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Fabrication of flower-like MoS₂/TiO₂ hybrid as an anode material for lithium ion batteries†

Xiaoquan Zhu,^a Xiaoyu Liang,^b Xiaobin Fan ^{*a} and Xintai Su ^{*b}

A three-dimensional (3D) flower-like MoS₂/TiO₂ nanohybrid was synthesized via a two-step hydrothermal method. It is found that the MoS₂/TiO₂ nanohybrid is assembled with MoS₂ nanosheets and TiO₂ nanoparticles. The TiO₂ nanoparticles are homogeneously dispersed on the MoS₂ nanosheets. Moreover, the MoS₂/TiO₂ nanohybrid displays excellent electrochemical performance with a high reversible capacity of 801 mA h g⁻¹ at a current density of 100 mA g⁻¹ after 50 cycles. It also demonstrates outstanding rate behavior with a reversible discharge capacity of 660 mA h g⁻¹ at a current density of 1000 mA g⁻¹ and retains a capacity of about 760 mA h g⁻¹ as the current density is returned back to 100 mA g⁻¹. Compared with MoS₂, the MoS₂/TiO₂ nanohybrid displays enhanced cycling stability and superior rate capability. The excellent electrochemical performance may be attributed to the favorable synergistic effect between MoS₂ and TiO₂. The TiO₂ particles may enhance the structure stability and shorten the transport distance of ions across the surface.

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1. Introduction

Lithium-ion batteries (LIBs) are now one of the most important power sources for many electronic devices in our daily life. Development of rechargeable LIBs with longer cycle life and higher power density is of great interest to accommodate the growing demands for higher energy density electronic devices.¹ Currently, graphite has been widely used as the negative electrode in commercial LIBs due to its natural abundance and stable cycling performance. However, it has a relatively low theoretical capacity (372 mA h g⁻¹).² Therefore, alternative anode materials with higher specific capacity and good cycling behavior are desirable for LIBs.

In recent years, two-dimensional layered transition-metal dichalcogenides (TMDs) have attracted great interest in the field of electrochemical energy storage and conversion because of their unique physical and chemical properties. Due to their short path length and more channels for lithium ion diffusion and insertion, these 2D materials exhibit enhanced electrochemical performances as electrode materials for LIBs, such as WS₂, MoS₂.^{3–5} In particular, molybdenum disulfide (MoS₂) has gradually drawn attention as a potential candidate, owing to its high theoretical specific capacity (~670 mA h g⁻¹).⁶ Meanwhile, the weak van der

Waals forces allow a fast diffusion path for lithium-ion and easy lithium ion insertion/extraction.⁷ This is due to the layered structure of MoS₂. MoS₂ is consisting of molybdenum atoms sandwiched between two layers of closely packed sulfur atoms, two molecular layers are weakly linked by van der Waals interactions.⁸ Various MoS₂ nanostructures such as nanoplates,⁶ nanowall,⁹ nanotube¹⁰ and nanoflowers^{11,12} have been reported for lithium storage as LIBs anodes. However, the inferior cycling stability due to large volume changes significantly limits its practical applications. To overcome the defects of the MoS₂-based electrode materials, one doable strategy is to design hybridization. A strategy is to immobilize MoS₂ nanostructures on carbon-based substrate to construct nanocomposites.^{13–16} Most of the previous studies focused on MoS₂-carbon nanocomposites. Carbon tubes, carbon nanofibers, graphene and organic conducting polymers are used as carbonaceous materials.^{14,17} However, the excessive interface between porous carbonaceous materials and electrolytes cause considerable side reactions, forming a thick solid electrolyte interface (SEI) on the carbon and leading to a low initial coulombic efficiency of <70%.¹³

Recently, some transition metal oxides were used to improve the cycling performance of MoS₂, such as Fe₃O₄ and TiO₂.^{18,19} Titanium dioxide (TiO₂) has been widely used as anode material for LIBs. It possesses a low volume variation (<4%) and displays good cycling stability during the charge-discharge process.²⁰ Furthermore, it is a safer material compared to graphite because of its higher operation voltage (1.7 V vs. Li⁺/Li). Accordingly, by combining the individual constituents, the hybrid MoS₂/TiO₂ system shows some merits that not exist in a single system. The advantages of both high reversible capacity and superior cycling stability are expected. The strain of volume

^aState Key Laboratory of Chemical Engineering, School of Chemical Engineering and Technology, Collaborative Innovation Center of Chemical Science and Engineering, Tianjin University, No. 135, Yaguan Road, Jinnan District, Tianjin 300354, China. E-mail: xiaobinfan@tju.edu.cn

^bDepartment of Chemistry, Zhejiang Sci-Tech University, Xiasha Campus, Hangzhou 310018, China. E-mail: suxintai827@163.com

