and conducted electrochemical testings. The working cathode was fabricated by coating a mixture containing 10 wt% polyvinylidene fluoride (PVDF) as a binder dissolved in NMP, 10 wt% carbon black and 80 wt% active material (nanofiber TiO_2/S) on an aluminum foil following by drying at 60 °C for 12 h. Then the electrode disks were punched. Li metal was used as the anode. The electrolyte was a solution of 1.0 M LiTFSI dissolved in a mixture of dioxolane (DOL) (99.8%, Sigma-Aldrich) and 1,2-dimethoxyethane (DME) (99.5, Sigma-Aldrich) (1:1 by volume) with $LiNO_3$ (1 wt%) additive. Separator (Celgard 2400) was bought from Celgard Company. CR2025 coin cells were assembled in an argon filled glovebox with water and oxygen content kept below 0.1 ppm and used for electrochemical tests. Galvanostatic charge/discharge cycling was carried out using a LAND-CT2001A instrument (Wuhan, China) in the voltage range 1.5 to 3 V.

3 Results and Discussion

Figure 1 shows the fabrication and electrochemical process of TiO_2/S composite as cathode for Li–S battery. In step 1, the smooth of TiO_2/PVP nanofibers was fabricated by electrospinning. Followed by pyrolysis of PVP, which is pyrolyzed into CO_2 and H_2O at high

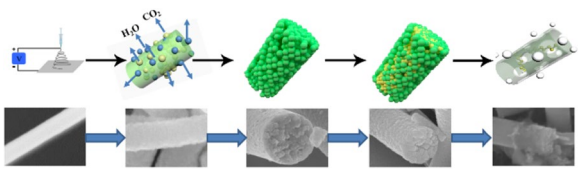

Figure 1 Schematic representation of the fabrication and cycle for TiO_2/S composite cathode, and the following diagram is corresponding SEM

temperature calcination in Air-flow, the TiO_2 nanofibers with mesoporous structure could be gained. In step 4, the TiO_2 infused with sulfur forming the TiO_2/S cathode. The sulfur elements are uniformly distributed in the TiO_2 nanofibers because of the mesoporous structure and polar metal-O bond. After testing for 200 cycles, clear and smooth surface of TiO_2/S composite electrode can be observed from the typical SEM images (in step 5), which improving the electrochemical performance.

The SEM images of the synthesis PVP/TiO_2 composite nanofiber by electrospinning are shown in Figure 2. Figure 2(a) shows a typical low-magnification SEM image of PVP/TiO_2 composite fibers (the average diameter is about 200 nm). The high-magnification SEM image of the composite nanofibers with smooth surface (Figure 2(b)). After electrospinning, the composite nanofibers were calcined to obtain pure TiO_2 nanofibers. From the Figure 2(c) and (d), the TiO_2 nanofibers with the average diameters about 200 nm were synthesized. Cross sections of enlarged TiO_2 nanofibers in Figure 2(d) clearly shows that the fibers are very rough with many wormhole-like pores which could be used as good sulfur host to infuse high content of sulfur.

After preparing of TiO_2/S, the morphology of the TiO_2 nanofibers as the host could not be changed after the infusion of sulfur (as shown in Figure 3(a) and (b)). The TEM images of TiO_2 nanofibers before and after infusion of sulfur are shown in Figure 3(c), (d). The mesoporous structure can be clearly seen in the TEM image of TiO_2 nanofibers, these porous structure was disappeared in the TEM image of TiO_2/S nanofibers, reflecting the good infusion of sulfur by mesoporous structure in TiO_2 nanofibers. The HRTEM image (Figure 3(e)) reveals the clear lattice fringe spacing is 0.35 nm, which is consistent with the (101) crystalline interplanar spacing of TiO_2 structure. Additionally EDS area mapping showing in Figure 3(f), and can see the elemental of Ti, O, and S homogeneous distribution in all over the fiber.

