TiO2 coated three-dimensional hierarchically ordered porous sulfur electrode for the lithium/sulfur rechargeable batteries

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Abstract
A three-dimensional (3D) hierarchically ordered mesoporous carbon-sulfur composite slice coated with a thin TiO2 layer has been synthesized by a low-cost process and investigated as a cathode for the lithium-sulfur batteries. The TiO2 coated carbon sulfur composite thin slice works as a binder-free cathode without any current collectors for lithium-sulfur batteries. The hierarchical architecture provides a 3D conductive network for electron transfer, open channels for ion diffusion and strong confinement of soluble polysulfides. Meanwhile, TiO2 (titanium dioxide) coating layer could further effectively prevent the dissolution of polysulfides and also improve the strength of the entire electrode, thereby enhancing the electrochemical performance. As a result, after TiO2 coating, the electrode demonstrates excellent cycling performance, with a discharge capacity of 608 mAh/g at 0.2 C current rate and 500 mAh/g at 1 C current rate after 120 cycles, respectively.

Keywords
coated, three, dimensional, hierarchically, ordered, porous, sulfur, electrode, rechargeable, lithium, batteries, tio2

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**ABSTRACT:** A three-dimensional (3D) hierarchically ordered mesoporous carbon-sulfur composite slice coated with a thin TiO$_2$ layer has been synthesized by a low-cost process and investigated as a cathode for the lithium-sulfur batteries. The TiO$_2$ coated carbon sulfur composite thin slice works as a binder-free cathode without any current collectors for lithium-sulfur batteries. The hierarchical architecture provides a 3D conductive network for electron transfer, open channels for ion diffusion and strong confinement of soluble polysulfides. Meanwhile, TiO$_2$ coating layer could further effectively prevent the dissolution of polysulfides and also improve the strength of the entire electrode, thereby enhancing the electrochemical performance. As a result, after TiO$_2$ coating, the electrode demonstrates excellent cycling performance, with a discharge capacity of 608 mAh/g at 0.2 C current rate and 500 mAh/g at 1 C current rate after 120 cycles, respectively.

**Keywords:** 3D architecture, binder-free, ordered mesoporous structure, mass production

1. **Introduction**

Rechargeable lithium ion batteries (LIBs) have achieved great development during the past decades as power sources for various portable devices such as laptops, smart phones and electric vehicles [1-4]. However, the specific energy of the commercialized lithium ion batteries will become insufficient for the future electric vehicles due to the low capacity of conventional electrode materials. Therefore, new electrode materials with higher gravimetric and volumetric capacity should be developed. Sulfur, as one of the most abundant elements on the earth, can offer ultra-high energy density (theoretically 2567 Wh kg$^{-1}$) and high theoretical specific capacity (1675 mAh·g$^{-1}$), making it a very promising cathode candidate for the next generation batteries [5-8]. The Li-S battery system may suffer, however, from
several disadvantages, including the low conductivity of sulfur and lithium sulfide [9] as well as the large volume changes of sulfur particles during charge and discharge processes. A more significant challenge that needs to be overcome is the high solubility of the intermediate lithium polysulfides in organic electrolytes. The soluble polysulfides can diffuse from the cathode and react with the lithium anode to generate insoluble lower-order polysulfides in the form of Li2S or Li2S2, resulting in the precipitation of these species on the surface during cyclic processes [10,11]. These issues lead to the low utilization of sulfur, which is the active material, low coulombic efficiency of the sulfur cathode, and fast capacity fading [12-15].

There are two basic strategies to address this problem in terms of designing nanostructured sulfur cathodes. One is to constrain the sulfur or lithium polysulfide within a framework by using host materials, such as various types of porous carbon [16,17], hollow carbon spheres [13,18], carbon nanotubes [19,20], graphene [21,22], graphene oxide [23,24], and conductive polymers [25,26]. An alternative route is to build a physical barrier to prevent soluble polysulfides from dissolving in the organic electrolyte by forming a thin film to acts as a coating on the surface of the active material. Such barrier materials include polymers [27,28] and metal oxides such as TiO2 [29], Al2O3 [30], SiOx, and VOx [31]. Compared with a polymer coating, a metal oxide coating layer could almost completely block out-diffusion of the polysulfides and enhance the strength of the entire electrode to withstand structural damage during long cycle testing.

