

MoS₂/C/C nanofiber with double-layer carbon coating for high cycling stability and rate capability in lithium-ion batteries

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ABSTRACT

MoS₂ has attracted a lot of interest in the field of lithium-ion storage as an anode material owing to its high capacity and two-dimensional (2D)-layer structure. However, its electrochemical properties, such as rate capability and cycling stability, are usually limited by its low conductivity, volume variation, and polysulfide dissolution during lithiation/delithiation cycling. Here, a designed two-layer carbon-coated MoS₂/carbon nanofiber (MoS₂/C/C fiber) hybrid electrode with a double-layer carbon coating was achieved by a facile hydrothermal and subsequent electrospinning method. The double carbon layer (inner amorphous carbon and outer carbon fiber) shells could efficiently increase the electron conductivity, prevent the aggregation of MoS₂ flakes, and limit the volume change and polysulfide loss during long-term cycling. The as-prepared MoS₂/C/C fiber electrode exhibited a high capacity of up to 1,275 mAh/g at a current density of 0.2 A/g, 85.0% first cycle Coulombic efficiency, and significantly increased rate capability and cycling stability. These results demonstrate the potential applications of MoS₂/C/C fiber hybrid material for energy storage and may open up a new avenue for improving electrode energy storage performance by fabricating hybrid nanofiber electrode materials with double-layer carbon coatings.

1 Introduction

MoS₂ is one of the typical two-dimensional (2D)

transition-metal dichalcogenides (TMDs), with a layered structure loosely held together by the Van der Waals interaction. MoS₂ exhibits a unique

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graphite-like structure in which the Mo hexagonal layers are sandwiched by two S layers, and each layer is bonded by strong covalent bonds (Mo–S) [1–3]. Due to its unique structure, MoS₂ demonstrates a variety of physical and chemical properties, such as photoluminescence, a bulk indirect band gap of 1.3 eV (which is similar to silicon), and excellent electrochemical performance for applications in photo/electrocatalysts, energy storage, and conversion devices [4–8]. Because of the weak interlayer interaction and large interlayer distance of 0.65 nm between each S–Mo–S layer, lithium ions can easily intercalate/extract through MoS₂ layers. Thus, MoS₂ is a promising anode material and its capacity can be three and a half times that of commercial graphite anodes [9–13]. Reversible capacity as high as 1,290 mAh/g has been reported for the MoS₂-graphene composite electrode [14]. Compared to other emerging negative electrode materials, such as silicon or SnO₂, MoS₂ generally displays much better rate capability, lower cycling degradation, as well as low cost (e.g., sub-micro MoS₂ powder retails for dollars per kg) [15]. While silicon anodes possess an initial capacity around 3,500 mAh/g when tested at low rates (e.g., 0.1 C), they retain minimal capacity at high rates (e.g., 10 C) or after long term cycling due to their 280% volumetric expansion upon full lithiation and related unstable solid electrolyte interface [12]. In addition, nanostructured MoS₂ routinely outperforms its bulk equivalent in terms of capacity retention, rate capability, and cycle life, due to shorter lithium diffusion distances and higher concentrations of active edge sites, which further enhance their lithium storage capability [11, 16, 17].

However, electrodes based on layered MoS₂ do not work perfectly. Although the volume change of MoS₂ is significantly less than that in silicon-based electrodes, the theoretical 103% volume expansion via the conversion reaction of MoS₂ to Li₂S and molybdenum will still lead to depressed cycling stability and rate performance [18–21]. The intrinsically limited conductivity, restacking of MoS₂ nanosheets, side reactions between Li₂S and electrolyte, and polysulfide dissolution during cycling can further aggravate the degradation of electrochemical performance [22–24].

In order to ameliorate the electrical conductivity and structural stability of MoS₂ electrodes during

cycling, carbonaceous materials, such as amorphous carbon, carbon fibers, porous carbon, carbon spheres, carbon nanotubes, and graphene, have been employed to form hybrid MoS₂-carbon systems [13, 25, 26]. The carbon component can enhance the electronic conductivity and concurrently buffer the volume changes of MoS₂ during the lithiation/delithiation reaction. At the same time, carbon materials can also act as a binder between the S/Li₂S and the molybdenum to prevent the loss of polysulfide during cycling [1, 23, 27, 28]. Based on these properties, hybrid MoS₂-carbon systems can lead to better electrode kinetics and more stable cycling performance [29–33].

Although some progress has been made in enhancing electrochemical performance by fabricating hybrid MoS₂/carbon electrode materials [34–36], there are still some challenges for this hybrid system. The restacking and aggregation of the nanocarbon materials, such as graphene or carbon nanotubes, or even MoS₂ nanomaterials during the fabrication process can lead to a serious loss of active surface area and sluggish ion transport kinetics. In addition, it is still difficult to coat or deposit a carbon layer with ideal thickness and compact contact interface onto nanosized MoS₂ materials. Thus, effectively controlling the carbon-coating process and avoiding the aggregation of the MoS₂/carbon is still a challenge.

