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Synthesis of nano-TiO₂-decorated MoS₂ nanosheets for lithium ion batteries

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A facile process is developed to synthesize TiO₂/MoS₂ nanohybrid via a one-pot hydrothermal route and post-annealing in an Ar atmosphere at 500 °C for 4 h. The precursor and target products were characterized by transmission electron microscopy (TEM) and Field-emission scanning electron microscope (FESEM). TEM and FESEM analysis showed that TiO₂ nanoparticles with the average

¹⁰ diameter about 20 nm were uniformly distributed on MoS_2 nanosheets. Electrochemical measurements demonstrated that the nano-TiO₂-decorated MoS_2 nanosheets exhibited excellent cycling stability and rate performance, which delivered a capacity of 604 mA h g⁻¹ after 100 cycles at a current density of 100 mA g⁻¹. The TiO₂ is believed as a stabilizer to retain the MoS_2 structure on prolonged cycling. This material can be the promising candidate for the lithium ion batteries (LIBs).

15 Introduction

Rechargeable lithium ion batteries (LIBs) are considered as potential power sources for various applications.¹ They are becoming more and more popular in many applications in consumer products such as mobile phone, music players and

²⁰ laptops.² It is known that anode materials play an important role as a crucial component.³ Focusing on general aspects of material technology for LIBs, graphite has been widely used as a major electrode material in commercial LIBs. However, graphite has a relatively low theoretical capacity (372 mA h g⁻¹),^{4, 5} which

²⁵ cannot fully meet the energy density requirement in electric vehicles (EVs) and the need of large-scale batteries in the future.⁶ Therefore, alternative anode materials with higher specific capacity and good cycling behavior are desirable for LIBs.

In recent years, layered transition-metal dichalcogenides are ³⁰ of great interest as the active materials for lithium storage based on their unique physical and chemical properties, such as relatively high energy density, long cycle life and design flexibility.^{7, 8} In particular, MoS₂ is one of the most stable and versatile members of this family, atoms within a layer are bound

- ³⁵ by strong ionic/covalent forces,⁹ while the individual layers are bound by weak Van der Waals interactions, forming a sandwich structure.⁹⁻¹¹ Because of its layered structure and high theoretical capacity.¹² MoS₂ has been regarded as a potential candidate for electrode materials in lithium secondary batteries. Thus far, MoS₂
- ⁴⁰ with different morphologies have been reported for lithium storage, such as nanorods,¹³ nanoplates,¹⁴ nanoflakes,¹⁵ nanotubes¹⁶ and nanoflowers.¹⁷ In spite of the theoretical capacity of MoS_2 is up to 670 mA h g⁻¹, it suffers from the poor cycling stability and low rate capability.¹⁸ Additionally, MoS_2 nanosheets
- ⁴⁵ can be easily restacked together under the Van der Waals interaction during charge/discharge processes. The restacked

surface is hardly accessible to electrolyte to penetrate. As a result, such layered structure and their high active surface will be lost.¹⁹ These defects obstruct their practical applications as electrode ⁵⁰ materials of LIBs. To combat this problem, one doable strategy is to design hybrid nanostructures. A number of MoS₂-based hybrid nanostructures have been fabricated for LIBs such as MoS₂/carbon,⁸ MoS₂/Fe₃O₄,¹⁹ and MoS₂/grapheme.²⁰

- Titanium dioxide (TiO_2) has been proposed as a prospective 55 candidate for the hybridization due to the low volume variation (<4%) during the lithiation/delithiation process, which can buffer the excessive volume change. Meanwhile, TiO₂ nanoparticles are introduced as spacer between MoS₂ nanosheet, thus making both faces of nanosheets accessible to electrolytes. TiO₂ act as spacer 60 can significantly stabilize the nanohybrid structure during the lithium insertion/removal process. Therefore, TiO₂ based electrode materials generally display favorable cyclical stability compared to other transition metal oxides and sulfides.²¹ The MoS₂ nanosheets@TiO₂ nanotubes hybrid nanostructures have 65 been synthesized through a template-assisted hydrothermal method by Xu et al. and it shows high reversible lithium storage capacity and superior rate capability.²² However, the complicated synthesis procedure might limit the practical applications of the composite.
- Herein, we report a facile synthesis of MoS₂ nanosheets decorated with TiO₂ nanoparticles, as illustrated in Fig. 1. The current nano-TiO₂-decorated MoS₂ nanosheets that consist of single or few layers are successfully synthesized via a one-pot hydrothermal process by employing ammonium heptamolybdate,
 titanium tetrachloride and thiourea as starting materials and post-annealing in an Ar atmosphere at 500 °C for 4 h. In the hydrothermal synthesis process, TiCl₄ acts as the source of Ti, as well as providing hydrochloric acid. Electrochemical measurements demonstrate that the TiO₂/MoS₂ nanohybrid

