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Flexible and Hierarchically Structured Sulfur Composite Cathode Based on the Carbonized Textile for High-performance Li-S Batteries

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ABSTRACT

Carbon hosts have been utilized to obtain composite cathodes with high sulfur loadings for Li-S battery. However the complicated synthesis process may hinder their practical applications. Besides, their mechanical and electrochemical properties shall be further improved. Herein, a facile scalable dip-coating process is developed to synthesize a flexible composite cathode with a high sulfur loading. Via the process, a hybrid composed of carbon nanotubes, carbon black, sulfur and titania nanoparticles is successfully conformally coated on the carbonized textile (c-

textile). The formed flexible c-textile@S/TiO₂ cathodes with sulfur loadings of 1.5 and 3.0 mg cm⁻² can deliver reversible discharge capacities of 860 and 659 mA h g⁻¹ at 2C, respectively. For the latter one, it can retain 94% of the initial capacity after 400 cycles with a high Coulombic efficiency (~96%). When its sulfur loading is further increased to 7.0 mg cm⁻², its areal capacity reaches 5.2 mA h cm⁻². Such excellent performance is ascribed to the synergy effect of three dimension conductive hierarchical pore structure and TiO₂ additive. They can physically and chemically entrap the soluble polysulfides in the composite cathode. The as-synthesized free-standing composite electrode is of low cost and a high areal capacity, enabling it suitable for the flexible energy storage applications based on Li-S batteries.

INTRODUCTION

Rechargeable batteries with high energy densities are very attractive for the next-generation electric-energy storage systems and have great potentials in plug-in hybrids, portable electronic devices and all-electric vehicles (EVs).¹ Among existing devices, lithium-sulfur (Li-S) battery has been considered one of the most promising candidates owing to its high theoretical energy density (2600 Wh kg⁻¹), low cost, and environmentally friendliness.¹⁻⁴ Despite these advantages, Li-S battery is faced with several challenges. For example, the insulating nature of sulfur and reduction products (Li₂S₂ and Li₂S) reduces the utilization of the active materials.⁵ “Shuttle effect” of the soluble polysulfides (PSs), the reaction intermediates (Li₂S_n, 4≤n≤8), between the cathode and anode can lead to the loss of active sulfur, rapid capacity decay and low Coulombic efficiency.^{6,7} Another failure mechanism is the large volumetric variation (~80%) of sulfur electrode during the lithiation process, causing the detachment of the active material from the conductive substrate/matrix.⁸

To address the aforementioned challenges, one effective strategy is to impregnate sulfur into the conductive hosts (porous carbon, graphene, conductive polymer, carbon fiber cloth etc.).⁹⁻¹² Among them, carbon nanotube (CNT) is one of the most promising candidates due to its high conductivity which can greatly improve the utilization and rate-capability of sulfur cathodes.^{13,14} Besides, pores inherent in CNTs or their self-assembled networks can provide reservoirs for the soluble intermediate PSs and accommodate the strain/stress due to the volume changes.¹⁵⁻¹⁷ Additionally, CNTs have potential applications for the flexible electronic devices because of their outstanding mechanical properties.^{18,19} Though the high sulfur loading could be achieved in CNT-based cathodes, their capacity retention and rate-capability were not satisfying unless high percentage (≥ 30 wt%) of CNTs was used.²⁰⁻²⁴ Recently, there were breakthroughs on the high-loading sulfur cathodes by using thick carbon hosts with large and open pores.^{8,25-27} For example, the sulfur/hollow carbon fiber foam electrode exhibited a high areal capacity of $12.0 \text{ mA h cm}^{-2}$ with a sulfur loading of 16.5 mg cm^{-2} . The good performance was partially ascribed to the large pore volume in the foam. The volume could absorb a large amount of soluble PSs and electrolytes, which were essential for the long cycling-stability of the high-loading sulfur cathode.²⁶ However, their thickness ($\sim 2 \text{ mm}$) might be detrimental to the initial packaging of Li-S batteries. Meanwhile, the flexibility and their energy density of the electrodes could be further improved. Additionally, most of the carbon hosts were nonpolar, therefore they were ineffective to entrap the polar PSs. Recently inspired by the concept of surface chemistry, many polar host materials (e.g., TiO_2 , Co_3O_4 , and metal-organic frameworks (MOFs))²⁸⁻³¹ were adopted to strengthen the affinity between PSs and the cathode composite, leading to improved electrochemical performance. Unfortunately, the conductivities of these materials were very low, which unavoidably compromised the rate capability. Overall, long term (≥ 300 cycles) cyclability

and high rate performance ($\geq 2C$ -rate) were rarely demonstrated when the areal sulfur loading was higher than 3.0 mg cm^{-2} . Therefore, it is still a great challenge to improve the sulfur utilization, and at the same time achieve satisfactory capacity for the high sulfur loading even at high current densities with good capacity retention. A feasible solution is to reduce the dimension of sulfur particles, enhance the uniform distribution of sulfur in the conductive carbon framework and use polar metal oxides additive as PS immobilizer at the same time.³²

Solution process of CNTs was previously used to turn textile, paper, fabric and sponge into the conductive electrode materials for supercapacitors or the current collectors.³³⁻³⁵ However, to our knowledge, active materials together with carbon nanotubes, have not been coated onto the textile materials to form the composite cathode for lithium ion batteries via the dip-coating process. Herein, we demonstrated a simple dip-coating and drying process to synthesize a flexible and robust three-dimensional (3D) composite cathode. It was composed of carbonized textile (c-textile), on which carbon nanotube together with sulfur and titania nanoparticles were conformally coated. The formed c-textile@S/TiO₂ composite cathode could deliver a discharge capacity of 860 mA h g^{-1} at a current rate of 2C and a reversible specific capacity of 814 mA h g^{-1} was achieved at 4C with sulfur loadings of 1.5 mg cm^{-2} . Remarkably, we further confirmed that the cathode retained superior cycling stability, corresponding to 94% capacity retention at 2C after 400 cycles with sulfur loadings of 3.0 mg cm^{-2} . For all we knew, such long-term cyclability at a high rate of 2C was rarely reported when the areal sulfur loading was higher than 3.0 mg cm^{-2} . Additionally, the c-textile@S/TiO₂ composite cathode with 7.0 mg cm^{-2} sulfur loading delivered a high areal capacity of 5.2 mA h cm^{-2} , higher than the current commercial level (~ 3.0 - 4.0 mA h cm^{-2}). Such outstanding performance was ascribed to the hierarchical pore structure

and conductive network of the composite sulfur cathode, together with chemical adsorption of TiO_2 on the soluble PSs.