Herein, we designed a two-layer carbon-coated MoS₂/carbon hybrid nanofiber material (MoS₂/C/C fiber), to serve as a high performance anode material for Li-ion batteries. Carbon-coated three-dimensional (3D) hierarchical MoS₂ nanospheres (MoS₂/C spheres) were fabricated first and then embedded into ~ 250 nm diameter electrospun fibers. The double-layer carbon coating plays a key role in preventing the aggregation of MoS₂ flakes, restraining the MoS₂ volume changes, and consumption of sulfides and molybdenum during lithiation/delithiation. Due to its structural stability and enhanced electron transport, the MoS₂/C/C fiber electrode manifests an outstanding reversible capacity and an excellent cycling performance. The double-layer carbon-coated MoS₂ composite electrode is a promising candidate anode active material for next generation lithium batteries with high capacity, high rate, and high cycling stability.

2 Experimental section

2.1 Preparation of MoS₂ spheres

In a typical reaction [2], 1 mmol hexaammonium heptamolybdate tetrahydrate ((NH₄)₆Mo₇O₂₄·4H₂O, AR), 14 mmol thiourea (NH₂CSNH₂, ≥ 99.0%), and 0.01 mmol surfactant PVP (K32) were dissolved in 40 mL of deionized water (DI water) under vigorous stirring and ultrasonication for 30 min to form a homogeneous solution. Then, the solution was transferred into a 50 mL Teflon-lined stainless-steel autoclave and kept at 220 °C for 18 h. After being cooled to room temperature, the obtained precipitates were centrifuged and washed with DI water, acetone, and ethanol three times. The final products were dried at 70 °C under vacuum for 12 h.

2.2 Preparation of MoS₂/C spheres

In a typical synthesis [34], 100 mg of glucose and 200 mg of the above-obtained MoS₂ spheres were dissolved in 30 mL of DI water after violent stirring and ultrasonication for 30 min. Then, the solution was transferred into a 50 mL Teflon autoclave, followed by heating at 190 °C for 10 h. The autoclave was then cooled down to room temperature and the coating product was collected from the solution, washed with DI water and ethanol, and dried at 70 °C overnight. Finally, the produced powder was carbonized at 450 °C for 3 h under a nitrogen atmosphere to obtain the MoS₂/C spheres.

2.3 Preparation of MoS₂/C/C fiber

The mixture solution was prepared by adding 0.5 g of polyacrylonitrile (PAN) and 0.4 M of the above-obtained MoS₂/C spheres in 4.5 mL of N,N-dimethyl formamide (DMF). After stirring and ultrasonication for 30 min, the mixture solution was spun by a controlled electrospinning method. The applied working voltage, flow rate, and distance between the needle and the collector were fixed at 19 kV, 0.75 mL/h, and 15 cm, respectively. The electrospun fibers were collected from the aluminum foil and then prepared for further carbonization. In a typical carbonization process, the oxidative stabilization process was first carried out using a conventional muffle furnace at

280 °C for 1 h. Then, thermal treatment of the nanofiber film was performed at 1,000 °C for 3 h, with a continuous stable high-purity nitrogen gas.

2.4 Characterizations

X-ray diffraction (XRD) measurements were conducted with a Rigaku D/max 2550 V diffractometer using Cu K α radiation at a wavelength of 1.5406 Å. Scanning electron microscopy (SEM) measurements were performed with a SU-8010 field emission SEM. Transmission electron microscopy (TEM), and elemental mapping were carried out using a FEI Tecnai G2 F20 TEM at 200 kV. X-ray photoelectron spectroscopy (XPS) measurements were performed using a Kratos Axis Ultra multi-functional X-ray photoelectron spectroscope with a typical detection depth of ~ 5 nm. All XPS spectra were corrected using the C 1s line at 284.7 eV. The carbon content of the samples was determined through thermogravimetric and differential scanning calorimetry (TG–DSC) using a Libra/209F1 with a speed of 10 °C/min in ambient air in a temperature range of 50 to 700 °C. Raman spectroscopy was performed using an inVia-Reflex with an excitation wavelength of 785 nm. Nitrogen adsorption and desorption isotherms at 77.3 K were carried out with an ASAP 2020 physisorption analyzer (USA).