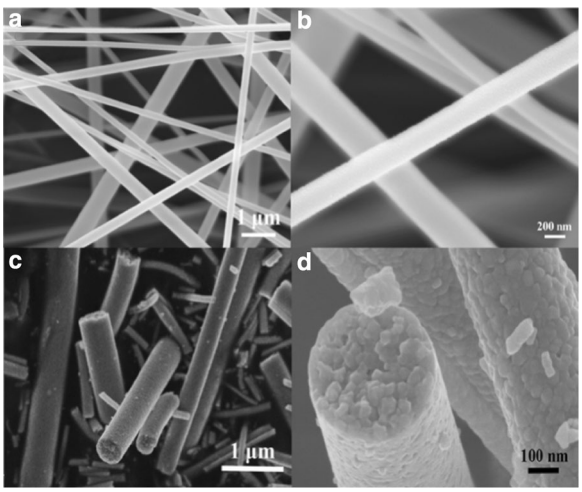

Figure 2 SEM images of the as-spun PVP/TiO_2 composite nanofibers: **a** the lower magnification and **b** the higher magnification, and after calcination the TiO_2 nanofibers: **c** the lower magnification and **d** the higher magnification

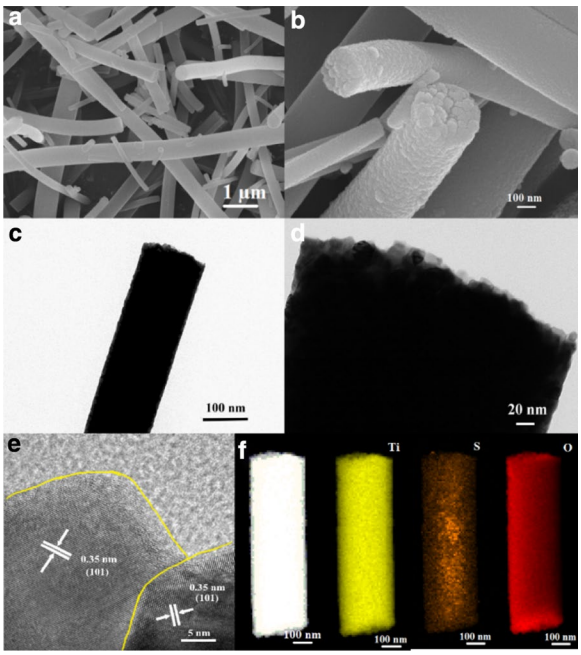

Figure 3 SEM images of the TiO_2/S composite nanofibers: **a** lower magnification, **b** higher magnification, **c** TEM images of the TiO_2 nanofibers, **d** TEM images of the TiO_2/S nanofibers, **e** HRTEM image of the (**c**), **f** corresponding EDS mapping for elemental titanium, oxygen and sulfur

The XRD patterns of TiO_2 and TiO_2/S nanofibers are shown in Figure 4 to confirm the crystal phase formation about synthesized TiO_2 nanofibers and the existence of sulfur about TiO_2/S nanofibers. The XRD pattern of TiO_2 nanofibers demonstrates that TiO_2 possesses almost pure rutile (JCPDS No. 65-0191) structure [19, 20]. Then, the XRD pattern of TiO_2/S composites was well defined for orthorhombic structure of crystalline sulfur (JCPDS Card No. 08-0247), which is identical to the element sulfur powder [5, 21]. It reveals the TiO_2 nanofibers with sulfur loading have been synthesized successfully.

The nitrogen adsorption and desorption isotherms of the TiO_2 and TiO_2/S composite were obtained, which correspond to type IV isotherms in the IUPAC classification with a typical mesopore hysteresis loop, from Figure 5(a) [22, 23]. Notably, compared with TiO_2/S composite, TiO_2 has larger pore volume and specific surface area. The pore size distribution of TiO_2 fibers is in the range of 20–30 nm by Barrett-Joyner-Halenda as shown in Figure 5(a) inset. After sulfur incorporation, the fibers