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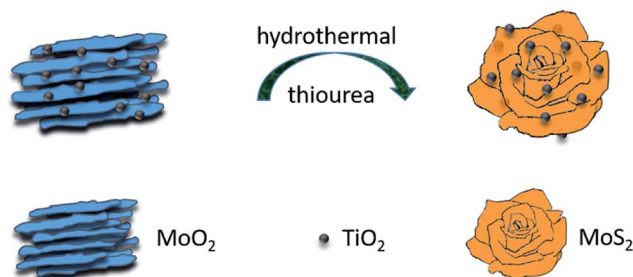


Fig. 1 Schematic illustration of the formation process of MoS₂/TiO₂ nanohybrid.

variation of MoS₂ can be alleviated. To the best of our knowledge, a number of MoS₂/TiO₂ hybrid systems have been widely investigated as photocatalysts.²¹ However, this hybrid system has also been studied as electrode materials for LIBs in recent years.^{19,22} There has some literatures reported about the applications of TiO₂@MoS₂ composite in lithium ion batteries. Li *et al.* synthesized the hierarchical TiO₂ nanowire@MoS₂ nanosheet nanocomposite by a glucose-assisted hydrothermal approach, and it displays a specific capacity of around 600 mA h g⁻¹ at a current density of 100 mA g⁻¹ after 100 cycles.⁷ Xu *et al.* synthesized MoS₂ nanosheet@TiO₂ nanotube hybrid by a two-step method, and it exhibits a capacity of 472 mA h g⁻¹ at a current density of 100 mA g⁻¹ after 100 cycles.²⁰ The TiO₂ decorated few-layers MoS₂ nanosheets through one-pot method have been reported by our team.²³ However, we found that the MoS₂/TiO₂ nanohybrid derived from the MoO₂/TiO₂ precursor was very different from one-pot method. We consider that the morphology of the MoO₂ precursor plays an important role in the formation of product. Meanwhile, TiO₂-decorated three dimensional (3D) MoS₂ nanoflowers have rarely been studied as electrode materials for LIBs.

Herein, we report a two-step hydrothermal route to prepare 3D Hierarchical MoS₂/TiO₂ nanoflowers. The synthetic process is illustrated in Fig. 1. Firstly, the hydrothermal method was adopted to prepare the MoO₂/TiO₂ precursor. Secondly, the as-prepared the MoO₂/TiO₂ nanobundles were vulcanized by thiourea under a subsequent hydrothermal process. We supposed that the formation of 3D flower-like architecture may undergo a self-assembling process from the precursor. The as-prepared flower-like MoS₂/TiO₂ nanohybrid was further treated at 500 °C in an Ar atmosphere to increase its crystallinity. Finally, the MoS₂/TiO₂ nanohybrid exhibited enhanced electrochemical performances as an anode material. It delivered a high reversible capacity of 801 mA h g⁻¹ at a current density of 100 mA g⁻¹ after 50 cycles, and an outstanding rate behavior of a reversible discharge capacity of 660 mA h g⁻¹ at a current density of 1000 mA g⁻¹ and retains a capacity of about 760 mA h g⁻¹ as the current density is back to 100 mA g⁻¹.

2. Experimental section

2.1 Synthesis and characterization of samples

All reagents were analytical grades. The synthesis process of MoS₂/TiO₂ nanoflowers involves two steps: formation of the

precursor MoO₂/TiO₂ and sequent vulcanization to MoS₂/TiO₂ by hydrothermal method.

The synthesis of MoO₂/TiO₂ precursor. The 2.89 mmol of (NH₄)₆Mo₇O₂₄ was dissolved in 30 mL of distilled water. The 2.82 g of ethanol solution of titanium tetrachloride (34% w/w) was added to the above aqueous solution under stirring. Then the mixture was stirred for 2 h. The obtained solution was transferred into a 100 mL autoclave Teflon vessel, which was filled with distilled water up to 60% of the total volume, sealed and hydrothermally treated at 180 °C for 48 h. After cooling to room temperature. The obtained precursor was collected by centrifugation and washed with distilled water and absolute ethanol several times, and dried at 60 °C for 12 h in an oven.

The synthesis of flower-like MoS₂/TiO₂ nanohybrid. 0.1423 g of MoO₂/TiO₂ precursor and an appropriate amount of thiourea were dissolved in 30 mL of distilled water, the mixture was stirred for 2 h, then transferred into a 100 mL Teflon-lined stainless steel autoclave, which was filled with distilled water up to 60% of the total volume. The autoclave was heated at 200 °C for 48 h. After cooling to room temperature. The product was washed more than three times with distilled water and absolute alcohol and then dried at 60 °C in the vacuum oven for 12 h. In order to improve the crystallinity, the product was calcined at 500 °C in Ar atmosphere for 4 h.

The synthesis of bare MoS₂. 0.137 mmol of (NH₄)₆Mo₇O₂₄ and 6.72 mmol of thiourea were dissolved in 30 mL of distilled water, then the mixture was stirred for 2 h. The obtained solution was transferred into a 100 mL Teflon-lined stainless steel autoclave, which was filled with distilled water up to 60% of the total volume. The subsequent procedure was the same as MoS₂/TiO₂ nanohybrid.