EXPERIMENTAL SECTION

Synthesis of carbonized textile. The carbonization of bamboo textile was performed as previously reported.³⁶ Typically, a piece of commercially-available bamboo textile was soaked in 50 ml NaF solution and kept for 1h. Then the textile was dried in oven at 120 °C for 2h. Finally the NaF-treated bamboo textile was carbonized at 900 °C for 1h in the tube furnace under argon atmosphere. After cooled to room temperature, the as-obtained carbonized textile was washed with distilled water several times and dried at 120 °C.

Synthesis of S/CNT hybrid. Raw MWCNTs (30-50nm, Chengdu, China) were dispersed into 1.0 wt% sodium dodecyl sulfate (SDS, AR) aqueous solution at a concentration of 1.0 mg/ml by combining vigorous stirring and sufficient ultrasonication to ensure a homogeneous CNT dispersion. While the sublimed sulfur (AR) was dissolved into tetrahydrofuran (THF) to get a precursor solution with a concentration of 0.30 M. The sulfur precursor solution was then added into CNT dispersion with vigorous stirring. The weight ratio of sulfur and MWCNTs was controlled as 90:5 in the mixture. CNT/S hybrid was separated and washed with distilled water three times by high-speed centrifugation. SDS was also removed in this washing process. Pure sulfur nanoparticles were prepared by the same method, but without the addition of MWCNTs.

Synthesis of c-textile@S and c-textile@S/TiO₂ cathodes. To synthesize c-textile@S, 190 mg (95 wt%) CNT/S hybrid and 10 mg (5 wt%) Super P were dispersed in 10 ml NMP. Subsequently, c-textile was soaked into the dispersion and then taken out. After dried at 60 °C

overnight, c-textile@S composite was formed. The sulfur loading could be controlled by varying the times of soaking. The sulfur loading of the cathode could be calculated with the equation as followed:

$$\text{Sulfur loading} = (W_2 - W_1) \times 88\%$$

W_1 and W_2 were weights of c-textile before and after the dip-coating and drying process.

For the preparation of c-textile@S/TiO₂ cathode, the percentages of raw materials were slightly adjusted as 92 wt% CNT/S, 5 wt% Super P carbon black and 3 wt% TiO₂ (5-10nm, Aladdin, Shanghai, China). The rest of the preparation procedures were the same. For comparison, 80 wt% of sulfur nanoparticles, 10 wt% of super P carbon black, and 10 wt% of PVDF binder were dispersed in NMP solution to form slurry. The formed slurry was then spread onto a carbon-coated aluminum foil with doctor-blading method, dried and pressed to form the nano-S/CB/PVDF electrode with the sulfur loading of $\sim 1.0 \text{ mg cm}^{-2}$.

Electrochemical Characterization. The electrodes were cut into the round disks with a diameter of 12 mm with a corresponding area of 1.13 cm^2 . The areal sulfur loading was in the range of $1.5 \sim 7.0 \text{ mg cm}^{-2}$, equivalent to a mass loading range of $1.7 \sim 7.9 \text{ mg}$. The electrodes, Li metal foil as anode and Celgard 2400 membrane as separator were assembled into 2016-type coin cells inside an argon-filled glovebox. The used electrolyte was composed of 1M bis(trifluoromethane) sulfonamide lithium salt (LiTFSI) with 1 wt% LiNO₃ dissolved in a mixture of 1,3-dioxolane (DOL) and dimethoxymethane (DME) (1:1 ratio, by volume). The amount of electrolyte in the coin cell with the areal sulfur loading of 1.5 mg cm^{-2} was 50 μL . When the areal sulfur loadings were increased to 3.0, 5.0 and 7.0 mg cm^{-2} , the corresponding amounts of electrolyte were 80, 130 and 160 μL , respectively. The galvanostatic discharge/charge

measurements were conducted at a voltage range of 1.7-2.8 V using a Land battery test system (Land Electronic, Wuhan, China). The CV and EIS measurements were performed on AutoLab 302N electrochemical workstation. The scan rate for CV measurements was set as 0.2 mV/s. The frequency range of EIS measurements was from 100 kHz to 0.01 Hz with an AC voltage amplitude of 5 mV.

Structure Characterization. Field-emission scanning electron microscope (FESEM, Philips XL30 FEG) and transmission electron microscope (TEM, JEOL JEM-2010) were used to characterize the morphologies and structures of the samples. Thermogravimetric analysis (TGA, Shimadzu DRG-60) was used to determine the content of each component in the hybrids. To measure the TiO₂ content in the CNT/S/CB/TiO₂ composite, TGA was performed in air flow, while the sulfur content in the CNT/S/CB composite was determined in N₂ flow.

RESULTS AND DISCUSSION

The synthesis process of the flexible composite cathode was illustrated in Figure 1. Sublimed sulfur was first dissolved into tetrahydrofuran to get a sulfur solution.³⁷ Meanwhile, multi-walled

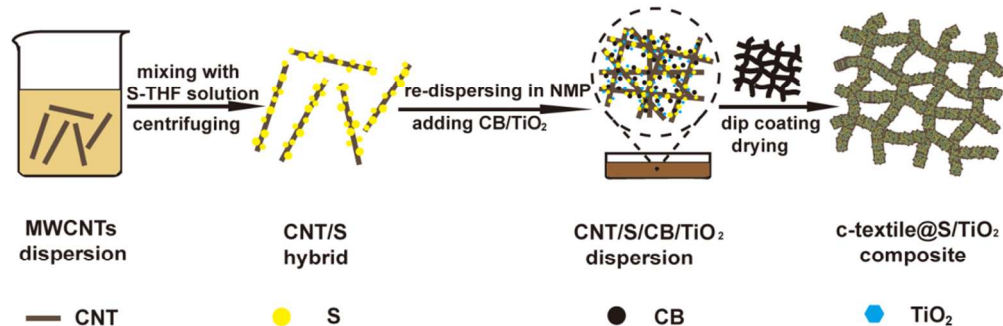


Figure 1. Schematic illustration of the structure and synthesis process of c-textile@S/TiO₂ composite.