Herein, we employ 3D hierarchical porous carbon slice (C) as an improved confined matrix for high-level sulfur impregnation. 3D porous nanostructured carbon is highly desirable for high-performance electrode materials, as it can not only provide a continuous electron pathway to ensure good electrical contact, but also facilitates the transport of ions and electrolyte. Additionally, the well-developed 3D structure with macropores and ordered interconnected mesopores can encapsulate a large amount of sulfur, provide a large specific surface area, and facilitate fast ion transport, thus enhancing the electrochemical performance of electrodes. In order to trap the dissolved polysulfides more effectively, a TiO2 layer was further coated on the surface of the as-prepared porous carbon-sulfur composite to obtain carbon-sulfur-TiO2 composite (Fig.1). The as-prepared TiO2 coated carbon-sulfur composite slice could be used as cathode directly without further electrode preparation process, therefore, no inert weight, i.e. binders and metal substrate, is included in the electrodes.

2. Experimental

2.1. Synthesis of hierarchical porous-structured carbon
The ordered mesoporous carbon-silica composite slice with macroporous architecture were synthesized through an evaporation-induced coating and self-assembly method using foam as template, as described by Zhao et al [32]. The foam was cut into thin slice (as displayed in Fig. S1 (left)) to prepare carbon-silica composite slice. Afterwards, the obtained thin slice was put into boiling 2 mol/L NaOH solution for 2 h to remove the silica to obtain the hierarchical porous carbon slice (as showed in Fig. S1 (right)).

2.2. Fabrication of TiO2 coated porous carbon-sulfur composite electrodes
The as-prepared carbon slice and sulfur were mixed together in a weight ratio of 3:7 and heated to 160 °C in a sealed stainless steel autoclave for 24 h to facilitate sulfur diffusion into the carbon host. Then, the composite was heated at 200 °C and kept for 10 minutes under flowing argon gas (50 cm³ s⁻¹) to vaporize the sulfur deposited on the outside surface of the composite (with the sample at this stage denoted as C-S). After that, titanium diisopropoxide bis(acetylacetonate) was used as the titanium precursor to coat a TiO2 layer on the surface of the C-S composite slice according to a previous report²⁵ to obtain C-S-TiO2 slice (denoted as C-S-TiO2).

2.3. Characterization
The crystal phases of the resulting materials were analyzed by powder X-ray diffraction (XRD, MMA GBC, Australia). Thermogravimetric analysis (TGA) was carried out to determine the sulfur content with a TGA/differential scanning calorimetry (DSC) type instrument (METTLER TOLEDO, Switzerland) at a heating rate of 10 °C min⁻¹ from room temperature to 500 °C under argon atmosphere. The Brunauer–Emmett–Teller (BET) method was utilized to calculate the specific surface areas. The pore size distributions were derived from the adsorption branches of the isotherms based on the Barrett–Joyner–Halenda (BJH) model. The morphologies of the samples were investigated by field-emission scanning electron microscopy (FESEM; JEOL JSM-7500FA). Transmission electron microscope (TEM) images were collected on a JEOL 2011 200 kV instrument. X-ray photoelectron spectroscopy (XPS) analysis was conducted on a VG Scientific ESCALAB 2201XL instrument using aluminum Kα X-ray radiation.

2.4. Electrochemical measurement
The C-S and C-S-TiO2 composite thin slices can be as a binder-free electrode for lithium-sulfur batteries that does not require any current collectors. Coin-type (CR2032) cells were assembled in an argon-filled glove box. The electrolyte used was 1 M lithium bis(trifluoromethanesulfonyl)imide in a solvent mixture of 1,3-dioxolane (DOL):
dimethoxyethane (DME) (1:1, v/v) containing LiNO$_3$ (1 wt%). The coin cells were galvanostatically charged-discharged between 1.5 and 3.0 V (vs. Li/Li$^+$) by using a cell test instrument (CT2001A, LAND, China).

3. Results and discussion

A scanning electron microscope (SEM) image in Fig. 2 shows that the carbon slice is a 3D interconnecting network composed of prism-shaped struts with macropores about 300 μm in diameter. Thermogravimetric (TG) curves of the C (inset in Fig. 2) displays a weight loss of 96 wt% from 400 to 650 °C, indicating that the content of carbon is up to 96% and nearly all the silica has been removed from the carbon-silica composite.

As shown in Fig. 3(a), the X-ray diffraction (XRD) pattern of the carbon exhibits low-intensity and broad peaks, which reveal a typical amorphous structure. The pure elemental sulfur has various diffraction peaks, corresponding to an orthorhombic structure. As for the C-S and C-S-TiO$_2$ composites, some diffraction peaks of the elemental S are visible, although the intensities become distinctly lower and some diffraction peaks even disappear, which suggests good dispersion of the S within the mesoporous carbon hosts [33]. The sulfur content in the C-S and C-S-TiO$_2$ composites was determined by thermogravimetric analysis (TGA) conducted under argon atmosphere (as shown in Fig. 3(b)). The amount of sulfur in the C-S and C-S-TiO$_2$ composites is 60 wt% and 53 wt%, respectively.