shows better cycling stability than MoS_2 , which delivers a reversible capacity of 604 mA h g⁻¹ after 100 cycles at a current density of 100 mA g⁻¹, The results demonstrate that the TiO₂/MoS₂ nanohybrid is promising materials for LIB s anode.

Experimental section

10 Materials preparation

All reagents were analytical grades. A typical preparation process is described as follows: 0.1698 g of $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ was dissolved in 20 mL of distilled water. The ethanol solution of titanium tetrachloride was added to $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ aqueous

- ¹⁵ solution under stirring in an ice water bath. Then 0.3662 g of thiourea was added. The mixtures were ultrasonicated for 10 min and stirred for 1 h to disperse them. The obtained solution was transferred into a 100 mL of Teflon-lined stainless steel autoclave, which was filled with distilled water up to 60% of the total
- ²⁰ volume, sealed and hydrothermally treated at 220 °C for 24 h. The autoclave was left to cool down to room temperature. The precursor was collected by centrifugation and washed with distilled water and absolute ethanol, dried at 60 °C for 12 h. In order to improve the crystallinity of the TiO₂/MoS₂ nanohybrid,
- ²⁵ the precursor was annealed at 500 °C at a heating rate of 10 °C min⁻¹ in an Ar atmosphere for 4 h. The desired TiO₂/MoS₂ nanohybrid was obtained. The preparation process of MoS₂ nanoclusters is similar to the one of TiO₂/MoS₂, except the addition of the ethanol solution of titanium tetrachloride and ³⁰ calcination.

Materials characterization

The product was characterized by X-ray diffractometer (XRD) using a Rigaku D/max-ga X-ray diffractometer at a scan rate of 6° min⁻¹ in 20 ranging from 10° to 80° with Cu K α radiation (λ = ³⁵ 1.54178 Å). The elemental composition was determined using energy dispersive X-ray spectroscopy (EDX). Field-emission scanning electron microscope (FESEM) was carried out on a Hitachi S-4800 electron microscope. Transmission electron microscopy (TEM) was performed on FEI Tecnai G2 T20





Fig. 1. Schematic illustration of the synthesis route of TiO₂/MoS₂ nanohybrid.

electron microscope operated at 200 kV with the software package for automated electron tomography. Thermogravimetric ⁴⁵ analysis (TGA) was carried out with a SDTQ600 at a heating rate of 10 °C min⁻¹.

Electrochemical measurements

The electrochemical tests were carried out in coin cells. TiO₂/MoS₂ nanohybrid was used as a working electrode, lithium 50 foil as counter and reference electrodes, a polypropylene film (Celgard-2400) as a separator, and 1 mol L^{-1} of LiPF₆ dissolved in a mixture of ethylene carbonate and diethyl carbonate (EC-DEC, 1:1 in volume) as an electrolyte. The working electrodes were prepared by a slurry tape casting procedure. The slurry 55 consisted of 70 wt% active materials, 20 wt% acetylene black and 10 wt% polyvinylidene fluoride (PVDF) dissolved in N-methyl-2-pyrrolidinone (NMP). The slurry was tape-cast on the copper foil, and then the coated electrodes were dried at 120 °C for 12 h in a vacuum. The cells were assembled into coin in an argon-60 filled glove box. Cyclic voltammetry measurements were performed on an electrochemical work-station (CHI 660D) at a scan rate of 0.1 mV s⁻¹ over the potential range of 0.01-3.0 V (vs. Li⁺/Li). The galvanostatic charge-discharge tests were conducted on the battery measurement system (LAND CT2001A, China) at 65 various current densities of 50-1000 mA g⁻¹ with a cut off voltage range of 3.00-0.01 V vs. Li/Li⁺ at room temperature. For the electrochemical impedance spectroscopy (EIS) measurement, the

excitation amplitude applied to the cells was 5 mV. The activation energy measurements were collected between 0.01 Hz 70 and 100 kHz at room temperatures.

