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TiO₂@C@MoS₂ Spheres as Efficient Sulfur Host for Lithium– Sulfur Batteries

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In this paper, TiO₂ @ C @ MoS₂ composite has been successfully synthesized by wrapping TiO₂ spheres with C layer and MoS₂ nanosheets. Firstly, TiO₂ spheres are synthesized by solvothermal and subsequent calcination process; subsequently, TiO₂ spheres are coated with dopamine and carbonized to form TiO₂@C spheres; then, ultrathin MoS₂ nanosheets grew outside the TiO₂@C spheres; finally, sulfur infiltrated into the TiO₂@C@MoS₂ spheres by melt diffusion method and the TiO₂@C@MoS₂/S spheres were successfully synthesized for the sulfur main body of lithium-sulfur batteries. The composite material has strong binding for polysulfides and good adsorption and catalysis, so it is an ideal carrier for sulfur host materials. By using such a composite material as a positive electrode in a Li-S battery, better electrochemical performance has been achieved. The results show that, the sulfur loading is about 63%, and the specific capacity of the sulfur positive electrode reaches 535.9 mAh g⁻¹ after 100 cycles at 0.5 C current density. The capacity retention rate is about 76.28%.

Keywords: Lithium-sulfur battery, Composite material, TiO₂, C, MoS₂

1. INTRODUCTION

As the fast growth of new energy, there is an urgent desire for high specific density, environmental friendly and cheap energy storage devices to solve these problems[1]. However, due to the low capacity of lithium-ion batteries, their energy density cannot meet the needs as a power source

for emerging electric vehicles. Therefore, finding high-energy devices has become the most important concern at present[2].Sulfur, with higher energy density(2600 wh kg⁻¹) and theoretical specific capacity (1675 mA g⁻¹) than lithium-ion batteries, has the advantages of low cost, non-toxic and natural, etc. Lithium sulfur battery has potential energy storage advantages and is considered to be one of the most promising energy storage devices in the next generation[3]. Although Li-S batteries have many advantages, the actual applications are still severely hindered. First, i) The insulation of sulfur and the poor electrical conductivity of Li₂S and Li₂S₂ lead to the inferior utilization rate of active substances; ii) The Shuttle Effect caused by the dissolution of polysulfide during the process of charging and discharging, the density variation between sulfur and L_{i2}S gives rise to volume expansion of sulfur, which makes a destruction of electrode microstructure and a high attenuation of its capacity[4].

Aiming to overcome these challenges, a great deal of proposals have been tried from the electrode, electrolyte, multi-layer intermediate layer. Most strategies still focus on building carbon/S composites, such as carbon nanotubes, carbon spheres, hollow carbon [5-10]. However, the non-polar carbon can merely provide inferior mutual interactions with polysulfides, and the inhibition effect on the shuttle effect is not obvious. It is therefore necessary to introduce a heteroatomdoped carbonaceous material and a polar compound for chemisorbing the polysulfide to enhance the chemical interaction between the polysulfide and the host material [11]. Many polar metal compounds such as metal sulfide (MoS₂) metal oxides (TiO₂), metal carbides (TiC, NbC, W₂C) and metal nitrides $(Co_4N,$ VN, TiN) metal borides (MgB₂, TiB₂) have been found to produce powerful chemical interaction with polysulfides(Li_2S_X), inhibit the shuttle effect of Li_2S_X , and have good adsorption and electrocatalytic properties[12-28]. In recent years, many literatures on TiO₂/MoS₂ composites have been reported, including TiO₂-MoS₂ hybrid nanocomposites, core-shell TiO₂@MoS₂ ball, TiO₂@MoS₂ nano onion heterostructure, TiO₂/MoS₂ hybrid, TiO_2 nanowires@MoS_2 nanosheets, MoS₂ nanosheets@TiO₂ nanotubes, etc[29-34]. When the TiO₂/MoS₂ composite is used as an electrode material, it can accelerate the diffusion rate of Li⁺, expand the contact area of the electrode / electrolyte interface, and provide a certain adjustment for volume changes. Compared with a single substance, the synergy between the two substances leads to an increase in battery capacity. Carbon is doped into TiO₂/MoS₂ composites, which can not only be used to enhance the electronic conductivity of TiO₂/MoS₂, but also to physically limit polysulfide dissolution of substances[35,36]. Therefore the researchers often make the heteroatom doped into conductive carbon materials, polar metal oxide and sulfide compound to improve the polarity of the whole material so as to capture polysulfide chemically.