The nitrogen adsorption-desorption isotherms of the C, C-S, and C-S-TiO$_2$ composites are shown in Fig. 4(a) to confirm the pore structures. The isotherms of C and the C-S composite are type IV isotherms with hysteresis at relative pressure above 0.4, which is characteristic of mesopores. Note that the insertion of sulfur leads to a significant decrease in the pore volume (from 1.26 to 0.33 cm$^3$/g) and Brunauer-Emmett-Teller (BET) surface area (1564 to 487 m$^2$/g for C and C-S composite, respectively). Meanwhile, the pore size (Fig. 4(b)) also shows a strong decrease from 7 nm to 4.5 nm, suggesting that a large portion of the pores are filled with sulfur. The C-S-TiO$_2$ sample, however, does not exhibit a typical isotherm, indicating that the TiO$_2$ layer almost completely covers the surface of the C-S composite.

Well-developed ordered mesostructure can be observed for the C sample, and the pore size estimated from the transmission electron microscope (TEM) image (Fig. 5(a)) is less than 8 nm, in good accordance with the value from the N$_2$ sorption isotherms. Moreover, compared to the C, the contrast and the pore size of the C-S composite are obviously decreased, and no significant amount of bulk sulfur on the external surface is detected (Fig. 5(b)). This indicates
that sulfur is homogeneously embedded in the mesopores of the sample due to the intense capillary forces. As for the C-S-TiO$_2$ composite, the mesopores are not as clear as those in the C and the C-S composite due to the TiO$_2$ coating on the surface of the C-S composite, resulting in a nearly complete lack of differentiation of the mesoporous composite (Fig. 5(c)). The scanning TEM (STEM) (Fig. 5(d)) and corresponding elemental mapping images of the C-S-TiO$_2$ composite demonstrate that the TiO$_2$ coating layer is evenly distributed on the surface of the C-S composite, which is also in good agreement with the results from the N$_2$ sorption isotherms.

X-ray photoelectron spectroscopy (XPS) was used to further confirm and characterize the TiO$_2$ coating layer on the surface of the C-S composite electrode (as displayed in Fig. S2). Three peaks positioned at 288.3, 284.9, and 283.7 eV are observed from the C1s spectrum, which could be attributed to the C=O, C-O, and C=C/C-C groups [34,35], respectively, indicating that C still retains some oxygen-containing groups from the carbonization process of the carbon precursor. The S 2p spectrum exhibits two peaks at 164.8 and 163.7 eV, corresponding to the resolved S 2p$_{1/2}$ and S 2p$_{3/2}$ peaks. Additionally, two peaks at 460.8 and 454.8 eV corresponding to Ti 2p$_{1/2}$ and Ti 2p$_{3/2}$ are shown in the Ti 2p spectrum, demonstrating the presence of Ti$^{4+}$ [36]. As the penetration depth of XPS is about 10 nm, it is likely that the possible elemental sulfur signal is from places where the TiO$_2$ layer is thinner than 10 nm. The XPS results together with the TEM images and N$_2$ sorption isotherms results reveal that most of the surface area of the C-S composite is covered with a TiO$_2$ layer less than 10 nm in thickness.

The cycling performance of the C-S and the TiO$_2$ coated composite electrodes at current rates of 0.2 C and 1 C is shown in Fig. 6(a). The initial discharge capacity is up to 1168 and 1111 mAh/g for the C-S composite cathode at the 0.2 C and 1 C rates, while the TiO$_2$ coated electrode delivers a corresponding discharge capacity of 1128 and 1076 mAh/g, respectively, which is slightly lower than for the C-S composite cathode due to the poor conductivity of the TiO$_2$ layer. This can be seen from the electrochemical impedance spectra (EIS) of the C-S and C-S-TiO$_2$ electrodes, as shown in Fig. S3. The resistance of the C-S-TiO$_2$ electrode is much higher than that of the C-S electrode, resulting in lower initial discharge capacity. In contrast, it is obvious that the TiO$_2$ coated sample shows superior cycling performance in the long run. In the beginning, the capacities of the two samples are almost the same, however, the gap become more and more significant, especially after 20 cycles, as shown in Fig. 6(a).

The discharge capacity at the 120$^{th}$ cycle can reach 608 mAh/g at 0.2 C and 500 mAh/g at the 1 C rate for the TiO$_2$ coated electrode, while the C-S composite cathode only exhibits
corresponding capacities of 450 and 370 mAh/g, respectively. This means that the mesopores of C can trap the polysulfides for a short time, but only a real capping layer can confine the polysulfides in the carbon matrix over a long span of time. Another important aspect that contributes to the stable cycling performance is that the TiO$_2$ layer can effectively integrate the individual components in the electrode into a whole system and enhance the strength of the entire electrode to withstand structural damage during cycling. It is noted that specific capacity of the electrode without any binders and metal substrate in our study could be comparable with that using binders and substrate in previous report [21, 23-25]. This suggests that the polysulfides are better trapped inside the carbon matrix due to the TiO$_2$ layer that is coated on the surface of the C-S composite.