CNTs (MWCNTs) with diameters of 30-50 nm were dispersed in the aqueous solution with sodium dodecyl sulfate (SDS) as a surfactant by ultrasonication.³⁴ Owing to the different solubility of sulfur in the solvents, sulfur particles precipitated from the solution and formed CNT/S mixture when the sulfur solution was added into CNT dispersion with continuous stirring.^{18,38} The anchoring of sulfur particles on CNTs might be due to the hydrophobic nature of the two materials. CNT/S hybrid was then separated and dispersed in NMP solution with carbon black (CB) and titania to form the CNT/S/CB/TiO₂ hybrid dispersion for dip-coating. Conductive c-textile as the host for dip-coating was synthesized by heating the textile of bamboo textile at 900 °C for 1h in argon. c-textile was then dipped in the CNT/S/CB/TiO₂ dispersion and dried to form the composite cathode (c-textile@S/TiO₂). The photographs of the obtained raw textile, c-textile and c-textile@S/TiO₂ composite cathodes were shown in Figure S1a, S1b and 2a, respectively. c-textile exhibited superior mechanical flexibility, allowing it to be bent, wrinkled and kneaded (see Video S1 and Figure 2a). Scanning electron microscopy (SEM) images in Figure 2b and 2c showed the microstructure of c-textile. It remained the morphology of the textile, which was interwoven with bundles of the long fibers. The thickness of c-textile was estimated to be ~180 μm with an areal mass of 4.0~4.5 mg cm⁻². Its sheet resistance (R_s) was measured to be ~1 Ω/sq. SEM images (Figure 2d-f) of the c-textile@S/TiO₂ composite cathode with sulfur mass loading of 3.0 mg cm⁻² showed a similar morphology as that of c-textile. However, coarser morphology was observed in SEM and transmission electron microscopy (TEM) images (Figure 2g-2h) at the higher magnifications. The outside layer of the fiber in the composite was of intertwined CNTs and sulfur nanoparticles with size of 25-40 nm. The size was smaller than that of the sulfur nanoparticles from the solvent-exchange process without CNTs.³⁷ In the precipitation process, CNTs might provide the grafting sites and prevent the coalescence

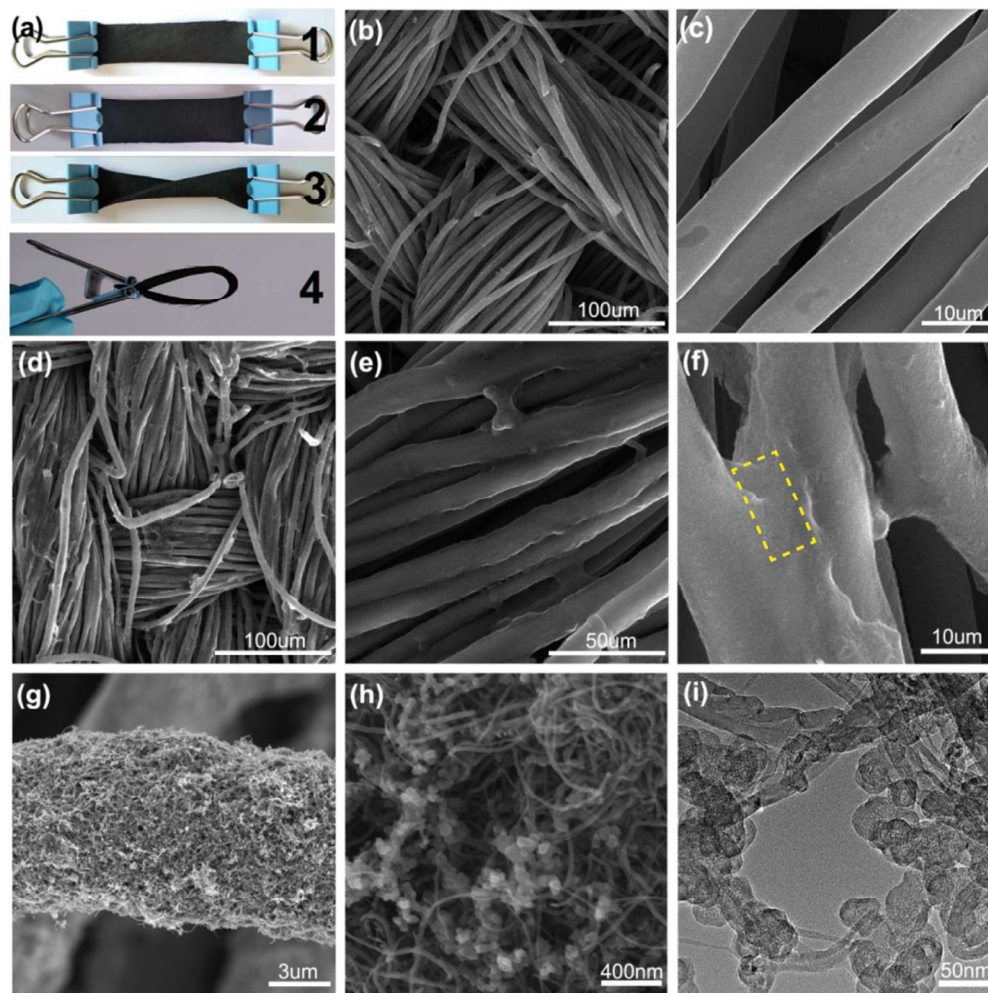


Figure 2. a) Photographs of the obtained 1) c-textile and 2,3,4) c-textile@S/TiO₂ composite; b, c) SEM images of the c-textile; d, e, f, g) SEM images of the c-textile@S/TiO₂ composite with sulfur mass loading of 3.0 mg cm⁻² (CNT bridging is marked in the yellow rectangle in f); h) and i) SEM and TEM images of the outside layer of a fiber in the composite, respectively.

of sulfur nanoparticles.³⁹ It was surprising to find out that R_s only increased to $\sim 8 \Omega/\text{sq}$, considering the weight ratio of CNT: S was 5: 90. The excellent electrical property of the composite was partially due to the CNT bridging between neighboring fibers, as shown in the yellow rectangular area in Figure 2f. The CNT/S/CB/TiO₂ hybrid was adhered tightly on c-textile. Only a very small fraction of CNTs were found to be peeled from the composite in the

tape adhesion test (see Video S2). The excellent mechanical property of the composite cathode made it possible for roll-to-roll fabrication of the energy storage devices. Figure 2h showed that an open porous structure was formed in c-textile@S/TiO₂ composite, and no large sulfur agglomerates were found. TEM images (Figure 2i) of outside layer of the fibers in the composite confirmed the good dispersion of sulfur nanoparticles, which were intimately anchored onto MWCNTs. The pores with size of several tens to hundreds of nanometers among MWCNTs could be observed, however no pore was measured in the fibers of textile, as indicated in its nitrogen absorption-desorption isotherms (Figure S2). The 3D macroporous structure inherited from the textile and the mesopores formed among CNTs composed the hierarchical pore structure in the composite. The structure was able to retain a large amount of the electrolyte and soluble PSs and facilitate the transport of lithium ions.^{8,24,25,27,40} which was good for the high-power Li-S batteries. Recently, TiO₂ was found to be an efficient sulfur mediator, which could greatly enhance the electrochemical performance of sulfur cathode.^{31,41-43}