Based on the above considerations, $TiO_2@C@MoS_2$ spheres was chosen to synthesize, and fully integrate the advantages of each component by integrating the three main materials into a singleelectrode material. Thanks to its unique chemical composition, the design has a significantly positive effect on performance. Firstly, The innermost layer of TiO₂ spheres has a small volume change during the cycle, so it can be used as a suitable support skeleton for other metal oxides and metal sulfides; secondly, the large void space of the TiO₂ sphere can accommodate high-load sulfur and its volume expansion and anchors the polysulfide through strong interactions; the nitrogen-doped carbon shell formed by the carbonization of the intermediate layer of dopamine is used for a nano-scale reaction room, which provides a physical limit for the diffused polysulfide[37]; the outermost MoS_2 nanosheet can chemically fix polysulfide and promote multiple kinetics of sulfide conversion. Because of the synergistic effect of the above three, this unique TiO_2 @C@MoS_2 composite exhibits good electrochemical performance.

2. MATERIALS AND METHODS

2.1. Synthesis

2.2.1. Preparation of TiO₂ spheres

2 mL of butyl titanate and 10 mL of glycerol were added into 30 mL of ethanol with vigorous stirring and the stirring process was continued for 30 min. The mixture was then transferred into a 100 mL polytetrafluoroethylene reactor and placed in an oven at 180 °C for 12 h. The oven has cooled to room temperature. After centrifugation and washing with ethanol several times, the obtained precipitate was dried in an oven at 80 °C. Finally, it is placed in a calciner and heated at a heating rate of 5 °C min⁻¹ to 450 °C for 2 h, the obtained product is TiO₂ spheres.

2.1.2. Preparation of TiO₂@C spheres

Nano-TiO₂ (0.08 g) and dopamine hydrochloride (DA) (0.01 g) were added into 50 mL of deionized water to form a suspension, and then 0.1 g of hexamethylenetetramine (HMTA) was dissolved in the suspension and sonicated for 3 min. The TiO₂ @ PDA powder was obtained by centrifugal washing and vacuum freeze-drying. Finally, the TiO₂@PDA were annealed at 500 °C for 3 h in a N₂ atmosphere at a heating rate of 1 °C min⁻¹ to get the product of TiO₂@C.

2.1.3. Preparation of TiO₂@C@MoS₂/S spheres

60 mg of TiO₂@C was added into 50 mL of water and ultrasound for 30 min, then 0.2 g of thioacetamide was added and stirred for 30 min, and 0.1 g of sodium molybdate dihydrate was added and stirred for 5 min. Finally, the obtained solution was transferred into an 80 mL polytetrafluoroethylene reactor and placed in an oven at 200 °C for 12 h. After centrifuged and washed and dried in an oven at 60 °C overnight. Sulfur and TiO₂@C@MoS₂ were mixed in a weight ratio of $M_S:M_{TiO2@C@MoS2} = 3:7$, then put the mixture under a N₂ atmosphere and heated at 155 °C for 12 h, and the made product was referred to as TiO₂@C@MoS₂/S.

2.2. Sample Characterization

The chemical component and crystal microstructure of the material were analyzed by XRD (Japan Tsutsuki, D / MAX-3C), Raman spectroscopy (Raman, Andor SR-500i) and infrared

spectroscopy (FTIR, Perkon-Elmer 700,USA). The sulfur load of the sample was determined by TGA / DSCI type synchronous thermal analyzer. The morphology, size, and particle aggregation state of the samples were characterized by using SEM (Hitachi, Japan, S-480) and TEM (TEM, JEOL JEM 2100). The pore structure of the sample were investigated by BET (NOVAtouch LX4). The valence distribution of the elements in the product was measured by XPS (Thermo ESCALAB 250XI).