The rate capability of the C-S and the TiO$_2$ coated composite electrodes at different current rates, ranging from 0.2 C to 5 C, is shown in Fig. 6(b). Compared with the C-S electrode, after TiO$_2$ coating, the rate performance is obviously improved, especially at high current rates. The discharge capacity at the second discharge cycle for the C-S-TiO$_2$ composite cathode is 1142 mAh/g at the current rate of 0.2 C, which is slightly lower than that of the C-S composite. Nevertheless, the discharge capacity for the C-S-TiO$_2$ electrode remains as high as 889, 770, 714, 677, and 650 mAh/g, as the current density is increased to 0.5, 1, 2, 3, and 5 C, respectively, which is much higher than the performance of the C-S composite, as shown in Fig. 6(b). Fig. 6(c) and (d) display the discharge/charge voltage profiles of C-S and C-S-TiO$_2$ electrodes at various rates, in which two plateaus at around 2.0 and 2.3 V are observed in the discharge process, which are typical characteristics of sulfur-carbon cathodes. Compared with previous report [13,18,37], rate capabilities (in table 1) for TiO$_2$ coated samples are higher. On the one hand, 3D porous hierarchical structure could support rapid electronic/ionic transport and improve electrochemical kinetics. On the other hand, a possible reason is that the TiO$_2$ works as an effective coating that helps to maintain the integrity of the electrode during charge and discharge processes. Together with the 3D hierarchically ordered porous carbon, it provides a real barrier to effectively trap polysulfides and minimize the dissolution of the polysulfides, thus reducing the loss of active mass in the cathode, and enhancing the electrochemical performance.

4. Conclusions

In summary, we have fabricated a 3D hierarchically ordered porous carbon-sulfur composite cathode, TiO$_2$ layer has been further introduced on the surface of C-S composite to help trap the dissolved polysulfides and enhance the strength of the entire electrode, which leads to notably improved performance for the lithium-sulfur battery, especially over long cycling and
at high rates. Furthermore, the 3D hierarchically ordered porous carbon slice can be mass produced in a simple way at low cost and carbon sulfur composite thin slice could work as a binder-free cathode without any current collectors for lithium-sulfur batteries, which makes our S-based electrode highly promising for practical application in lithium-sulfur batteries.

Acknowledgments

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Table 1. Rate performance of Lithium-sulfur cathodes with different nanostructures

<table>
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<th>0.1 C</th>
<th>0.2 C</th>
<th>0.5 C</th>
<th>1 C</th>
<th>2 C</th>
<th>3 C</th>
<th>5 C</th>
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<td>1142</td>
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<td>770</td>
<td>714</td>
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<td>—</td>
<td>1150</td>
<td>970</td>
<td>750</td>
<td>600</td>
<td>450</td>
<td>820</td>
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<tr>
<td>sulfur in double-shelled hollow carbon spheres [18]</td>
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<td>820</td>
<td>550</td>
<td>350</td>
<td>—</td>
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<td>—</td>
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<td>graphene-based sandwich-type architecture [37]</td>
<td>—</td>
<td>1146</td>
<td>856</td>
<td>743</td>
<td>502</td>
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References


[18] Zhang CF, Wu HB, Yuan CZ, Guo ZP, Lou XW. Confining Sulfur in Double-Shelled


Fig. 1 Pictorial representation of the structure of C-S-TiO₂ composite.
Fig. 2. SEM image of as-prepared carbon. Inset shows the TG curve of C under air atmosphere to determine the content of carbon.
Fig. 3. (a) XRD patterns of C, S, C-S, and C-S-TiO$_2$ composites, and (b) TG curves of C-S and C-S-TiO$_2$ composites under argon atmosphere.

Fig. 4. (a) N$_2$ sorption isotherms and (b) pore-size distributions of C and C-S composite.
Fig. 5. TEM images of (a) C, (b) C-S composite, (c) C-S-TiO₂ composite, and (d) STEM image of C-S-TiO₂ and corresponding elemental mapping images of C, S, and Ti.
Fig. 6. (a) Cycling performances of C-S and C-S-TiO$_2$ electrodes at current densities of 0.2 C and 1 C; (b) rate capabilities of C-S and C-S-TiO$_2$ electrodes; discharge/charge voltage profiles of (c) C-S and (d) C-S-TiO$_2$ electrodes at various rates.