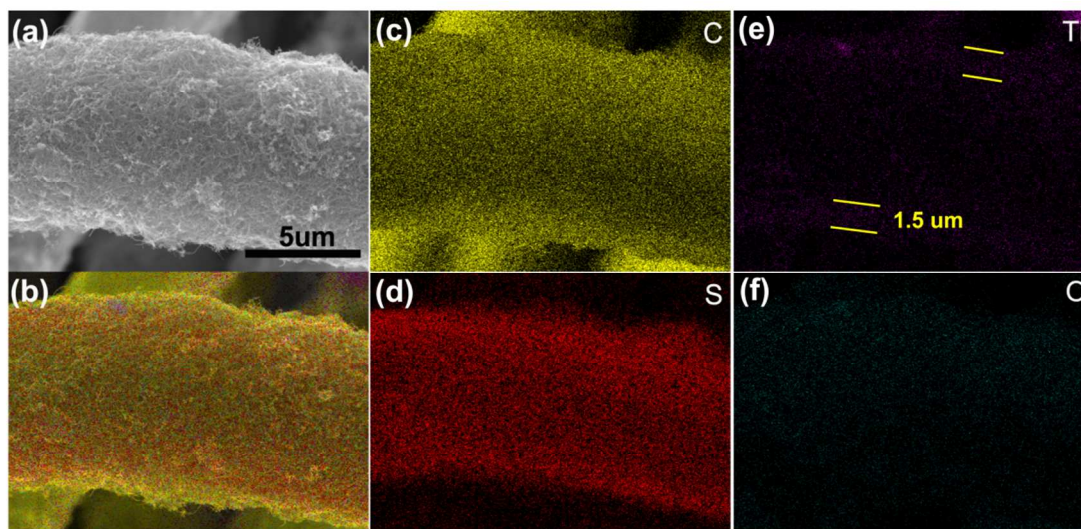


Figure 3. a) SEM image of a fiber in the c-textile@S/TiO₂ composite cathode; b) overlapped element mapping of the fiber, and the corresponding element mapping images of c) carbon, d) sulfur, e) titanium and f) oxygen.

In the current research, TiO_2 nanoparticles were also successfully incorporated in the intertwined MWCNTs by the dip-coating process, as confirmed by the element mapping images (Figure 3). Above result confirmed that the CNT/S/CB/ TiO_2 hybrid was successfully conformally coated onto the long carbon fiber of c-textile. The self-assembly of conformal coating was due to Van der Waals force among the nanoparticles induced by the evaporation of the solvent. From the Ti element image as shown in Figure 3e, the thickness of conformal coating layer was roughly estimated to be $\sim 1.5 \mu\text{m}$. SEM analyses of the CNT/S/CB hybrids without (Figure S3a) and with TiO_2 (Figure S3c) additive revealed that the introduction of tiania in the composite improved the distribution homogeneity of the sulfur nanoparticles. The sulfur contents in the hybrids were calculated to be 88% and 86% with thermogravimetric analyses (TGA; Figure S3b and S3d) of CNT/S/CB and CNT/S/CB/ TiO_2 hybrids, respectively. The values were basically consistent with 90% and 87%, the determined sulfur percentages in the raw materials, respectively. Hence, the sulfur contents in the composite were calculated with the mass changes before and after the dipping and drying process together with the percentage of sulfur in the raw materials.

To evaluate the electrochemical performance of the composites, CR2016 coin cells with c-textile@S/ TiO_2 and c-textile@S as cathodes were assembled and tested, respectively. Figure 4a showed the cyclic voltammetry (CV) profiles of the c-textile@S composites within a potential window of 1.7-2.8V. Two well-defined reduction peaks in the cathodic scan were observed with a scan rate of 0.2 mV s^{-1} . The peak at $\sim 2.30 \text{ V}$ corresponded to the conversion of element sulfur (S_8) to the high-order lithium polysulfide (e.g. Li_2S_x , $4 \leq x \leq 8$). The strong cathodic peak at $\sim 1.99 \text{ V}$ suggested the further reduction of soluble polysulfides to solid-state $\text{Li}_2\text{S}_2/\text{Li}_2\text{S}$. In the subsequent anodic scan, two oxidation peaks existed distinctly at 2.39 and 2.46 V, suggesting the