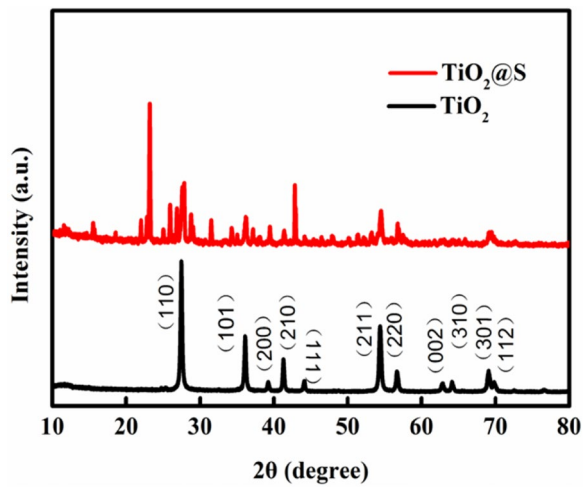

Figure 4 XRD patterns of as-spun electrospun TiO_2 and TiO_2/S nanofibers

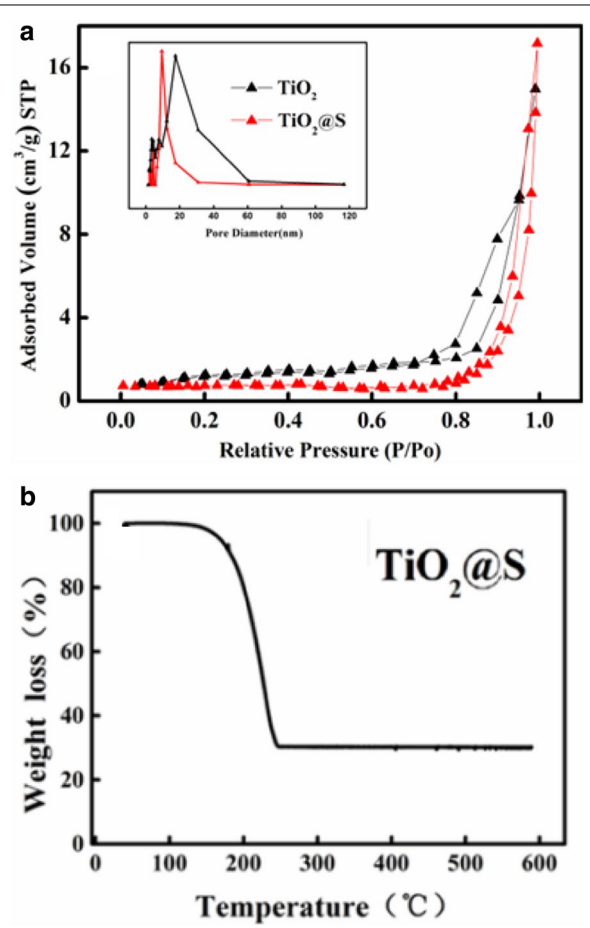

Figure 5 **a** Nitrogen adsorption-desorption isotherms and corresponding pore size (inset) distribution of TiO_2, TiO_2/S composite, **b** Thermogravimetric plot of TiO_2/S composite in Ar atmosphere heating from room temperature to 600 °C

pore distribution decrease to 10–20 nm, because S particles is covered on or embedded into the mesopores of TiO_2 fibers. To evaluate the content of sulfur in TiO_2/S composite, thermo gravimetric (TGA) was performed from room temperature to 600 °C at a heating rate of 10 °C/min under N_2 atmosphere. The sulfur content in TiO_2/S nanocomposite (Figure 5(b)) is estimated as high as 70 wt%, which demonstrates such higher sulfur loading.

Figure 6(a) and (b) display the galvanostatic the discharging-charging curves of the TiO_2/S composite electrode at a current rate of 0.2 and 0.5 C (1 C = 1672 mA/g). The profile apparently shows the two plateaus in the discharging curves, which could be assigned to the two-step reaction of sulfur with lithium. The first plateau, at 2.35 V, was due to the reduction of sulfur to higher polysulfide. The low voltage plateau, at 2.1 V, showed the reactions of the higher polysulfides (Li_2S_n, $4 \le n \le 8$) finally the further to the lower polysulfides (Li_2S_n, $n \le 3$) [24–27]. And the initial discharge capacity and charge capacity of as prepared electrode were 763 mAh/g and 827 mAh/g at 0.2 C, respectively. And at 0.5 C as shown in Figure 6(b), the electrode discharge capacities was found to be 423 mAh/g, and charge capacities was 405 mAh/g.