2.5 Electrochemical measurements

2.5.1 Half-cell

The electrochemical properties of MoS₂ spheres, MoS₂/C spheres, and MoS₂/C/C fiber were investigated using a coin-type half-cell (CR2032). For the preparation of working electrodes, active materials, Super-P carbon black, and polyvinylidene fluoride (PVDF) with a mass ratio of 70:20:10 were mixed into a homogeneous slurry by adding DMF and the obtained slurry was pasted onto pure Cu foil and dried at 60 °C overnight. Lithium metal foil works as both counter and reference electrode. The cell used LiPF₆ (1 M) in ethylene carbonate/dimethyl carbonate/diethyl carbonate (1:1:1 vol.%) as the electrolyte and a Celgard 2400 polypropylene membrane as the separator. All the batteries were assembled in an argon-filled glovebox with humidity and oxygen levels lower than 1 ppm. The charge and discharge measurements of the cells

were performed on a LAND CT2001A electrochemical workstation between 0.005 and 3.00 V at room temperature. Cycling voltammogram (CV) tests of the batteries were performed by a CHI660D electrochemical workstation with the same potential range.

2.5.2 Full-cell

The MoS₂/C/C fiber electrode as active materials, Super-P carbon black, and PVDF with a mass ratio of 70:20:10 were mixed into a homogeneous slurry, which was then pasted onto pure copper foil as the anode electrode. The full cell was fabricated using a MoS₂/C/C fiber electrode on Cu foil as the anode, lithium cobalt oxide (LiCoO₂) on aluminum foil as the cathode electrode, with the same separator and electrolyte as in the half-cell. The charge and discharge measurements of the batteries were performed on a LAND CT2001A electrochemical workstation between 0.005 and 4.20 V. The average mass loading of the half-cell was 2.0–2.4 mg/cm². For the MoS₂/C/C/LiCoO₂ full cell, the mass loadings for the anode and cathode were 4.0 and 19.9 mg/cm², respectively.

3 Results and discussion

As illustrated in Fig. 1(a), the typical preparation

process of MoS₂/C/C fiber hybrid electrodes consists of three steps, including one step for the MoS₂ spheres preparation and two steps for the double-layer carbon coating. In the first step, MoS₂ nanospheres were synthesized by a hydrothermal method. Then the prepared MoS₂ nanospheres were reacted with glucose and annealed under a N₂ atmosphere to get the first layer of the carbon coating. The typical morphologies of the MoS₂ and MoS₂/C nanospheres were characterized with SEM and TEM, as shown in Figs. 1(b) and 1(c) and Figs. S1 and S2 in the Electronic Supplementary Material (ESM). The pure MoS₂ exhibited similar spherical nanostructures with an average diameter of ~ 200 nm. The high resolution TEM images (Fig. S1 in the ESM) demonstrate that the MoS₂ flakes with lateral sizes of 50–100 nm and thicknesses of ~ 5 nm were highly interconnected and formed into a 3D nanosphere. The interconnected 3D structure can efficiently prevent the aggregation of MoS₂ nanosheets, ensuring electrode mechanical integrity. The MoS₂ nanosheets showed a typical lattice plane spacing of 0.66 nm for the (002) crystal plane, which exceeds the crystalline MoS₂ lattice spacing of 0.62 nm. The expanded spacing could decrease the energy barrier for Li ion intercalation. After being coated with the first carbon layer, the diameter of the MoS₂/C nanospheres increased by

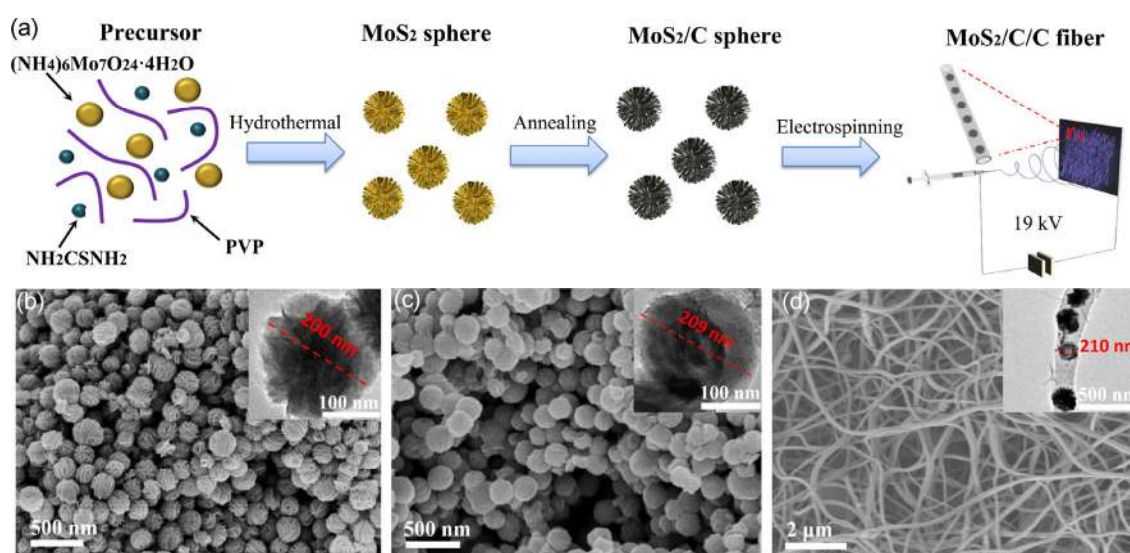


Figure 1 (a) Schematic illustration of the preparation process of MoS₂/C/C fiber electrodes. (b)–(d) SEM images of MoS₂ spheres, MoS₂/C spheres, and MoS₂/C/C fiber. The insets are the magnified TEM images of these three samples, respectively.