Results and discussions





Fig. 2. (a) XRD patterns of the as-prepared TiO₂/MoS₂ nanohybrid after a hydrothermal process (I), TiO₂/MoS₂ nanohybrid after annealing at 500 °C in an Ar atmosphere (II), MoS₂ nanoclusters (III). (b) EDX spectrum of TiO₂/MoS₂ nanohybrid.

The synthesis of the TiO_2/MoS_2 nanohybrid was conducted through a facile hydrothermal and post-annealing method. Initially, The ethanol solution of titanium tetrachloride is added into $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ aqueous solution to form TiO_2 s nanoparticles through a fast nucleation process, then MoS_2 nanoparticles are gradually formed under a thiourea-assisted hydrothermal conditions. MoS_2 nanoparticles grown into sheetlike structure by oriented aggregation as time go on. As a result, TiO_2 nanoparticles are in-suit decorated in the layers of MoS_2 .

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- Fig. 2a (III) shows the XRD patterns of the MoS_2 without adding titanium tetrachloride, all the diffraction peaks can be readily indexed to the hexagonal MoS_2 phase (JCPDS card No. 37-1492) and these results are in good agreement with those of previous
- ¹⁵ reports.²³ The stacking peak at 14.2° from curve III implied that MoS₂ nanoclusters may contain a well stacked layered structure. TiO₂/MoS₂ nanohybrid was synthesized by the similar hydrothermal method and subsequent calcination. As shown in Fig. 2a (I) and (II), the annealed TiO₂/MoS₂ shows sharper peaks
- $_{20}$ in comparison with the as-prepared $\rm TiO_2/MOS_2$ nanohybrid, which demonstrates that the crystallinity of $\rm TiO_2/MOS_2$ is slightly improved after annealing. It can be seen from Fig. 2a (II), all the diffraction peaks can be readily indexed to the standard peak of hexagonal 2H–MOS_2 (JCPDS card No.37-1492) and anatase $\rm TiO_2$
- ²⁵ (JCPDS card No.21-1272). The absence of peak at 14.2 ° of MoS₂ indicates that stacking of the single layers has not taken place.²⁴ Fig. 2(b) shows EDX spectrum of TiO₂/MoS₂ nanohybrid. The EDX spectrum indicates that the annealed sample only contains Mo, S, Ti and O elements.



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Fig. 3. TGA curves of TiO_2/MoS_2 nanohybrid and MoS_2 nanoclusters at a temperature ramp of 10 °C min⁻¹ in air.

TGA (Fig. 3) was carried out from room temperature to 700 °C in air flow to determine the amount of MoS₂ present in the ³⁵ TiO₂/MoS₂ nanohybrid. The TGA curve can be divided into two domains of 25-300 °C, 300-500 °C. The first weight loss was measured to be 3.58% and 3.39% for the TiO₂/MoS₂ nanohybrid and MoS₂ nanoclousters, respectively. The result is attributed to to the physisorbed water evaporation and the loss of chemisorbed

- ⁴⁰ water. The second weight loss occurs at approximately 300 °C, which probably be attributed to the oxidation of MoS₂ to MoO₃. A common feature of both TGA curves is the large weight loss in the range of 300–500 °C. The mass fraction of MoS₂ in the TiO₂/MoS₂ nanohybrid can thus be estimated to be about 71.79
- 45 wt% , on the assumption that the remaining product after the

TGA measurement was pure MoO_3^{25}



Fig. 4. (a) SEM and (b) TEM images of the as-prepared TiO₂/MoS₂ nanohybrid synthesized after a hydrothermal process. (c) SEM and (d) high-magnification SEM images of TiO₂/MoS₂ nanohybrid after annealing at 500 °C in an Ar atmosphere. (e) TEM and (f) HRTEM images of TiO₂/MoS₂ nanohybrid and corresponding fast Fourier Transform (FFT) patterns obtained from the HRTEM images.