2.3. Electrochemical Measurements

Mixing the prepared TiO₂@C@MoS₂ composite with Conductive agent and binder (PVDF) in a mass ratio of 7:2:1, then the mixture was evenly spread on aluminum foil and dried at 60 °C overnight. Then a tablet machine was used to cut the dried aluminum foil into electrode pole pieces. The lithium metal plate is served as the cathode, the Celgard 2400 as the separator. The electrolyte is 1.0 mol/L LiTFSI/DME+ DOL (1:1 by volume) with an appropriate amount of LiNO₃. The CR2430 button battery is assembled for subsequent performance testing. Cyclic volt-ampere and AC impedance tests were performed at the Shanghai chenHua CHI660D electrochemical workstation. The cyclic voltampere voltage scanning range was from 1.5 V to 3.0 V, and the scanning speed was at 0.2 mV s⁻¹. The AC impedance test was used in the frequency ranging from 10^{-1} Hz to 10^{5} Hz. The Xinwei Test System was used to test, that made the cell to a Cycle and magnification test at room temperature, with the voltage range 1.7 V~2.8 V.

3. RESULTS AND DISCUSSION





The schematic diagram of the synthesis process of $TiO_2@C@MoS_2/S$ is shown in Fig.1. Firstly, TiO_2 spheres were synthesized by solvothermal method and calcination method; subsequently, $TiO_2@PDA$ spheres were formed by coating a layer of polydopamine (PDA) on the outside of the TiO_2 spheres; nextly, after the obtained product was calcined at 500 °C, the outer layer of PDA is transformed into an N-doped carbon shell layer; Then ultra-thin MoS_2 nanosheets grew outside the

 $TiO_2 @ C$ spheres by hydrothermal reaction; finally, sulfur was diffused into the $TiO_2@C@MoS_2$ by melt diffusion to obtain the final product $TiO_2@C@MoS_2/S$.



Figure 2. (a)XRD pattern of TiO₂@C@MoS₂, (b)XRD pattern of TiO₂@C@MoS₂/S composite;(c)Raman spectrum of TiO₂@C@MoS₂ composite; (d)Fourier infrared spectra of TiO₂,TiO₂@PDA, TiO₂@C@MoS₂, TiO₂@C@MoS₂/S composites;(e) TG curve for TiO₂@C@MoS₂/S composite in nitrogen.

Fig.2a and b show the XRD patterns of the TiO₂@C@MoS₂ and TiO₂@C@MoS₂/S complexes. The peaks of XRD in Fig.2a are 25.3°, 38.5°, 48.0°, 53.8°, 55.0°, 62.6°, 68.7°, 70.2°, 74.0°, 82.1° corresponding to TiO₂ (JCPDS: 65-5714) (101), (112), (200), (105), (211), (204), (116), (220), (107), (303) crystal planes. The sharp peak indicates that the prepared TiO₂ has good crystallinity. The characteristic peaks at 14.4° , 33.0° , and 58.2° conform to the (003), (101), and (110) crystal planes of the hexagonal MoS₂ (JCPDS: 24-0515), manifesting that MoS₂ was successfully coated outside of TiO₂@C. The comparison with the peak shape in Fig.2b illustrates the successful loading of S. The diffraction peak of elemental sulfur is identical with the characteristic peak of standard kapia orthorhombic system S₈ (JCPDS: 08-0247), which shows that the composite has no residual and impurity phase.

Fig.2c illustrates the Raman spectrum of the TiO₂@C@MoS₂ composite. The Raman peaks appearing at 150 cm⁻¹, 403 cm⁻¹, 521 cm⁻¹, and 631 cm⁻¹ correspond to $E_{g(1)}$, $B_{1g(1)}$, $A_{1g}+B_{1g(1)}$, and $E_{g(2)}$ vibration mode in the TiO₂ anatase phase[38,39], respectively. Compared to the characteristic peaks of TiO₂ and MoS₂, the disordered D peak and G peak of the carbon material were also exhibited at 1355 cm⁻¹ and 1587 cm⁻¹. The smaller the I_D/I_G intensity ratio, the higher is the degree of graphitization of the substance, which further verifying the formation of the TiO₂@C@MoS₂ complex.