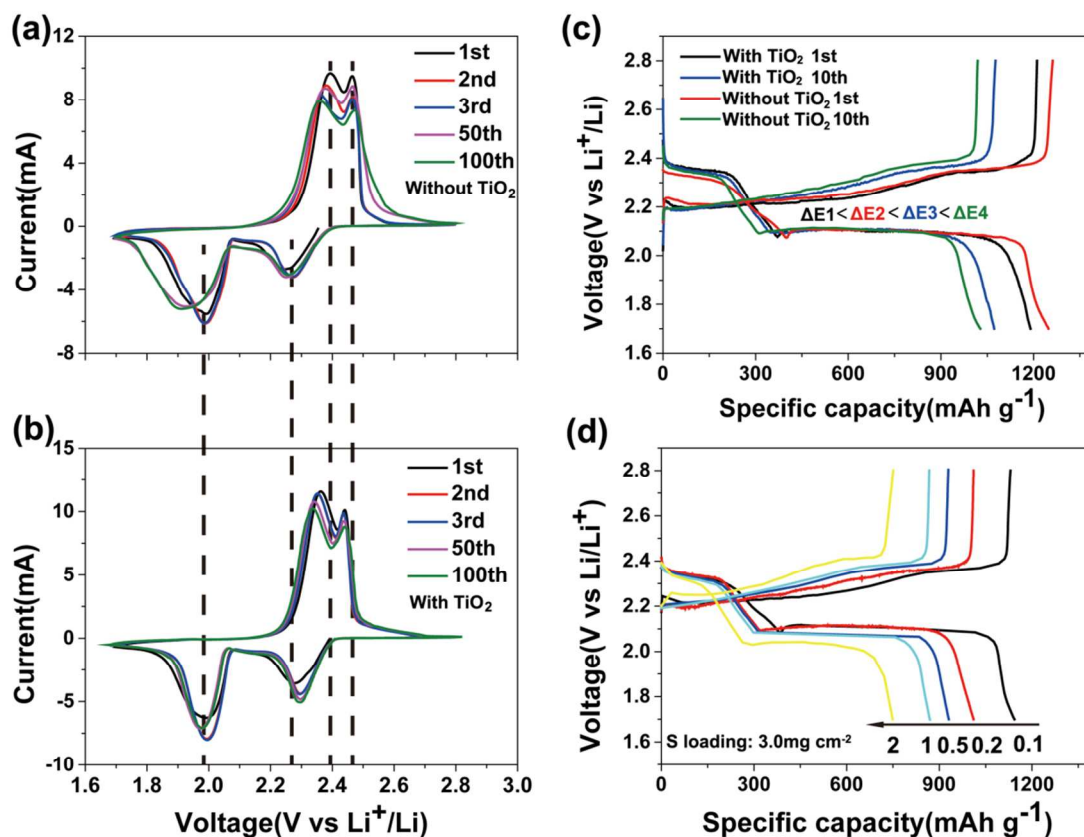


Figure 4. a) and b) CV profiles of the c-textile@S and c-textile@S/TiO₂ cathodes at 1st, 2nd, 3rd, 50th and 100th cycle, respectively; c) galvanostatic discharge-charge profiles of the c-textile@S and c-textile@S/TiO₂ cathodes at 0.1C; d) galvanostatic discharge-charge profiles of the c-textile@S/TiO₂ cathode at the different current densities.

reversible conversion from Li₂S to PSs, and from PSs to element S, respective.^{14,16,42,44} However, in the CV curves (Figure S4) of conventional S/CB/binder cathode, only one anodic current peak at 2.5 V could be detected during the initial three cycles. The appearance of single peak was due to the increased electrode resistance and slower dynamics, which agreed with previous reports.⁴⁵⁻⁴⁷ Large variation of the locations of the anodic peaks for c-textile@S was observed in the subsequent cycles. This phenomenon was ascribed to the rearrangement of sulfur nanoparticles from their original positions to more energetically stable sites.^{13,48-50} No significant changes

appeared in the CV profile (Figure 4b) of the c-textile @S/TiO₂ cathode, implying TiO₂ facilitated the uniform distribution of active sulfur, as confirmed by Figure S3c. Moreover, compared with c-textile@S cathode, its cathodic peaks became stronger and exhibited a slight positive shift, whereas its anodic peaks gradually shifted to lower potentials, indicating a more facile redox activity.⁴⁹ The almost overlapped voltage profiles after 50 and 100 cycles for c-textile@S/TiO₂ cathode indicated that the addition of TiO₂ could enhance the stability of sulfur electrode. The anodic peak at 2.46 V related to the conversion from PS to element S became weaker (Figure 4b) because the electrostatic attraction existed between TiO₂ and PS, and less PS was converted to sulfur.⁴² It was consistent well with its lower initial capacity shown in the initial galvanostatic discharge/charge curve (Figure 4c). The curves also indicated that the electrodes underwent a typical two-plateau behavior. The voltage hysteresis (ΔE) between reduction and oxidation plateau voltages for c-textile@S/TiO₂ cathode was smaller than c-textile@S cathode, which indicated that the cell had a better reversibility and less polarization on c-textile@S/TiO₂ cathode.⁵¹ Figure 4d showed the charge/discharge plots of c-textile@S/TiO₂ cycled at various current densities. Though the voltage hysteresis increased when current densities increased, its voltage hysteresis at each current density was smaller compared with that of the c-textile@S (Figure S5). The rate performance of the composite electrodes was shown in Figure 5a and 5b. The c-textile@S composite with the loading of 1.5 mg cm⁻² delivered a high discharge capacity of 1262 mA h g⁻¹ in the first cycle at 0.1C, indicating easy electrochemically activation of sulfur owing to its nanosize and superior conductivity of the carbon network. Its capacity dramatically dropped in the following cycles. It was due to the loss of soluble PSs into the electrolyte because of the extremely high content (~88 wt%) of sulfur in the hybrid.^{8,52-54} Contrary to c-textile@S, the composite with TiO₂ additive exhibited a slight capacity decay,