Fig. 4a-d shows the SEM and TEM images of the as-prepared TiO₂/MoS₂ nanohybrid after a hydrothermal process and treated ⁵⁵ at 500 °C in the Ar atmosphere. It reveals that the as-prepared TiO₂/MoS₂ nanohybrid delivers a large-scale uniform sheet structure (Fig. 4a). Fig. 4b indicates that MoS₂ nanosheets are almost transparent, showing the extremely small thickness of this layer structure. A large quantity of TiO₂ nanoparticles with a ⁶⁰ diameter of 20 nm are uniformly distributed on the surface of

layered MoS₂ nanosheets. Fig. 4c shows the morphology of the TiO₂/MoS₂ nanohybrid after annealing at 500 °C in an Ar atmosphere and it maintains its sheet-like structure. The high-magnification FESEM image displays that the TiO₂ nanoparticles ⁶⁵ are distributed on the MoS₂ layers (Fig. 4d). Fig. 4e-f shows the

TEM and High resolution transmission electron microscopy . (HRTEM) images of TiO_2/MoS_2 nanohybrid. It can be clearly seen that MoS_2 nanosheets keep the original morphology despite a slight shrinkage after calcination (Fig. 4e). And the inter-planar 70 distances are measured to be around 0.63 nm and 0.35 nm,

corresponding to the (002) plane of hexagonal MoS_2 and the (101)

plane of anatase TiO_2 . The inset of Fig. 4f corresponding to FFT pattern demonstrates that the MoS_2 layers grow along the (002) direction.

- $_{\rm 5}$ Fig. 5a shows the cyclic voltammograms (CVs) of TiO_2/MoS_2 nanohybrid for the 1st, 2nd, and 3rd cycles in the potential window of 0.01-3 V vs. Li⁺/Li. During the 1st cycle, the reduction peak at 1.1 V suggests the presence of the lithium insertion mechanism, which is attributed to the insertion of
- ¹⁰ lithium ions into the MoS_2 to form Li_xMoS_2 . Another reduction peak at 0.57 V is attributed to the conversion of Li_xMoS_2 into metallic Mo and Li_2S . These peaks disappear in the 2nd and 3rd cycles resulting from few amorphous MoS_2 is reformed after the

in which MoS₂ was reduced to Mo particles embedded in a LiS₂ matrix. The first discharge and charge capacities are 932.7 mA h g⁻¹ and 813.9 mA h g⁻¹, respectively, corresponding to a Coulombic efficiency of 74%, which may be due to the formation of a gel-like polymeric layer. The charge and discharge capacities in the second cycle are 804.8 mA h g⁻¹ and 833 mA h g⁻¹, respectively, showing a Coulombic efficiency of 95%. The capacity loss might arise from the irreversible reactions during the discharge/charge processes. As shown in the Fig. 5c, the reversible capacity of TiO₂/MoS₂ retained at 604 mA h g⁻¹ after 100 cycles at a current density of 100 mA h g⁻¹. From the second s cycle onwards, the TiO₂/MoS₂ nanohybrid exhibited coulombic

efficiency approximately of 95%. The fresh electrode and the



Fig. 5. (a) Cyclic voltammograms (CVs) at a scan rate of 0.1 mV s⁻¹ for the 1st, 2nd, and 3rd cycle of TiO₂/MoS₂ nanohybrid. (b) Charge-discharge voltage profiles at a current density of 100 mA g⁻¹ of TiO₂/MoS₂ nanohybrid. (c) Cycling performance of TiO₂/MoS₂ nanohybrid and MoS₂ electrodes, and Coulombic efficiency of TiO₂/MoS₂ nanohybrid at a current density of 100 mA g⁻¹. (d) Rate behavior of TiO₂/MoS₂ nanohybrid at different current densities.