The composition and phase of the precursor and the final product were characterized by a Rigaku D/max-ga X-ray diffractometer (XRD) at a scanning rate of 6° min⁻¹ in 2θ ranging from 10° to 80° with Cu Kα radiation (λ = 1.54178 Å). The transmission electron microscopy (TEM) were carried out on a Hitachi H-600 transmission electron microscope with accelerating voltage of 100 kV, and field-emission scanning electron microscope (FESEM, Hitachi S-4800) were obtained with an acceleration voltage of 5 kV. Thermogravimetric analysis (TGA) was carried out using a SDTQ600 at a heating rate of 10 °C min⁻¹ from 25 °C to 650 °C under air atmosphere. The X-ray photoelectron spectroscopy (XPS) was analyzed by Perkin-Elmer PHI1600 spectrometer.

2.2 Electrochemical measurement

The electrochemical tests were carried out in coin cells. The working electrodes were fabricated by coating a slurry containing 80 wt% of active materials (MoS₂/TiO₂ nanohybrid, MoS₂), 10 wt% of acetylene black, and 10 wt% of polyvinylidene fluoride (PVDF) dissolved in *N*-methyl-2-pyrrolidinone onto a copper foil and dried at 110 °C in vacuum for 12 h before pressing. The standard CR-2032 type coin cells were assembled in an Ar-filled glove box using the as-prepared anode, lithium foil as counter electrode, and Celgard-2400 as a separator. The electrolyte was 1 M LiPF₆ dissolved in a mixture of ethylene



carbonate and diethyl carbonate (EC–DEC, 1 : 1 in volume). The cells were aged for 12 h before the measurements. Cyclic voltammetry measurements (CV) and electrochemical impedance spectroscopy (EIS) were performed on an electrochemical workstation (CHI 660D). The voltage scan rate for the CV measurement was at a scan rate of 0.1 mV s^{-1} over the potential range of 0.01–3.0 V (vs. Li^+/Li). The EIS data were obtained by applying excitation amplitude of 10 mV in the frequency range from 10 mHz to 1 MHz. The galvanostatic charge–discharge tests were conducted on the battery measurement system (LAND CT2001A, China) at current densities of 50–1000 mA g^{-1} with a cut off voltage range of 0.01–3.0 V vs. Li/Li^+ at room temperature.

3. Results and discussions

3.1 Structural characteristics of samples

Fig. 2a shows that all the diffraction peaks of precursor can be assigned to the anatase TiO_2 (JCPDS 21-1272) and monoclinic MoO_2 phase (JCPDS 32-0671). Peaks in Fig. 2b can be indexed to a mixture of the hexagonal MoS_2 phase (JCPDS 74-0932) and a phase of anatase TiO_2 (JCPDS 21-1272). It indicated that the MoO_2 has been successfully transformed to MoS_2 . The (002) diffraction peak at 13.8° is lower than standard card ($2\theta = 14^\circ$), which indicates enlarged layer distances of MoS_2 .

Fig. 3a and b show low and high magnification FESEM images of the annealed $\text{MoS}_2/\text{TiO}_2$ nanohybrid, respectively. It exhibits 3D flower-like structure assembled from several thin nanosheets. Some TiO_2 nanoparticles were decorated on the MoS_2 nanosheets. The TEM images of annealed $\text{MoS}_2/\text{TiO}_2$ are shown in Fig. 3c and d. And we found that the hierarchical $\text{MoS}_2/\text{TiO}_2$ nanohybrid was assembled from curly MoS_2 nanosheets and an amount of TiO_2 . The TiO_2 nanoparticles with diameter of $\sim 20 \text{ nm}$ are uniformly distributed on the MoS_2 nanosheets. The morphology of bare MoS_2 were shown in Fig. S1.† It exhibits the cluster-like morphology. The TEM

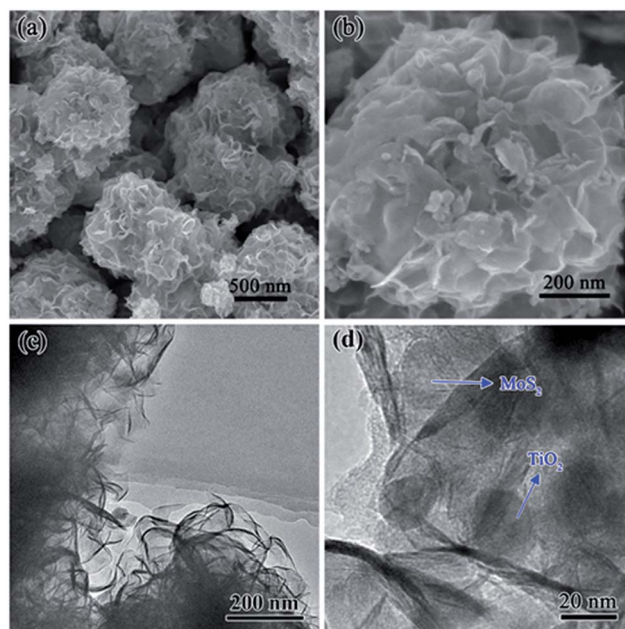


Fig. 3 (a) Low- and (b) high-magnification FESEM images of 3D $\text{MoS}_2/\text{TiO}_2$ nanohybrid. (c) Low- and (d) high magnification TEM images of $\text{MoS}_2/\text{TiO}_2$ nanohybrid.