The excellently stable cycling performance of TiO_2/S composite electrodes at different current densities have been shown in Figure 6(c). The TiO_2/S electrodes exhibit the excellent capacity retention at 0.1, 0.2 and 0.5 C. The initial discharge capacity was 703 mAh/g and the capacity remained at 652 mAh/g after 200 cycles at 0.1 C. Figure 6(d) is the discharge rate capability performance with 100 cycles at different current densities. When the current density is increased to 0.2, 0.5 and 1 C, the discharge

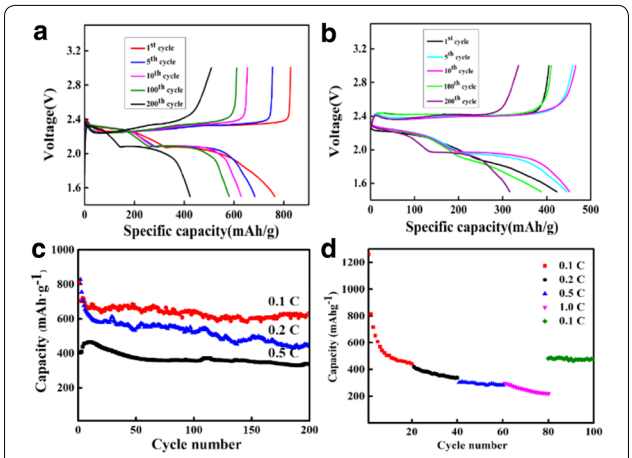

Figure 6 Electrochemical performance of TiO_2/S nanocomposite structures. Galvanostatic charge-discharge voltage profiles of TiO_2/S cathodes between 1.5 and 3.0 V at **a** 0.2 C, **b** 0.5 C, **c** Cycling performance of TiO_2/S cathodes at a current density of 0.1 C, 0.2 C and 0.5 C, **d** Rate capability of TiO_2/S composite electrodes at various current densities from 0.1, 0.2, 0.5 to 1 C

capacities are 498, 402 and 298 mAh/g. When the current density returns to 0.1 C, the reversible capacity was recovered to 613 mAh/g, indicating the reliability and stability of the TiO_2/S composite electrode.

The SEM images of the TiO_2/S cathode after cycled 200 times are displayed in Figure 7(a). The TiO_2/S fibers are still maintains the original fiber structure, although the some nanowire structure was destroyed. From Figure 7(b)–(d), the cathode elemental of Ti, O, and S still displays homogeneous distribution. It reveals that sulfur could be trapped in the nanofibers after 200 cycles, and further shows the advantages of mesoporous nanofibers in repeated cycling, which accordingly enhances the cyclic stability and rate capability. Figure 7(e) is corresponding reaction mechanism of the TiO_2/S cathode during cycling. In the discharge process, S_8 (elemental sulfur) in the nanofibers is combined with the Li^+ from the anode, and reduced to form soluble Li_2S_n ($2 \leq n < 8$), which is also trapped in the mesoporous structure without diffused into the electrolyte and transferred to anode [28]. Then the soluble Li_2S_n is further reduced to insoluble Li_2S. Because the process of elemental sulfur reacted to form lithium polysulfide and eventually to lithium sulfide, which is always carried out in TiO_2 nanofibers, it could prevent the soluble lithium sulfide from being dissolved in the electrolyte, indicating the remission of the "shuttle effects". Meanwhile, the volume expansion caused by the conversion of sulfur into lithium sulfide could be alleviated, because of TiO_2 nanofibers with mesoporous structure. The electrochemical performance comparison of the TiO_2–S composite between the current work and previously reported in Table 1. It shows that the TiO_2 nanofibers with mesoporous structure in our work improved cycle stability of cathode for Li–S battery.