5–10 nm. As shown in the high resolution TEM image in Fig. S2 in the ESM, the very thin carbon layer was uniformly wrapped around the MoS₂ nanospheres without damaging the 3D network. The first carbon coating layer not only facilitates the intrinsic electron conductivity of the electrode material but also limits structural damage during the electrochemical process.

The MoS₂/C nanospheres were subsequently mixed with PAN and electrospun into nanofibers. As schematically illustrated in Fig. S3 in the ESM, the as-prepared nanofibers were pre-oxidized and then carbonized by high temperature thermal treatment. The as-prepared MoS₂/C/C fibers exhibited a homogeneous diameter distribution and smooth surface. As shown in the SEM image in Fig. 1(d), the diameters

of the MoS₂/C/C fibers were mainly in the range of 250 to 280 nm. It is worth noting that no obvious MoS₂ nanosheets were found at the surface of the fibers, implying the embedding of MoS₂/C spheres inside the nanofibers. The low magnification TEM images in Figs. 2(a) and 2(b) clearly show the MoS₂/C spheres embedded into the carbon fiber networks. To further characterize the microstructure, we performed high-resolution TEM. A very clear two-layer carbon coating on MoS₂ spheres was observed. Furthermore, the high-resolution TEM energy dispersive spectroscopy (EDS) elemental mapping is shown in Figs. 2(e)–2(g), which exhibit the elemental distribution in the MoS₂/C/C fiber sample in the same region as that shown in Fig. 2(d). All of the molybdenum, sulfur,