images of precursor $\text{MoO}_2/\text{TiO}_2$ are shown in Fig. S2.† It exhibits a small amount of TiO_2 nanoparticles are attached to the surface of MoO_2 bundles. The HRTEM image of the $\text{MoS}_2/\text{TiO}_2$ nanohybrid illustrates the crystal lattice structure of MoS_2 and TiO_2 (Fig. S3†). The interplanar spacing of 0.64 nm and 0.35 nm are corresponding to the lattice plane (002) of MoS_2 and (101) of TiO_2 , respectively. The spacing is slightly larger than the layer-to-layer spacing of 6.2 \AA in bulk MoS_2 . This is consistent with the results of XRD. It also indicates that the MoO_2 nanobundles turn into MoS_2 nanosheets successfully. Moreover, the XPS of bare MoS_2 and $\text{MoS}_2/\text{TiO}_2$ nanohybrid were shown in the ESI (Fig. S4†). The binding energies of S $2p_{1/2}$, S $2p_{3/2}$, Mo $3d_{3/2}$ and Mo $3d_{5/2}$ peaks in the bare MoS_2 locate at 163.4, 162.3, 232.7 and 229.5 eV, respectively. However, the S $2p_{1/2}$, S $2p_{3/2}$, Mo $3d_{3/2}$ and Mo $3d_{5/2}$ peaks of $\text{MoS}_2/\text{TiO}_2$ nanohybrid shift to 163.2, 162.1, 232.4 and 229.2 eV, respectively. The binding energy shifts to lower binding energy mean electronic interaction between MoS_2 and TiO_2 .²⁴

TGA was carried out from 25°C to 700°C in air flow to determine the amount of MoS_2 in the $\text{MoS}_2/\text{TiO}_2$ nanohybrid (Fig. 4). The weight loss stage below 300°C is a result of the evaporation of physically adsorbed water and the loss of chemisorbed water, and a large continuous weight loss in the range of approximately $300\text{--}500^\circ\text{C}$ which was caused by the oxidation of MoS_2 . The second weight loss was measured to be 10.56% and 12.32% for the $\text{MoS}_2/\text{TiO}_2$ nanohybrid and bare MoS_2 nanoclusters, respectively. The result is attributed to the oxidation of MoS_2 to MoO_3 . The mass fraction of MoS_2 in the $\text{MoS}_2/\text{TiO}_2$ nanohybrid can thus be estimated to be about 85.7 wt%. Let the weight percentage of MoS_2 in the $\text{MoS}_2/\text{TiO}_2$ nanohybrid to be x , one has $10.56 = 12.32x$. Therefore $x = 85.71\%$.²⁵

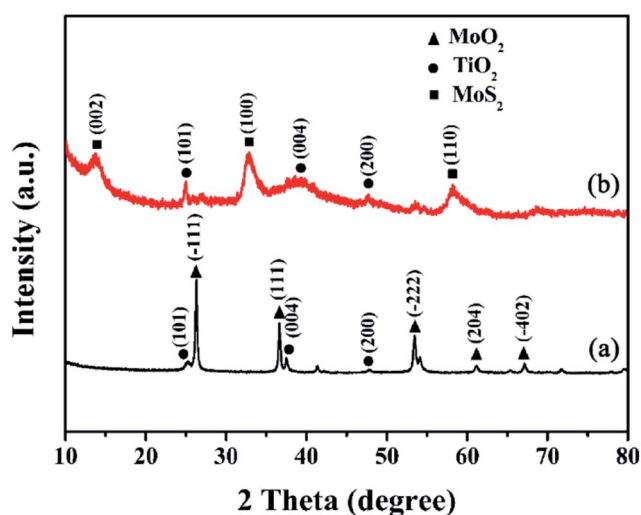


Fig. 2 XRD patterns of (a) precursor of $\text{MoO}_2/\text{TiO}_2$. (b) As-synthesized $\text{MoS}_2/\text{TiO}_2$ nanohybrid.



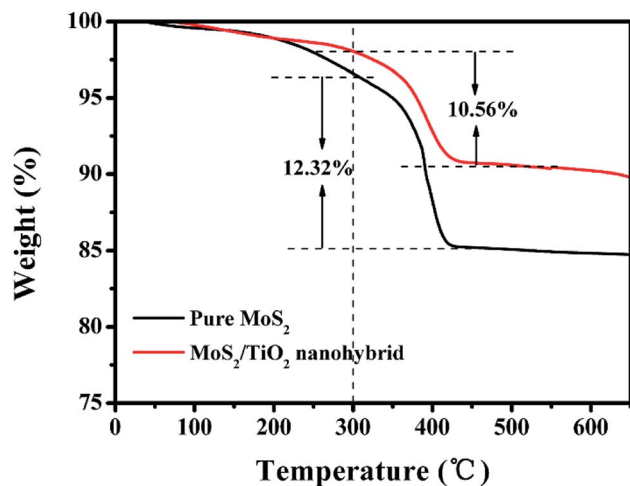


Fig. 4 TGA curves of the $\text{MoS}_2/\text{TiO}_2$ nanohybrid and pure MoS_2 nanoclusters at a temperature ramp of $10^\circ\text{C min}^{-1}$ in air.