Fig.2d shows the infrared analysis spectra of TiO₂, TiO₂@PDA, TiO₂@C@MoS₂, TiO₂@C@MoS₂/S. The characteristic vibration peak produced by the octahedral ligand [TiO₆] exists in the region of 450~700 cm⁻¹ of TiO₂[40]. The characteristic absorption peak at 1240 cm⁻¹ in the infrared spectrum of TiO₂@PDA corresponds to the ruthenium structure carried by polydopamine, and the absorption band between 800 and 700 cm⁻¹ is weak, indicating that the aromatic ring is substituted. The relative content of aromatic hydrogen is relatively small, and the absorption between 1600 and 1000 cm⁻¹ has a significant association phenomenon, which is caused by the mutual absorption of the absorption vibration, and also the cause of the decrease in the resolution of the spectrum.

The sulfur content in the TiO₂@C@MoS₂/S composite was analyzed by TGA. As shown in Fig.2e, as the temperature gradually increases, sulfur begins to sublimate at 155 °C. The heat temperature changes from 200 °C to about 310 °C, and the weight loss of the composite is fast, which may be related to the loss of sulfur supported in the big pores of the TiO₂@C@MoS₂ composite [41]. As the temperature continues to rise to around 500 °C, the weight loss in the composite slows, which may be due to a stronger interaction between the TiO₂@C@MoS₂ complex and the S embedded in the pores[42]. According to the calculation results, the sulfur content of the TiO₂@C@MoS₂/S composite is about 63%.

The pore structure of the samples was further evaluated by performing N₂ adsorptiondesorption isotherm test. Fig.3 shows the specific surface area and pore size distribution of TiO₂, TiO₂@PDA and TiO₂@C@MoS₂ composites. According to the BET calculation method, the specific surface area of TiO₂ reaches 92.7 m² g⁻¹. After the polydopamine was coated on the surface of TiO₂, the specific surface area of TiO₂@PDA is reduced to 27.4 m² g⁻¹. When the outermost layer is coated with MoS₂, the specific surface area of the composite reaches 143 m² g⁻¹, which not only provides more space for the load of S but also facilitates the penetration of the electrolyte, which is of great significance for improving the electrochemical performance.



Figure 3. a) Nitrogen adsorption–desorption isotherms and b) pore sizes of the TiO₂, TiO₂@PDA host, and TiO₂@C@MoS₂ composite.

The morphology of the samples was observed with SEM(Fig.4), TEM and HRTEM(Fig.5). Fig.4a and b show that the average diameter of TiO₂ spheres synthesized is about 1 um. The internal cavity structure of the TiO₂ material can limit the dissolution of polysulfides and adapt to the bulk inflation of sulfur, and it can also be used as a supporting framework for the growth of outer materials. Subsequently, PDA was coated TiO₂ spheres with and carbonized in N₂ to form TiO₂@C. The carbon shell can provide excellent conductivity for the entire electrode material and can physically limit lithium polysulfide. Next, a layer of MoS₂ nanosheets was coated outside of the TiO₂ @C spheres. From the SEM image (4c, d), the MoS₂ sheets are decentralized outside and in the gap of the TiO₂@C spheres. MoS₂ nanosheets have a strong adsorption capacity for polysulfides, which can effectively prevent them from dissolving during charge and discharge. Finally, S is diffused into the TiO₂@C@MoS₂ spheres by the melt diffusion method. SEM image shows (4e, f) that no obvious S particles were observed outside the TiO₂ @C@MoS₂ composite, indicating that S diffused well into the composite[43]. Next, HRTEM was also used to show the morphology of TiO₂@C@MoS₂ spheres(Fig.5). From the morphology, it can be seen that the MoS₂ nanoflakes successfully grew on the surface and in the gap of TiO₂, forming a nebula-like structure. Without the support of TiO₂ nanospheres, MoS₂ nanospheres might form irregular aggregates. In the image (Fig.5d), obvious lattice stripes with interlayer spacing of 0.77 nm and 0.35 nm were found, which were attributed to the crystal surface of MoS₂ nanospheres (002) and anatase TiO₂ (101), respectively[44].