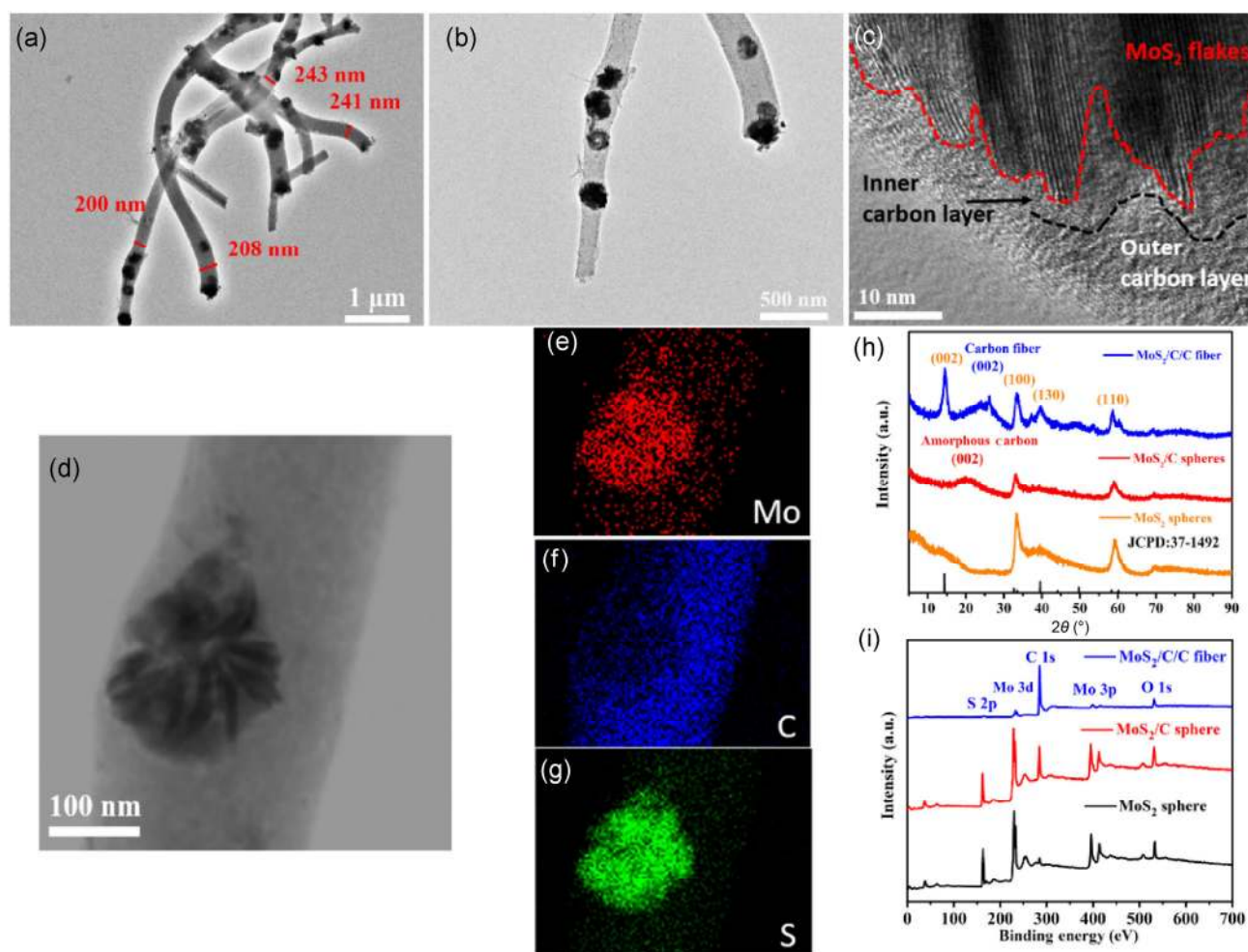


Figure 2 (a) and (b) TEM images of MoS₂/C/C fiber. (c) High-magnification TEM image corresponding to area of MoS₂/C/C fiber. (d)–(g) TEM images of MoS₂/C/C fiber electrode material and the corresponding elemental mapping images of Mo, S, and C. (h) XRD patterns of MoS₂, MoS₂/C, and MoS₂/C/C fiber. (i) The full range XPS spectra of MoS₂, MoS₂/C, and MoS₂/C/C fiber.

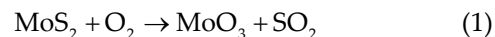
and carbon are distributed in specific regions of the 3D MoS₂/C/C fiber network, which further proves the successful preparation of the MoS₂/C/C fiber hybrid nanostructure.

The crystalline structure and chemical composition of the resultant MoS₂, MoS₂/C nanospheres, and MoS₂/C/C hybrid fiber were further studied by XRD and XPS. The XRD pattern of the MoS₂ nanospheres shows three dominant peaks of hexagonal crystalline 2H-MoS₂ (JCPDS: 37-1492). These three peaks, corresponding to the (002), (100), and (110) planes, emerge at 13.5°, 33.3°, and 58.9° [16], respectively. After thin layer carbon coating, the XRD pattern of the MoS₂/C spheres does not show any obvious changes from pure the MoS₂ spheres sample, except for the appearance of a broad peak at ~ 22° associated with amorphous carbon and a decrease in the intensity of the (100) plane peak of MoS₂, due to the thin layer carbon coating [36, 37]. For the XRD pattern of MoS₂/C/C fiber, the peak shown around 25° is ascribed to the outer layer carbon coating. The sharpened peaks corresponding to the (002) and (130) planes at 13.5° and 39.4°, respectively, are related to the high temperature thermal treatment and the shrinkage of the interlayer spacing of MoS₂ [38, 39].

XPS measurements were carried out to further clarify the components of these samples and the interfacial properties between MoS₂ flakes and the carbon layer. Overall, Fig. 2(i) shows the full XPS spectra of pure MoS₂, MoS₂/C, and MoS₂/C/C fiber materials. The spectrum from the pure MoS₂ spheres clearly exhibits peaks assigned to Mo 3d and 3p, S 2p, and O 1s. Both MoS₂/C and MoS₂/C/C fiber also include the C 1s peak, and the intensity ratio of C 1s for MoS₂/C/C fibers is much higher than that of MoS₂/C spheres.

The high-resolution XPS spectra of MoS₂, MoS₂/C nanospheres and MoS₂/C/C fibers are shown in Figs. S4–S6 in the ESM. Two peaks are observed at 228.6 and 231.9 eV, which can be attributed to the Mo 3d_{5/2} and Mo 3d_{3/2} binding energies, respectively, and are ascribed to the characteristic peaks of Mo⁴⁺ in MoS₂ flakes [40]. The peaks at 232.1 and 235.3 eV are related to the Mo 3d_{5/2} and 3d_{3/2} of Mo⁶⁺ (typical of the Mo–O–C bond) [26]. The peaks at 162.5 and 161.3 eV are attributed to the S 2p_{1/2} and S 2p_{3/2} peaks, which