In order to investigate the detailed local elemental composition and distribution of the flower-like $\text{MoS}_2/\text{TiO}_2$ nanohybrid, energy dispersive X-ray (EDX) mapping analysis was carried out (Fig. 5). The EDS analysis shows that the composite mainly contains O, S, Ti and Mo. Fig. 5b–f shows the full elements map and corresponding elemental mapping images. The O, S, Ti and Mo are homogeneously distributed throughout the samples on the whole. From the elemental mapping, it can

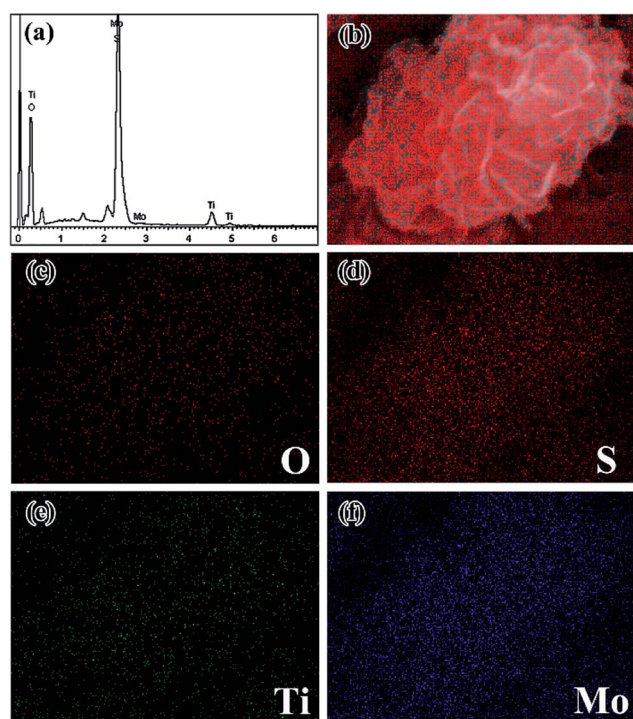


Fig. 5 (a) EDS spectrum of the $\text{MoS}_2/\text{TiO}_2$ nanohybrid; the EDX elemental maps of (b) full elemental map and the corresponding elemental mapping images of (c) oxygen (d) sulfur (e) titanium and (f) molybdenum.

be observed that the Mo and S elemental distribution shows strong signals (Fig. 5d and f). For the Ti and O signals, the distinct distributions are sparse compared to Mo and S. It agrees well with the EDS spectrum.

3.2 Electrochemical properties

The annealed $\text{MoS}_2/\text{TiO}_2$ nanohybrid was assembled into Li half-cells to investigate the electrochemical performance. Fig. 6a shows the cyclic voltammetry curves (CVs) of the annealed $\text{MoS}_2/\text{TiO}_2$ nanohybrid, which we collected at a scan rate of 0.01 mV s^{-1} in a potential window of $0.01\text{--}3.0\text{ V vs. Li}^+/\text{Li}$. In the first cathodic process (discharge process), four reduction peaks appear at approximately at 1.8 V , 1.7 V , 1.1 V and 0.6 V . The remarkable cathodic peak appears at 1.8 V , indicating the lithiation process leading from S to Li_2S .²⁵ The weak reduction peak at 1.7 V is due to the lithiation of TiO_2 nanoparticles. The reduction peak at 1.1 V is attributed to the Li intercalation into the MoS_2 nanosheets, resulting in the phase transformation from trigonal prismatic to octahedral.²⁶ The reduction peak at 0.6 V can be assigned to the decomposition of Li_xMoS_2 into Li_2S and Mo particles, which is based on the conversion reaction: $\text{MoS}_2 + 4\text{Li}^+ + 4\text{e}^- \rightarrow \text{Mo} + 2\text{Li}_2\text{S}$.²⁷ These peaks disappear in the successive cathodic process resulting from few amorphous MoS_2 reformed after the first charge process. In the follow cycles, a new reduction peak appears at 1.8 V corresponding to lithiation process of S to form sulfur-containing materials.²⁵ In the first charge process, three anodic peaks appear at 1.75 V , 2.0 V and 2.3 V . The small oxidation peak at 1.75 V is likely due to the transformation of Mo to MoS_2 . The two peaks at 2.0 V and 2.3 V are attributed to the reversible conversion reactions of Li_xTiO_2 to TiO_2 and the conversion of Li_2S into S, respectively. A broad envelope feature at lower potential could be found, which