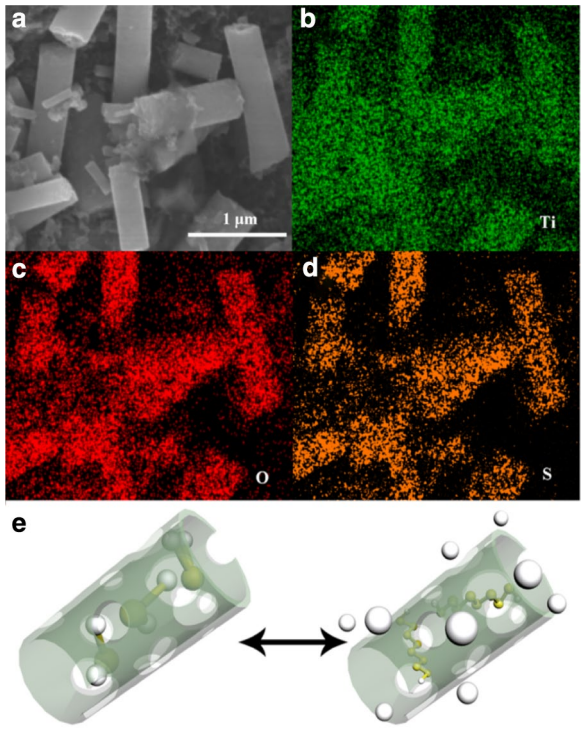

Figure 7 **a** SEM and **b**–**d** elemental mapping results of TiO_2/S cathode cycled 200 times at 0.1 C rate between 1.5 and 3.0 V, **e** schematic diagram of mutual transformation between S_8 and Li_2S at the mesoporous TiO_2 nanofibers structure

Table 1 Electrochemical performance comparison of TiO_2-S with different morphologies in previously reported

Cathode material	Cycle number	Cycling stability	Ref. No.
TiO_2 rods/S	50	530 mAh/g (0.2 C)	[5]
TiO_2 sphere/S	100	371 mAh/g (1.0 C)	[18]
Mesoporous TiO_2 /S	100	676 mAh/g (0.5 C)	[8]
TiO_2 sphere/S	100	705 mAh/g (0.5 C)	[27]
TiO_2 nanofibers /S	200	652 mAh/g (0.1 C)	This work

Therefore, it is owing to the following reasons of TiO_2 nanofiber with mesoporous structure as highly efficient sulfur host for improving cycle stability and high efficiency of battery. Firstly, TiO_2 possesses the excellent catalytic dissociation ability of lithium polysulfides. And rutile phase TiO_2 can in-situ adsorb the lithium polysulfides by stable chemical bonding force leading to further trapping of polysulfide anions [29]. Secondly, the interconnected fiber architecture provided fast pathways for electron/ion transfer and the mesoporous structure provide enough large surface to infuse sulfur while physically absorbing soluble lithium polysulfides and accommodating volume changes by the charge/discharge reactions.

4 Conclusions

TiO_2 nanofibers with mesoporous structure were prepared by post thermal-treatment of electrospun. The fibers as the superior host material to load sulfur up to the 70 wt % for Li–S batteries. The TiO_2/S cathode demonstrated cycle stability and high efficiency. The TiO_2/S cathode maintains a capacity of 652 mAh/g at 0.1 C after 200 cycles, corresponding to a capacity retention of 92.7%. The mesoporous TiO_2 fibers enhance the conductivity of sulfur, promote the utilization of sulfur and provide large active sits to absorb soluble lithium polysulfides. The mesoporous TiO_2 nanofibers as cathode

host material has great potential in high-performance lithium–sulfur batteries.

Authors' Contributions

LD and ZG was in charge of the whole trial; XS wrote the manuscript; XZ and JY assisted with sampling and laboratory analyses. All authors read and approved the final manuscript.

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Acknowledgements

The authors sincerely thanks to Feifei Zhang of National University of Singapore and Junkai Wang of University of Chinese Academy of Sciences for their critical discussion and reading during manuscript preparation.

Competing Interests

The authors declare that they have no competing interests.

Funding

Supported by National Nature Science Foundation of China (Grant No. 61774022) and Education Department of Jilin Province of China (Grant No. JJKH20181030KJ).

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Received: 25 May 2019 Revised: 20 June 2019 Accepted: 1 July 2019
Published online: 17 July 2019

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