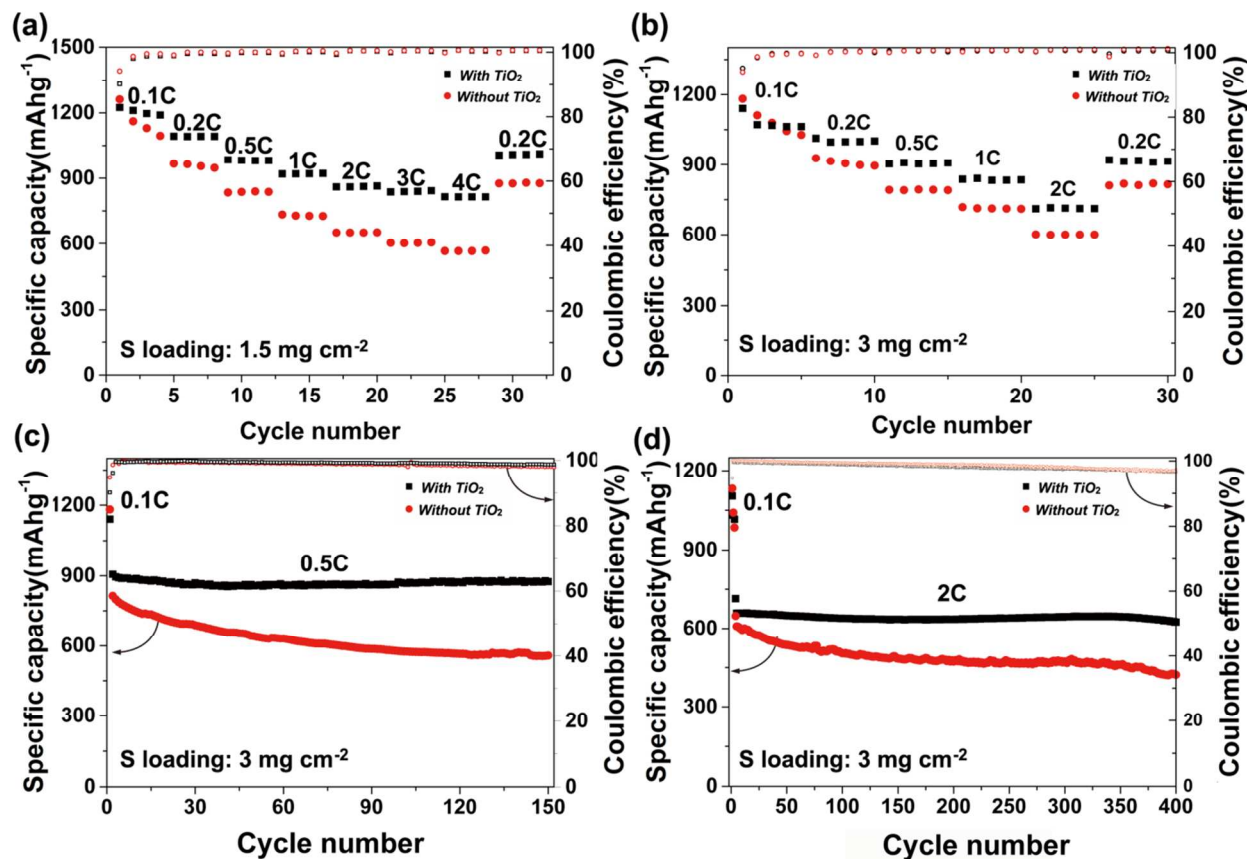


Figure 5. Rate performance of the c-textile @S/TiO₂ and c-textile @S cathodes with S loading of a) 1.5 mg cm⁻² and b) 3.0 mg cm⁻²; c) cycling performance of these two cathodes with loading of 3.0 mg cm⁻² at 0.5C; d) the long cycling stability of these two cathodes with S loading of 3.0 mg cm⁻² at 2C.

even at 0.1C, indicating that the TiO₂ effectively mitigated the dissolution of polysulfides into the organic electrolyte, which was further confirmed by the polysulfide affinity experiment. In the experiment, 5 mg of c-textile, CNT and TiO₂ sample was added into three sealed glass vials containing lithium polysulfide (Li₂S₆, 0.1M) in DOL/DME solvents (1:1 by volume, 5ml), respectively. The blank PS solution was added in the vial with the same volume as a control.

And two cells with c-textile@S and c-textile@S/TiO₂ composites as cathodes were cycled for 5 times, and the composites were then taken out and immersed into 1,3-dioxolane (DOL) for 24 h in a glove box. The images of the solutions with different samples were shown in Figure S6. The color of the solution with c-textile/S/TiO₂ was faint yellow and remained unchanged, similar to the solution containing TiO₂, while the color of the other solution was deeper. For c-textile@S and c-textile@S/TiO₂ composites with sulfur loading of 1.5 mg cm⁻², the discharge capacities were 1161, 966, 834, 732, 650, 602, 566 mA h g⁻¹ and 1211, 1092, 984, 919, 860, 836, 814 mA h g⁻¹ at 0.1, 0.2, 0.5, 1, 2, 3, 4C, respectively. While for the two composites with sulfur loading of 3.0 mg cm⁻², the discharge capacities of 1111, 927, 791, 717, 600 and 1071, 1012, 908, 841, 710 mA h g⁻¹ were obtained at 0.1, 0.2, 0.5, 1, 2C, respectively, as shown in Figure 5b. The rate capability of c-textile@S/TiO₂ was far better than c-textile@S. Such superior rate performance for the c-textile/S/TiO₂ cathode might benefit from the faster reaction kinetics and Li⁺ transport in the hierarchical pore structure.³² Moreover, for c-textile@S/TiO₂ with sulfur loading of 1.5 and 3.0 mg cm⁻², reversible capacities of 1005 and 920 mA h g⁻¹ were recovered when the specific current density was switched back to 0.2C, respectively, indicating the high reversibility and stability of the composite electrode. The cycling stability of the composite electrode was shown in Figure 5c and 5d. With the sulfur loading of 3.0 mg cm⁻², c-textile@S/TiO₂ cathode delivered stable capacities of 909 mA h g⁻¹ and 659 mA h g⁻¹ at 0.5C and 2C, respectively. After 150 and 400 cycles, 96% and 94% of the capacities were retained, corresponding to the capacity decay rates of 0.026% and 0.013%, respectively. Moreover, the cathode exhibited high Coulombic efficiency (>96%), proving that good electrolyte absorbability of the hierarchical pore structure in the c-textile@S/TiO₂ and strong affinity between titania and PS. They could effectively suppress the shuttle effect and contribute to the cycling stability, which was

confirmed by the polysulfide affinity study shown in Figure S6. For the composite electrodes without TiO_2 , the capacity retentions were only 66% and 69% after 150 cycles at 0.5C and 400 cycles at 2C, corresponding to capacity decay rates of 0.205% and 0.076%, respectively. The performance of c-textile@S/TiO_2 was also superior to most of the sulfur cathodes based on thick carbon hosts as listed in Table S1. To better understand the mechanism for the improved electrochemical performance of c-textile@S/TiO_2 cathode, electrochemical impedance spectra analyses were conducted before and after cycling in the frequency from 0.01 to 100 kHz.