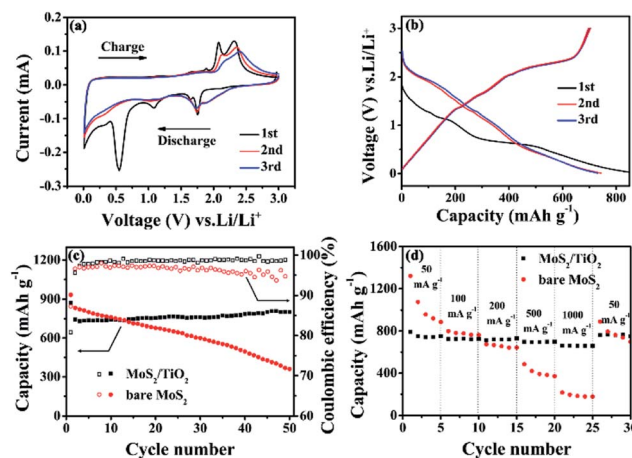


Fig. 6 (a) Representative CV curves for the 1st, 2nd, 3rd of the annealed $\text{MoS}_2/\text{TiO}_2$ nanohybrid at a scan rate of 0.1 mV s^{-1} , (b) galvanostatic charge–discharge voltage profiles of the annealed $\text{MoS}_2/\text{TiO}_2$ nanohybrid at a current density of 100 mA g^{-1} , (c) comparative cycling performance and coulombic efficiency of the annealed $\text{MoS}_2/\text{TiO}_2$ nanohybrid and bare MoS_2 at a current density of 100 mA g^{-1} , (d) rate performance of the annealed and bare MoS_2 at different current densities.



due to the formation of amorphous phase.²⁸ The CV curves of bare MoS₂ is shown in Fig. S5a.† Compared with MoS₂/TiO₂ nanohybrid, the reduction peak at 1.7 V and oxidation peak at 2.0 V are disappeared. It is attributed to the absence of TiO₂. Fig. 6b presents the galvanostatic discharge–charge (GDC) voltage profiles of the annealed MoS₂/TiO₂ nanohybrid at 100 mA g^{−1}. In agreement with the above CV results, two apparent voltage plateaus at 1.1 V and 0.6 V in the first discharge process are attributed to the phase transformation from 2H-MoS₂ to 1T-Li_xMoS₂ and further conversion into Mo and Li₂S. During the charge process, a weak potential plateau at 1.75 V is attributed to the oxidation of Mo to MoS₂. The other conspicuous potential plateau at about 2.3 V appeared is corresponding to the conversion of Li₂S into S. There is no obvious difference compared with bare MoS₂ (Fig. S5b†). It may be due to relatively low content of TiO₂. In the first cycle, the MoS₂/TiO₂ nanohybrid reveals discharge and charge specific capacities of 871.4 mA h g^{−1} and 696.7 mA h g^{−1}, respectively, leading to a relatively high coulombic efficiency (CE) of 80%. It should be mainly due to the gel-like polymeric layer formation on the MoS₂/TiO₂ nanohybrid.²⁹ The charge and discharge capacities in the second cycle are 743.3 mA h g^{−1} and 702.8 mA h g^{−1}, giving a relatively high coulombic efficiency of 94.5%. The cycling performances and coulombic efficiency of MoS₂/TiO₂ nanohybrid and bare MoS₂ are shown in Fig. 6c. The initial discharge capacity of MoS₂/TiO₂ nanohybrid is 871.4 mA h g^{−1}, it exhibits lower discharge capacity than the MoS₂. This is mainly on account of the influence of the TiO₂. Nevertheless, after 50 cycles, the specific capacity of the bare MoS₂ decreases quickly from 932.7 mA h g^{−1} to 360.9 mA h g^{−1}, while the MoS₂/TiO₂ nanohybrid delivers a discharge specific capacity of 802 mA h g^{−1} with a capacity retention of 92%. The MoS₂/TiO₂ hybrid nanostructures possess more stable cycle stability and higher discharge capacities than the bare MoS₂. The coulombic efficiency of MoS₂/TiO₂ hybrid is also higher than bare MoS₂. The cycling performance of bare acetylene black and TiO₂ were shown in Fig. S6.† We assess that 10 wt% of acetylene black and 14.29 wt% of TiO₂ contribute ~40 mA h g^{−1} to the discharge capacity in total. The rate behavior was shown in Fig. 6d. The 3D nanoflower-like MoS₂/TiO₂ hybrid displays a reversible discharge capacity of 660 mA h g^{−1} at a current density of 1000 mA g^{−1} and retains a capacity of about 760 mA h g^{−1} as the current density is back to 100 mA g^{−1}, indicating the good capacity recovery. Comparably, the bare MoS₂ exhibits the inferior cyclic capacity retention and rate capability. The excellent electrochemical performance may be attributed to the favorable synergistic effect between MoS₂ and TiO₂. The TiO₂ nanoparticles can enhance the structure stability and shorten the transport of ions across the surface.