- $_{20}$ first charge process.²² The oxidation peaks at 1.7 V and 2.3 V correspond to the lithium extraction process and the transformation of Mo to MoS₂, respectively. The peaks at 1.75 V in the cathodic sweep and 2.07 V in the anodic sweep can be ascribed to the discharge/charge process of TiO₂: TiO₂+ x (Li⁺+e⁻)
- 25 ↔Li_xTiO₂ (0< x<1). The broad reduction peak at 1.8 V may be attributed to the insertion of lithium ions into the TiO₂. Fig. 5b exhibits the voltage profiles of the TiO₂/MoS₂ nanohybrid during the 1st, 2nd, and 50th cycles at the current density of 100 mA g⁻¹ at room temperature. In agreement with previous reports,²⁶ two
- ³⁰ voltage plateaus at around 1.1 V and 0.57 V are observed in the discharge process of the first cycle. The former was ascribed to the Li insertion reaction that led to the formation of Li_xMoS_2 , however, the latter at 0.57 V was related to a reduction process,

used electrode (after 100 cycles) are observed by SEM (Fig. S1,

see Electronic Supplementary Information). The MoS₂ ⁵⁵ nanosheets are difficult to be distinguished and many spherical nanoparticles are observed on the surface of fresh electrode. It may attributed to the existence of acetylene black and binder in the electrode. ²⁷ Comparison of Fig. S1a and b reveals no obvious change in morphologies, indicating that the TiO₂/MoS₂ ⁶⁰ nanohybrid architecture is beneficial to the stable cycling performance. The initial capacity is lower than pure MoS₂, which is mainly in consequence of the influence of TiO₂. However, the cycle stability is preferable compared to pure MoS₂. Fig. 5d displays the rate performance at various densities. At current ⁶⁵ density of 1000 mA g⁻¹, the capacity of TiO₂/MoS₂ nanohybrid is 472.14 mA h g⁻¹. When the current density returns to 50 mA g⁻¹,

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the TiO_2/MoS_2 nanohybrid still delivers a capacity of 601.9 mA h $g^{-1}.$



Fig. 6 (a) Nyquist plots of TiO₂/MoS₂ nanohybrid and MoS₂ electrodes obtained by applying a sine wave with an amplitude of 5.0 mV over the frequency range from 0.01 Hz and 100 kHz. (b) an equivalent circuit model of the studied system.

Fig. 6 shows the EIS and the equivalent circuit model of the studied system. Re represents the resistance contribution from the

- ¹⁰ electrolyte, electrode and the passive film between them. Rct and CPE are associated with the charge-transfer resistance, Zw is associated with the Warburg impedance. For MoS_2/TiO_2 nanohybrid, resistance Re and Rct fitted by ZView software are 1.84 Ω and 133.7 Ω , which are significantly lower than those of
- ¹⁵ MoS₂ (2.35Ω and 162.3Ω). This result further demonstrates that incorporation of TiO₂ can greatly enhance the conductivity of MoS₂/TiO₂ nanohybrid electrode and greatly enhance rapid electron transport during the electrochemical lithium insertion/extraction reaction, resulting in significant improvement ²⁰ in the electrochemical performances.

Conclusions

In summary, TiO_2/MoS_2 nanohybrid has been successfully synthesized by a facile hydrothermal process and post-annealing in an Ar atmosphere at 500 °C for 4 h. Transmission electron

- ²⁵ microscopy and Field-emission scanning electron microscope images demonstrate that TiO_2 particles are uniformly distributed on MoS₂ nanosheets. Electrochemical evaluation showed better cycling stability of TiO_2/MoS_2 than pure MoS₂ clusters, which may be due to the unique structure of TiO_2/MoS_2 nanohybrid. The
- $_{30}$ addition of anatase $\rm TiO_2$ nanoparticles greatly facilitate electron and ionic transport and accommodated the volume change of MoS_2 during the charge/discharge process. $^{28,\ 29}$ Besides, the excellent rate performance may be due to the large interfacial contact area with the electrolyte and shorten Li-ion insertion
- ³⁵ distances. The present results suggest that the TiO₂/MoS₂ nanohybrid is a promising candidate for anode material in LIBs.

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Notes and references

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The TiO_2 -decorated MoS_2 nanosheets were prepared by a hydrothermal-annealing method and retained a capacity of 604 mA h g⁻¹ after 100 cycles