Figure 4. The SEM images of a, b) the TiO_2 sphere and c,d) $TiO_2@C@MoS_2$ composite and e,f) $TiO_2@C@MoS_2/S$ composite

The chemical state and valence in the samples were further characterized by XPS. The peaks of Mo, S, Ti, O and C elements in TiO₂ @C@ MoS₂ composite was shown in the full spectrogram (Fig.6). In the spectrum of Ti2p , the peaks at 464.3 and 458.5 eV refer to Ti $2p_{1/2}$ and Ti $2p_{3/2}$, respectively, which implied that the valence state of Ti elements is Ti⁴⁺ [45]. In the spectrogram of O1s, the two peak pairs at 532.9 and 531.5 eV conform to C-O bonds and C=O bonds, and one at 529.8 eV

corresponds to Ti-O bonds. In the spectrogram of C1s, C-C bond, C-N bond and C-O bond are respectively correspond to 283.9, 285.1 and 286,1 eV. In the spectrum of Mo3d, peaks located at 231.6 eV and 228.5 eV assign to Mo $3d_{3/2}$ and Mo $3d_{5/2}$ respectively, however, the small peak at 235.8 eV is attributed to S₂. In the light of earlier reports, the binding energies of pure MoS₂ ought be at 232.5 and 229.3 eV. The shift of the peak may be due to the growth of MoS₂ on the surface of TiO₂ @ C spheres[46]. In the spectrum of S2p, the peaks at 163.7 eV and 162.5 eV represent S $2p_{1/2}$ and S $2p_{3/2}$, respectively, and the peaks at 161.3 eV and 168.3 eV can be attributed to the formation of S-O keys[44].



Figure 5. HRTEM of TiO₂@C@MoS₂ at different magnifications



Figure 6. High-resolution XPS spectra of TiO₂@C@MoS₂ microsphere: (a) XPS survey spectra and (b) High resolution Ti 2p spectra and (c) O1s spectra and (d) C1s spectra (e) Mo 3d and (f) S2p spectra.

Fig.7 is the cyclic voltammetry (CV) curve of the TiO₂@C@MoS₂/S composite measured between 1.7 and 2.8 V at a scan rate of 0.1 mV/s. During the first three turns of the cycle, there were two distinct characteristic reduction peaks at approximately 2.35 and 2.05 V. These two reduction peaks correspond to the conversion of elemental S₈ into long-chain soluble lithium polysulfide (S₈+Li \rightarrow Li₂S_n,3 \leq n \leq 8) and the conversion of long-chain lithium polysulfide into short-chain insoluble lithium disulfide, Lithium sulfide (Li₂S_n+Li \rightarrow Li₂S₂,Li₂S₃ \leq n \leq 8). The only oxidation peak at about 2.39 V is due to the progressive oxidation of Li₂S and Li₂S₂ to elemental sulfur (S₈). In addition, the first three cycles of the TiO₂@C@MoS₂/S electrodes almost coincide with each other, indicating that the composite has high stability.



Figure 7. Cyclic voltammetry curve of TiO₂@C@MoS₂/S composite

Then, the GCD curves between 1.7 and 2.8 V at 0.1 C (1 C = 1675 mAh g⁻¹) were further tested to observe the performance. Fig.8a showed the GCD voltage profiles of TiO₂@C@MoS₂/S electrodes. Two discharge platforms and one charging platform are clearly visible from the GCD curve, which are consistent with two reduction peaks and an oxidation peak appearing in the cyclic voltammetry curve. All of the GCD voltage profiles undergo two remarkable plateaus, which is at 2.3 and 2.1 V (vs Li⁺/Li), could be respectively classified to_the two steps:

 $xS_8 + 16 e^- + 16 Li^+ \leftrightarrow 8 Li_2S_x (4 \le x \le 8)$ (1)

4 $\text{Li}_2\text{S}_x + (6x-8) e^- + (6x-8) \text{Li}^+ \leftrightarrow x \text{Li}_2\text{S}_2 + 2x \text{Li}_2\text{S}$ (2)