Electrochemical impedance spectroscopy (EIS) was carried out to study the electrode kinetics of the materials (Fig. 7). The Nyquist plots were simulated by the equivalent circuit as depicted in Fig. 7b. R_e represents the resistance contribution from the electrolyte, electrode and the passive film between them. The symbol R_{sf} represented by the semicircle at high frequency are due to the Li⁺ migration through the solid electrolyte interphase (SEI) film. The symbol R_{ct} are assigned to the charge-transfer

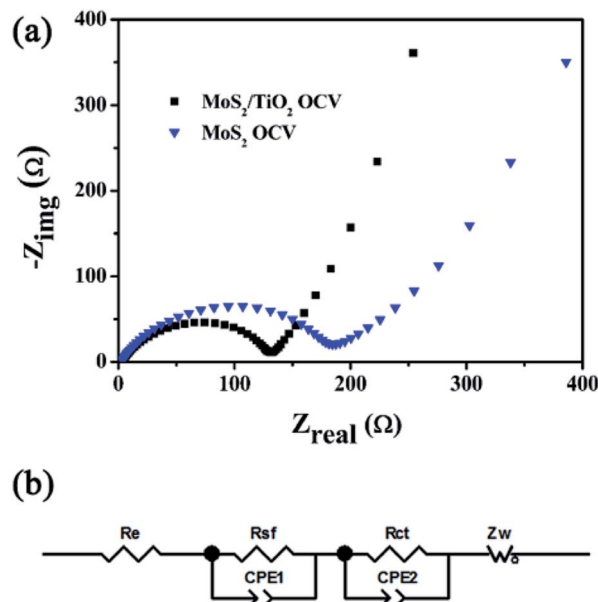


Fig. 7 (a) Nyquist plots of the MoS₂/TiO₂ hybrid and bare MoS₂ electrodes, (b) equivalent circuits for fitting Nyquist plots.

resistance at the electrode/electrolyte interface, which is shown by a semicircle in mid-frequency region. The slope line in the low frequency region relates to Li⁺ diffusion processes in the active material. The EIS experiments of MoS₂/TiO₂ hybrid and bare MoS₂ were conducted at OCV (open circuit potential) firstly (Fig. 7a). As can be seen, the MoS₂/TiO₂ hybrid shows a smaller semicircle diameter than the MoS₂, indicating that the MoS₂/TiO₂ hybrid has lower charge transfer resistance. The charge-transfer resistance (R_{ct}) of the MoS₂/TiO₂ hybrid and MoS₂ are 120.9 Ω and 148.8 Ω, respectively. Fig. S7† shows the Nyquist plot for the MoS₂/TiO₂ hybrid and bare MoS₂ after the first discharge and charge process. The impedance data values are summarized in Table S1.† At the end of the 1st discharge, the semicircle at high frequency appears because of the resistance of surface-passivation layer.³⁰ The R_{sf} of MoS₂/TiO₂ hybrid and MoS₂ are 37.6 Ω and 108.2 Ω, respectively. Such phenomenon indicates the formation of a thick SEI layer on the surface.³¹ Therefore, the decreasing tendency of R_{ct} could be observed. However, the R_{ct} of MoS₂/TiO₂ hybrid (114.9 Ω) is also much lower than MoS₂ (138.5 Ω). After the 1st charge, the diameter of semicircle at mid-frequency is significantly enlarged. The increasing charge transfer resistance may due to the volume expansion of MoS₂ after the first cycle. Nevertheless, the MoS₂/TiO₂ (195.4 Ω) shows a smaller semicircle diameter than the MoS₂ electrode (259.7 Ω), indicating that the MoS₂/TiO₂ hybrid has lower charge transfer resistance (R_{ct}). The effect of the modification with TiO₂ may be verified. The modification of TiO₂ may stabilize the structure of MoS₂ and alleviate volume change. The MoS₂/TiO₂ hybrid shows lower slope than bare MoS₂, indicating the better lithium ion kinetics in the electrode materials. It may due to attachment of TiO₂ particles onto the surface of MoS₂ can greatly enhance electron transport. Consequently, a favorable synergistic effect between the TiO₂ nanoparticles and MoS₂ nanosheets is supposed.



4. Conclusions

In summary, TiO₂ nanoparticles decorated MoS₂ nanoflowers have been successfully developed by a two-step hydrothermal process. As the anode materials for LIBs, the electrochemical performance of MoS₂/TiO₂ hybrid is better than bare MoS₂. This may be due to the hybridization with TiO₂ be able to stabilize the structure of MoS₂ and effectively accommodates the volume changes. Meanwhile, the TiO₂ nanoparticles can shorten the transport of ions across the surface. This work opens up an avenue for the rational design of other anode composite materials in high performance LIBs.