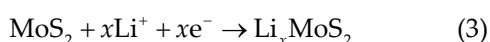
are related to the sulfur in MoS₂ [13]. The C 1s spectra can be decomposed into a dominant peak at 284.7 eV for C=C/C–C, and another broad peak related to oxygen-containing functional groups, which include C–O–Mo bonds [26]. The C–O–Mo bonds can be formed by bonding Mo atoms to oxygen-containing functional groups of the carbon precursor. The interfacial interaction of the C–O–Mo bond between MoS₂ and inner carbon layer should be beneficial for the electrochemical performance of the MoS₂/C/C fiber electrodes. As shown in Fig. S7 in the ESM, we further characterized the structure of MoS₂/C and MoS₂/C/C hybrid electrodes using Raman spectroscopy. For MoS₂/C, the two distinct peaks at 377 and 404 cm⁻¹ correspond to the E_{1g} vibration mode (the in-plane displacement of Mo and S atoms) and the A_{1g} vibration mode (out-of-plane symmetric displacements of S atoms along the *c*-axis), respectively. After embedding MoS₂/C spheres into carbon fiber, these two MoS₂ related peaks disappeared due to the thick outer carbon layer. In addition, both MoS₂/C spheres and MoS₂/C/C fiber hybrid materials also displayed another two peaks at the bands around 1,360 (D band) and 1,590 (G band) cm⁻¹. The D band can be assigned to sp³-hybridized disordered carbon or defective carbon, and the G band is associated with sp²-hybridized graphitic carbon. The relative intensity ratio of I_D/I_G can roughly indicate the ratio of disordered carbon to graphitic carbon. The calculated values of I_D/I_G for MoS₂/C and MoS₂/C/C hybrid materials are 0.88 and 0.97, respectively, suggesting that MoS₂/C/C fiber contained a higher ratio of sp³-hybridized carbon after the high temperature annealing. Figure S8 in the ESM reveals the thermogravimetric analysis of pure MoS₂, MoS₂/C spheres, and MoS₂/C/C fiber. The mass loss can be attributed to the decomposition of MoS₂ and carbon using Eqs. (1) and (2)



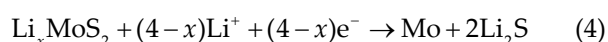
As shown in Fig. S8 in the ESM, in the case of pure MoS₂, 10% of the weight loss happened at approximately 350 °C owing to the oxidation of MoS₂ to MoO₃ under an air atmosphere. In contrast, MoS₂/C and MoS₂/C/C hybrid materials present a larger

weight loss of ~ 22% and 63%, respectively. The oxidative decomposition of carbon materials is thought to be the main reason for the different weight losses between MoS₂/C and MoS₂/C/C hybrid materials and pure MoS₂ material. Thus, the carbon contents in MoS₂/C and MoS₂/C/C hybrid materials are estimated to be 13.3% and 58.9%, respectively.

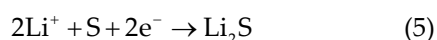
MoS₂, a well-known material, could offer some exciting electrochemical properties for lithium storage as an anode material. Intercalation of lithium into MoS₂ is known to occur within the voltage range of 0–3 V [13]. In the discharge process, a lithiation mechanism occurs at 1.1 V (vs. Li/Li⁺) corresponding to Li⁺ intercalation between the interlayers of MoS₂, forming Li_xMoS₂, which is fully reversible according to the reaction represented by Eq. (3)



At voltages below 1.1 V vs. Li/Li⁺, there appears to be a series of disproportionation reactions as well as the presence of intermediate metastable sulfide species [41]. Another dominant lithiation process at 0.3 V vs. Li/Li⁺ is related to the transformation of Li_xMoS₂ into metallic Mo nanoparticles and Li₂S via a conversion reaction represented by Eq. (4)



The reaction of elemental sulfur and lithium at 2.2 V vs. Li/Li⁺ can be described as in Eq. (5)

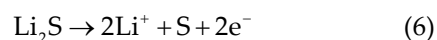


The theoretical specific capacity of the reaction from MoS₂ to Li_xMoS₂ (Eq. (3)) is 167 mAh/g, corresponding to the intercalation of one lithium ion per molybdenum atom. If the lithiation process goes deeper, attributed to the reversible conversion reaction of MoS₂ to Li₂S and metallic molybdenum as shown in Eq. (4), the theoretical specific charge capacity can reach up to 669 mAh/g. However, the reaction represented by Eq. (5) could yield a high theoretical capacity of 1,675 mAh/g, which is one of the reasons to produce MoS₂/carbon composites to achieve a high capacity over 1,000 mAh/g [42].

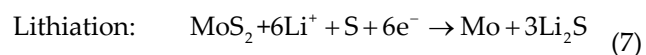
Based on the 3D network structure and double-

layer carbon coating, MoS₂/C/C fiber could be a promising active material for high-performance energy storage. We systematically evaluated the electrochemical performance of a MoS₂/C/C fiber electrode as the anode of a Li-ion battery. Figure 3(a) shows the first three consecutive CV curves of the MoS₂/C/C fiber electrode with a scanning rate of 0.2 mV/s. In the first discharge process, a cathodic peak at 1.05 V (vs. Li/Li⁺) corresponds to the reaction in Eq. (3). The peak at 0.42 V can be assigned to the transformation of Li_xMoS₂ into metallic Mo nanoparticles and Li₂S via a conversion reaction represented by Eq. (4). A wide shoulder peak emerges in the range of 0.6–0.8 V, which can be attributed to the formation of solid electrolyte interphase (SEI). The formation of an SEI layer can also make a significant contribution to the overall charge storage capacity [36, 43].