The cycle performance and corresponding coulombic efficiency of the $TiO_2@C@MoS_2/S$ composite at 0.1 C and 0.5 C current densities are presented in Fig. 8b and 8c. The first charge and discharge capacity of $TiO_2@C@MoS_2/S$ composite at current density of 0.1C is about 850.51 and 851.73 mAh g⁻¹. After 99 cycles, the charge-discharge specific capacity decreases to 535.8 and 535.9 mAh g⁻¹, and capacity retention rate reached approximately 62%. It can be seen from the curve in the

figure that the capacity decay during the early cycle is relatively fast, but as the number of cycles increases, the capacity decay inch by inch slows down, which demonstrates that the $TiO_2@C@MoS_2/S$ composite has a good cyclic stability at 0.1 C current density. Next, the $TiO_2@C@MoS_2/S$ composite was analyzed for cyclic performance at a current density of 0.5 C. The initial charge and discharge capacity are about 488.0 and 514.5 mAh g⁻¹, respectively. After 99 cycles, the charge-discharge specific capacity reduces to 392.4 mAh g⁻¹, the capacity retention rate is about 76%, and the average coulombic efficiency is about 99%. It can be seen from the curve in the figure that the specific capacity amplitude of the composite changes greatly during the cycle, which could be caused by the collapse of the composite structure during reaction.



Figure 8. The typical voltage profiles of the TiO₂@C@MoS₂/S composite electrode at 0.1 C a)the first 5 turns; the cycle performance and the corresponding coulombic efficiency of TiO₂@C@MoS₂/S electrode at a current densities of b) 0.1 C c) 0.5 C and d) the rate capacities

Fig.8d is the rate performance of the TiO₂@C@MoS₂/S composite from 0.1 to 2 C. After 9 cycles at a current density of 0.1 C, the discharge specific capacity is as high as 832.4 mAh g⁻¹. Subsequently, the current density increases to 0.2 C, 0.5 C, 1 C, 2 C. After 10 cycles, the specific capacities of the composites reached 717.7, 508.9, 397.3, 240.1 mAh g⁻¹, respectively. When the current density is restored to 0.1 C, the battery capacity is greatly restored, reaching about 767.1 mAh

 g^{-1} after 10 cycles. When the current density resets to 0.1 C, the battery capacity is greatly restored, recovering about 767.1 mAh g^{-1} after 10 cycles, which indicates that the TiO₂@C@MoS₂/S composite can significantly improve the cycle reversibility of the battery.

The TiO₂ and TiO₂ based composites have been studied widely in Li-S Battery and made remarkable achievements. The rate properties of TiO₂ and its composites for Li-S Battery are provided in Table 1. The electrochemical ability of TiO₂ and TiO₂ based composites is mainly dependent on the morphology and the second component of composite. From the Table 1, it can be seen that TiO₂@C@MoS₂ composite electrode exhibits rate performance. Due to the synergistic effect among TiO₂, C and MoS₂, the hybrid TiO₂@C@MoS₂/S material shows enhanced rate performance.

Materials	Disharge capacity[mAh g ⁻¹]						Ref.
	0.2C	0.5 C	1C	2C ().1C	0.2C 0.5C	
Mesoporous TiO ₂ Nanofiber	498	402	298		613		[47]
This work	717.7	508.9	397.3	240.1	767.1		
hollow TiO ₂ sphere	623	538	448	374		539	[48]
TiO ₂ –S composite	700	601	538		850		[49]
TiO ₂ NTs		200	180			204	[50]

Table 1. TiO₂ and its composite materials for LIBs.

4. CONCLUSIONS

In short, the TiO₂@C@MoS₂ cathode for Li-S batteries was fabricated. TiO₂ spheres can not only serve as a framework for the growth of outer layers, but also buffer the volume expansion of S and effectively adsorb polysulfides. The carbon layer can improve the conductivity of the overall material and physically coat the polysulfides. MoS₂ has catalytic conversion function for polysulfides. Compositing the three materials together, through this effective improvement measure, the results can show that the TiO₂@C@MoS₂ composite electrode achieves a high sulfur load of 63 wt%. When the current density is 0.1 C, the capacity retains still of 535.9 mAh g⁻¹ after 99 cycles.

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