Acknowledgements

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Notes and references

- 1 X. Cao, Y. Shi, W. Shi, X. Rui, Q. Yan, J. Kong and H. Zhang, *Small*, 2013, **9**, 3433–3438.
- 2 Y. Xu, G. Yin, Y. Ma, P. Zuo and X. Cheng, *J. Mater. Chem.*, 2010, **20**, 3216–3220.
- 3 T. Stephenson, Z. Li, B. Olsen and D. Mitlin, *Energy Environ. Sci.*, 2014, **7**, 209–231.
- 4 X. Xu, W. Liu, Y. Kim and J. Cho, *Nano Today*, 2014, **9**, 604–630.
- 5 J. Ye, L. Ma, W. Chen, Y. Ma, F. Huang, C. Gao and J. Y. Lee, *J. Mater. Chem. A*, 2015, **3**, 6884–6893.
- 6 H. Hwang, H. Kim and J. Cho, *Nano Lett.*, 2011, **11**, 4826–4830.
- 7 X. Li, W. Li, M. Li, P. Cui, D. Chen, T. Gengenbach, L. Chu, H. Liu and G. Song, *J. Mater. Chem. A*, 2015, **3**, 2762–2769.
- 8 S.-K. Park, S.-H. Yu, S. Woo, J. Ha, J. Shin, Y.-E. Sung and Y. Piao, *CrystEngComm*, 2012, **14**, 8323–8325.
- 9 U. K. Sen and S. Mitra, *ACS Appl. Mater. Interfaces*, 2013, **5**, 1240–1247.
- 10 S. Wang, X. Jiang, H. Zheng, H. Wu, S.-J. Kim and C. Feng, *Nanosci. Nanotechnol. Lett.*, 2012, **4**, 378–383.
- 11 Z. Hu, L. Wang, K. Zhang, J. Wang, F. Cheng, Z. Tao and J. Chen, *Angew. Chem.*, 2014, **126**, 13008–13012.
- 12 G. Tang, J. Sun, C. Wei, K. Wu, X. Ji, S. Liu, H. Tang and C. Li, *Mater. Lett.*, 2012, **86**, 9–12.
- 13 S. Ding, J. S. Chen and X. W. D. Lou, *Chem.-Eur. J.*, 2011, **17**, 13142–13145.
- 14 L. Zhang, W. Fan, W. W. Tjiu and T. Liu, *RSC Adv.*, 2015, **5**, 34777–34787.
- 15 G.-H. Lee, S.-J. Kim, M.-C. Kim, H.-S. Choe, D.-M. Kim, S.-B. Han, D.-H. Kwak, J. H. Jeong and K.-W. Park, *RSC Adv.*, 2016, **6**, 92259–92266.
- 16 L. Hu, Y. Ren, H. Yang and Q. Xu, *ACS Appl. Mater. Interfaces*, 2014, **6**, 14644–14652.
- 17 L. Yang, S. Wang, J. Mao, J. Deng, Q. Gao, Y. Tang and O. G. Schmidt, *Adv. Mater.*, 2013, **25**, 1180–1184.
- 18 Y. Chen, B. Song, X. Tang, L. Lu and J. Xue, *Small*, 2014, **10**, 1536–1543.
- 19 B. Chen, N. Zhao, L. Guo, F. He, C. Shi, C. He, J. Li and E. Liu, *Nanoscale*, 2015, **7**, 12895–12905.
- 20 X. Xu, Z. Fan, S. Ding, D. Yu and Y. Du, *Nanoscale*, 2014, **6**, 5245–5250.
- 21 Q. Xiang, J. Yu and M. Jaroniec, *J. Am. Chem. Soc.*, 2012, **134**, 6575–6578.
- 22 Q. Pang, Y. Zhao, X. Bian, Y. Ju, X. Wang, Y. Wei, B. Liu, F. Du, C. Wang and G. Chen, *J. Mater. Chem. A*, 2017, **5**, 3667–3674.
- 23 X. Zhu, C. Yang, F. Xiao, J. Wang and X. Su, *New J. Chem.*, 2015, **39**, 683–688.
- 24 C. Liu, L. Wang, Y. Tang, S. Luo, Y. Liu, S. Zhang, Y. Zeng and Y. Xu, *Appl. Catal., B*, 2015, **164**, 1–9.
- 25 W. Zhuang, L. Li, J. Zhu, R. An, L. Lu, X. Lu, X. Wu and H. Ying, *ChemElectroChem*, 2015, **2**, 374–381.
- 26 G. Du, Z. Guo, S. Wang, R. Zeng, Z. Chen and H. Liu, *Chem. Commun.*, 2010, **46**, 1106–1108.
- 27 M. Mao, L. Mei, D. Guo, L. Wu, D. Zhang, Q. Li and T. Wang, *Nanoscale*, 2014, **6**, 12350–12353.
- 28 T.-F. Yi, J.-Z. Wu, M. Li, Y.-R. Zhu, Y. Xie and R.-S. Zhu, *RSC Adv.*, 2015, **5**, 37367–37376.
- 29 K. Chang and W. Chen, *ACS Nano*, 2011, **5**, 4720–4728.
- 30 B. Chen, N. Zhao, L. Guo, F. He, C. Shi, C. He, J. Li and E. Liu, *Nanoscale*, 2015, **7**, 12895–12905.
- 31 T. S. Sahu and S. Mitra, *Sci. Rep.*, 2015, **5**, 12571.