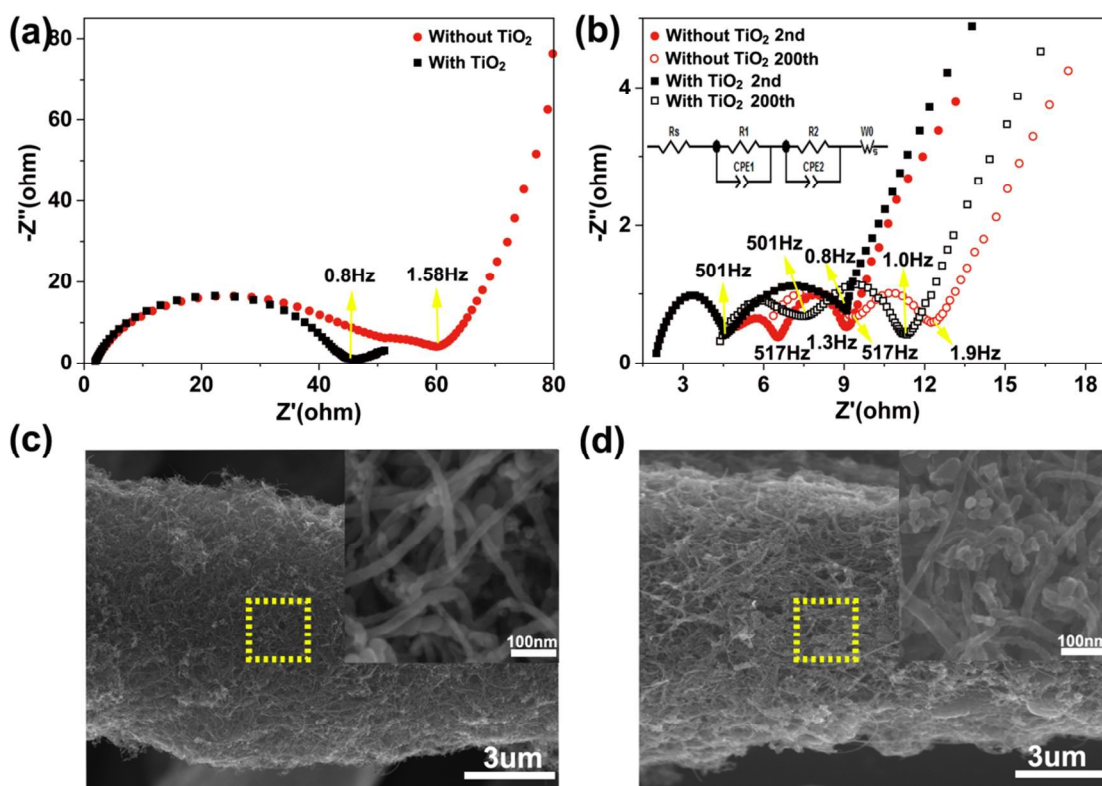


Figure 6. The electrochemical impedance spectra a) before cycling, b) after 2 and 200 cycles (Inset was the fitted equivalent circuit.); SEM images of the c-textile@S/TiO_2 cathodes c) before and d) after 2 and 200 cycles, respectively (the insets were magnified images of the rectangular areas).

Nyquist plots (Figure 6a) of the c-textile@S/TiO₂ and c-textile@S electrodes before cycling displayed mainly a semicircle with a similar radius, which represented the charge transfer resistance (R_{ct}) at the high-medium frequency region.^{26,55,56} After the initial activation process for both electrodes, an additional semicircle appeared in the medium-frequency region. It was related with the formation of the passivation films on the electrode.⁵⁷⁻⁶⁰ The equivalent circuit shown as the inset in Figure 6b was used to fit the Nyquist plots and the fitting parameters were summarized in Table S2. Before the cycling, R_{ct} were 41.02 and 44.09 Ω for c-textile@S/TiO₂ and c-textile@S electrodes, respectively. However, after 2 cycles, the values dramatically decreased to 2.48 and 2.80 Ω . It was ascribed to the appearance of the soluble PSs, which was already confirmed by the color of solution shown in Figure S6. The electrolyte resistances (R_s) for c-textile@S/TiO₂ were smaller than that for c-textile@S because there was less PS in the cells with the former one as the cathode. The appearance of PS could increase the viscosity of the electrolyte. Much smaller variation in the fitting parameters of R_1 and R_2 for Nyquist plots of c-textile@S/TiO₂ after 2 cycles and 200 cycles indicated more stable charge transfer and interface in the composite, compared with c-textile@S. It was responsible for the highly stable performance of the composite.^{57, 61} EIS measurements were also carried out at different discharge and charge states during the 2nd cycle at 0.1 C after the initial activation (Figure S7). Among all states, R_{ct} reached the maximum at the end of discharge, indicating that a considerable amount of soluble species had transferred to Li₂S/Li₂S₂ at the cutoff voltage of 1.7 V. It was also worth noting that the R_{ct} value decreased first and then increased during the charge process, indicating that most of insoluble Li₂S/Li₂S₂ could be transferred to soluble polysulfides since polysulfides facilitated the charge transfer.³⁰ After further charging, partial polysulfides were converted to insulating sulfur, which consistent with analyses of CV plots. Figure 6c and 6d shows the

morphologies of the c-textile@S/TiO₂ electrode before and after 200 cycles, respectively. 3D porous network was retained well and the blockage of the pore was not severe. SEM images (Figure S8a and S8b) of cross-sections of the electrodes showed that their thickness almost did not change. It indicated that the carbon host reported here was stable. As shown in Figure 7a and 7b, although the capacities of c-textile@S/TiO₂ could reach 1058 and 1003 mA h g⁻¹ for the cathodes with the sulfur loadings of 1.5 and 3.0 mg cm⁻², respectively, their corresponding areal capacities were