The intensities of these three peaks decreased in the following cycles. The two reduction peaks at 1.10 and 1.90 V can be attributed to formation of Li_xMoS₂ and Li₂S according to Eqs. (3) and (5). In the reverse anodic process, there are two oxidation peaks around 1.43 and 1.71 V, which are associated with the oxidation of Mo to Mo⁴⁺ and/or Mo⁶⁺ [15]. The dominant peak at 2.3 V could be assigned to the delithiation process of Li₂S



These two peaks were in accordance with the peaks for pure MoS₂, providing further evidence of the charge storage origin. During the subsequent cycles, the reversible reaction is based on Eq. (7)



During subsequent discharge cycles, the obvious peak at 0.42 V almost disappeared while two new peaks were repeatedly observed at 1.9 and 1.1 V. These two peaks correspond to the conversion of S to polysulfides and then to Li₂S, which is consistent with other results in literature [44]. The oxidation peak at around 2.3 V, which is due to the oxidation of Li₂S to S and lithium ions [45, 46], is quite repeatable

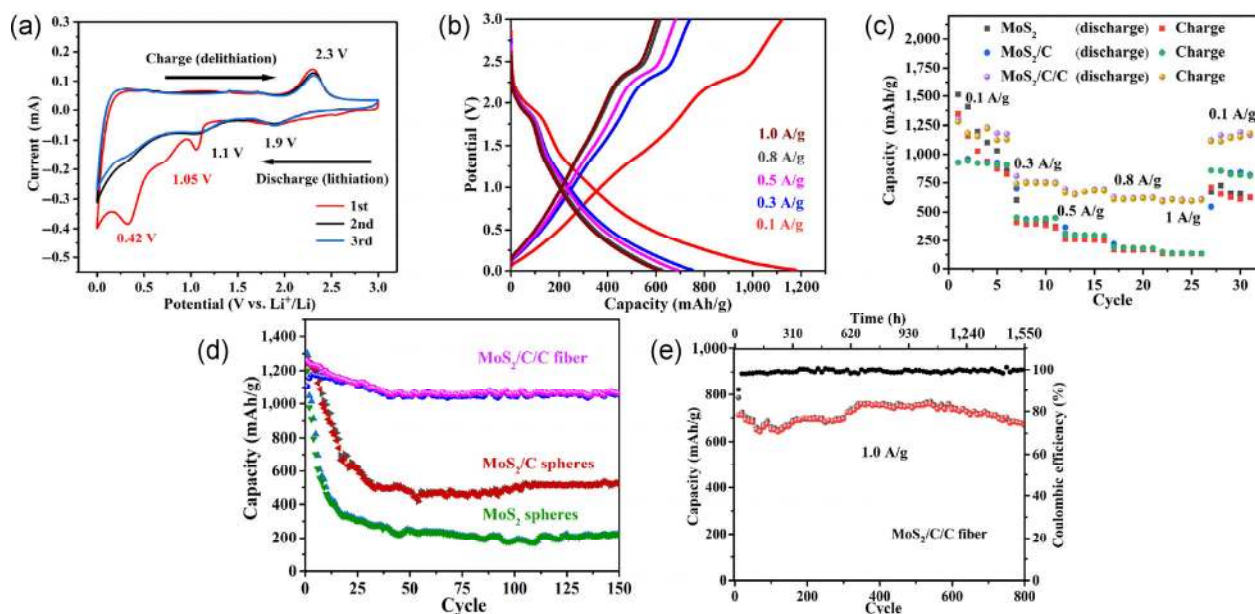


Figure 3 (a) CV of a $\text{MoS}_2/\text{C}/\text{C}$ fiber electrode at a scanning rate of 0.2 mV/s during the initial three cycles. (b) The discharge/charge profiles of the $\text{MoS}_2/\text{C}/\text{C}$ fiber electrode at different current densities. (c) Rate capability performance of the MoS_2 , MoS_2/C , and $\text{MoS}_2/\text{C}/\text{C}$ fiber electrodes. (d) Capacity retention of the MoS_2 , MoS_2/C , and $\text{MoS}_2/\text{C}/\text{C}$ fiber electrodes at a current density of 0.2 A/g for the subsequent 150 cycles. (e) Long-time cycling of the $\text{MoS}_2/\text{C}/\text{C}$ fiber electrode at a current density of 1 A/g.

after the first cycle, indicating the good cycling stability of the $\text{MoS}_2/\text{C}/\text{C}$ fiber hybrid electrode, as further revealed in the following electrochemical tests.