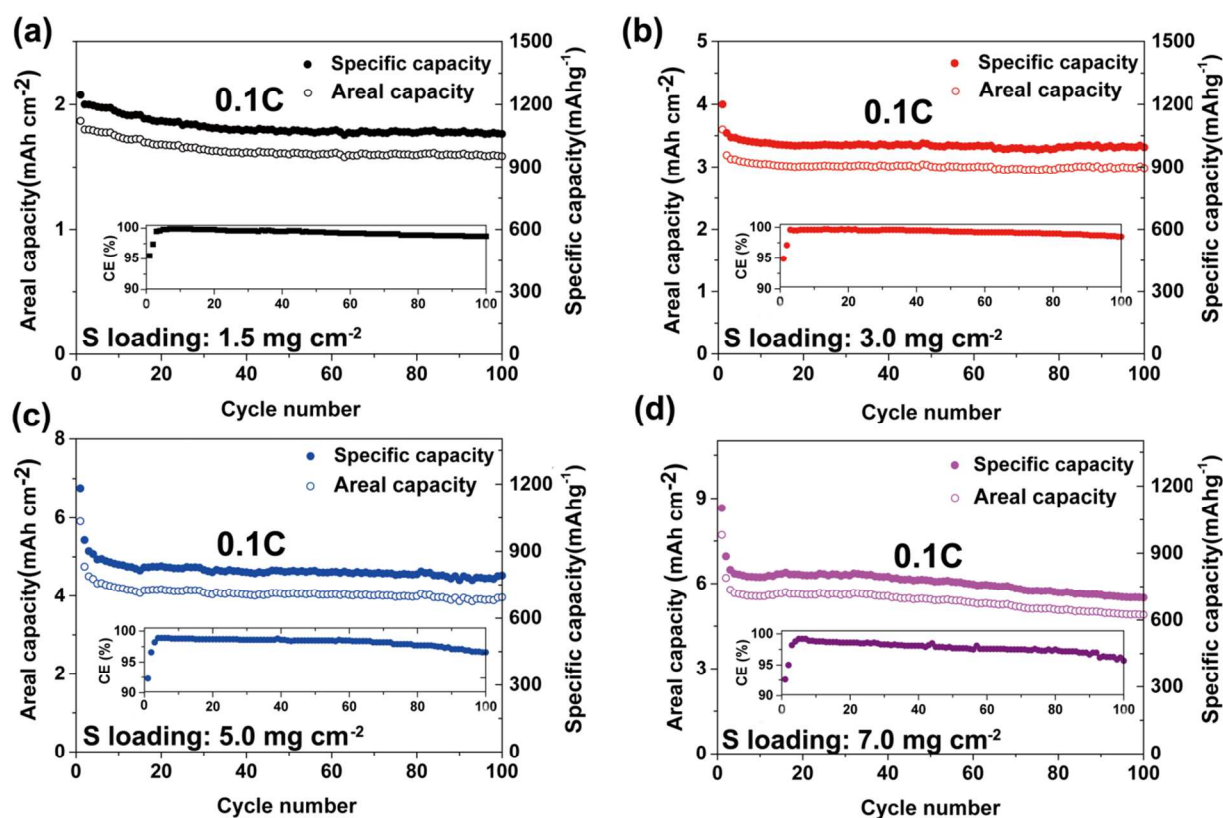


Figure 7. The cycling performance of the c-textile@S/TiO₂ cathode with the sulfur areal loadings of a) 1.5 mg cm⁻², b) 3.0 mg cm⁻², c) 5.0 mg cm⁻² and d) 7.0 mg cm⁻². (The inset is the corresponding Coulombic efficiency)

1.6 and 3.0 mA h cm⁻², lower than the current commercial level (~3.0-4.0 mA h cm⁻²).^{40, 62} To reach the level, the electrodes with sulfur loading of 5.0 and 7.0 mg cm⁻² were fabricated and tested. The sulfur loading, electrode thickness and areal density were measured and summarized in Figure S9. The results showed that the thickness of cathode had a negligible increase. They exhibited initial specific capacities of 1185 and 1065 mA h g⁻¹ at 0.05 C and retained capacities of 802 and 731 mA h g⁻¹ after 100 cycles at 0.1 C, respectively. They corresponded to areal capacities of 4.0 and 5.2 mA h cm⁻², respectively. The electrolyte/sulfur (E/S) in this work was in the range of 20~29 ul/mg. The high E/S ratios also were used in the other porous structured cathodes^{25, 63}. It was believed that every space among fibers and CNTs should be partially filled with the electrolyte to guarantee good electrochemical performance. Moreover, for the electrodes with sulfur loading of 5 and 7 mg cm⁻², their structures became compact, as confirmed by Figure S9. The compact structure not only lowered the amount of electrolyte but also contributed to high volumetric capacity⁶⁴. Although the E/S ratio decreased from 29 to 20ul/mg as sulfur loading increased, the electrochemical performance was not affected by the ratio change, as confirmed by the negligible change of initial capacity in Figure S10. Additionally, the determined sulfur and TiO₂ contents in the cathode were summarized in Table S3. The values fitted well with TGA analysis (Figure S11). The sulfur content in the cathode greatly increased with the increasing of sulfur loading, which could somehow increase the high energy density of Li-S batteries.

Above superior electrochemical performance of composite electrodes could be attributed to their hierarchical structures formed in the dip-coating and drying process. The microscale fibers in c-textile built 3D interconnected conductive network as the main channels for the transport of electrons. While nanoscale CNTs could intimately contact with sulfur nanoparticles, facilitating

the transfer of electrons. Such hierarchical conductive network made the high rate-capability and high utilization of active materials possible. Meanwhile, the macropores among fibers of c-textile could absorb large amounts of electrolytes while the mesopores among CNT could accommodate the volume expansion and keep the soluble sulfide well-localized. The hierarchical pore structure could enhance the transport of the lithium ions and further improve the Columbic efficiency, rate capability and long-term cycling performance. Addition to the physical entrapment of soluble PS with pores, small fraction (<5 wt%) of titania additive could chemically adsorbed PS and enhanced the uniformity of sulfur nanoparticles in the conductive matrix. Although such synergy effect promoted the stable redox activity and greatly improved the electrochemical properties during the discharge/charge process of the composite electrode, some crucial issues remain to be resolved. The insulator nature and strong affinity of TiO_2 reduced the initial capacity, as confirmed by Figure 4c. Hence, the oxide type and percentage can be adjusted to reduce shuttle effect for better chemical entrapment of soluble polysulfide species and improve the initial capacity and Coulombic efficiency simultaneously. For example, VO_x is found to be an excellent sulfur immobilizer,²⁸ which can be tried in the future work. Moreover, the textile can be directly conformally coated with CNT via dip-coating in CNT dispersion and become the conductive matrix.³³ The conductive textile will be then turned into cathode materials with sulfur as active material via the process reported in this paper.

CONCLUSIONS

In summary, we designed and synthesized flexible sulfur composite cathode, c-textile@S/ TiO_2 , with a hierarchical structure via a simple dip-coating process. In the process, carbon nanotube, carbon black, sulfur and titania nanoparticle were successfully conformally coated on carbonized

textile. The formed c-textile@S/TiO₂ cathode with sulfur areal loading of 1.5 mg cm⁻² delivered specific capacities of ~860, 836 and 814 mA h g⁻¹ at 2, 3, and 4C, respectively. Impressively, the electrode with the loading of 3.0 mg cm⁻² displayed a reversible capacity of 659 mA h g⁻¹ at 2C with a high capacity retention of 94% after 400 cycles. Its areal capacity reached 5.2 mA h cm⁻² when its sulfur loading was further increased to 7.0 mg cm⁻². Such excellent performance was ascribed to hierarchical pore structure and conductive networks, and TiO₂ in composite cathode. The as-synthesized free-standing composite electrodes are of low cost and high areal capacities, enable them suitable for the flexible energy storage applications based on Li-S batteries.

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ASSOCIATED CONTENT

Supporting Information.

Photographs of the raw textile and carbonized textile, SEM and TGA analysis of the CNT/S/CB hybrid and CNT/S/CB/TiO₂ hybrid, CV profiles of the S/CB/binder, the galvanostatic discharge-charge profile of c-textile@S cathode, the images of the solution with the electrodes, galvanostatic profiles and Nyquist plots at different discharge/charge states of the c-textile@S/TiO₂, SEM images of the cross-section of the electrode, comparison of various flexible Li-S systems, list of fitting parameters of the equivalent circuit (PDF).

Video showing the superior mechanical flexibility and tape adhesion test of the c-textile@S/TiO₂ electrode (AVI).

Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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