The specific capacity and rate capability of the $\text{MoS}_2/\text{C}/\text{C}$ fiber electrode were tested by galvanostatic charge–discharge with different currents from 0.1 to 1.0 A/g. It is evident that the plateaus on the charge–discharge curves are consistent with the respective peaks on the CV curves. Similar charge and discharge plateau with different applied current densities revealed the good rate stability of the $\text{MoS}_2/\text{C}/\text{C}$ fiber electrode. Figure 3(c) shows the superior rate capability of the $\text{MoS}_2/\text{C}/\text{C}$ fiber electrode compared to that of pure MoS_2 spheres and MoS_2/C spheres electrodes. The measured reversible capacities of the $\text{MoS}_2/\text{C}/\text{C}$ fiber electrode are 1301.2, 765.9, 680.8, 622.8, and 605.4 mAh/g at current densities of 0.1, 0.3, 0.5, 0.8, and 1.0 A/g, respectively. In contrast, the pure MoS_2 sphere electrode showed a rapid capacity drop with increasing current density. Although the rate capability of the MoS_2/C spheres electrode showed a minor improvement compared with pure MoS_2 sphere, it was still much lower than that of the double-layer carbon coated $\text{MoS}_2/\text{C}/\text{C}$ fiber electrode.

In addition, the rate capability of the $\text{MoS}_2/\text{C}/\text{C}$ fiber electrode was higher than $\text{MoS}_2/\text{carbon nanotubes}$ (500 mAh/g at 1 A/g) [23], carbon nanotube supported MoS_2 (300 mAh/g at 1 A/g) [47], and hierarchical $\text{MoS}_2/\text{polyaniline nanowires}$ (330 mAh/g at 1 A/g) [48].

The cycling performance of the $\text{MoS}_2/\text{C}/\text{C}$ fiber electrode was evaluated at a current density of 0.2 A/g as shown in Fig. 3(d). The respective performance data for pure MoS_2 and MoS_2/C sphere electrodes were also included for comparison. The initial discharge capacities of pure MoS_2 , MoS_2/C , and $\text{MoS}_2/\text{C}/\text{C}$ fiber electrodes were 1,301, 1,281, and 1,275 mAh/g, respectively. The corresponding initial Coulombic efficiencies of these electrodes were 68.9%, 75.0%, and 85.0%. Such improved Coulombic efficiency can be related to the increased conductivity after double-layer carbon coating. The irreversible capacity loss during the initial few cycles is inevitable, because of the formation of the SEI layer [43, 49]. In the subsequent cycles, the Coulombic efficiency of the $\text{MoS}_2/\text{C}/\text{C}$ fiber electrode gradually increased to 99.2%, superior to that of the MoS_2 and MoS_2/C electrodes with 93.3% and 98.2%, respectively. After 150 cycles, the $\text{MoS}_2/\text{C}/\text{C}$ fiber electrode retained 83.3% (1,062 mAh/g) efficiency, which is much higher than the 40.9% (525 mAh/g) of

the MoS₂/C electrode and the 17.9% (234 mAh/g) of the pure MoS₂ electrode. Due to the direct exposure of MoS₂ to the electrolyte, it is inevitable to introduce the irreversible reaction of MoS₂ to dissoluble metallic Mo and Li₂S, which will lead to serious structure and electrochemistry fading during the charge and discharge process. Due to the partial blocking of this irreversible reaction, the cycling stability of MoS₂/C increased by over 20% after a thin layer of carbon coating. For the MoS₂/C/C electrode, the double-layer carbon coating could not only suppress the irreversible reaction, but also limit the volume change during the lithiation/delithiation process. In order to evaluate the long-term stability of the MoS₂/C/C fiber electrode, we ran the electrode with a high current density of 1 A/g for 800 cycles. After the long-term cycling, 92.6% of the initial charge capacity remained, which means only a 0.009% capacity loss per cycle. The Coulombic efficiency of the MoS₂/C/C fiber electrode reached 98.8% in the third cycle and stabilized between 98.8%–100% until the 800th cycle, illustrating

its high Coulombic efficiency and cycling stability.

Based on the above discussion, the outstanding electrochemical properties of the MoS₂/C/C fiber electrode may be derived from the synergistic effects between the MoS₂ nanosphere network and the double-layer carbon coating. First, the introduction of the inner layer conductive carbon coating can prevent the restacking of MoS₂ nanosheets and increase the conductivity of the MoS₂ nanospheres, especially at the interface of MoS₂ nanosheets. Second, the robust outer layer carbon could effectively tolerate the volume change and prevent the loss of metallic molybdenum and sulfides during cycling. The conductive matrix of the carbon fiber can also provide a fast electron transport path for the whole electrode. Third, the fibrous network structure and high surface area of the MoS₂/C/C fiber electrode (371.6 m²/g) also increased the area exposed to the electrolyte, facilitating ion diffusion and transport for high capacity and good rate capability (Fig. S9 in the ESM).

Figure 4 presents a schematic illustration showing

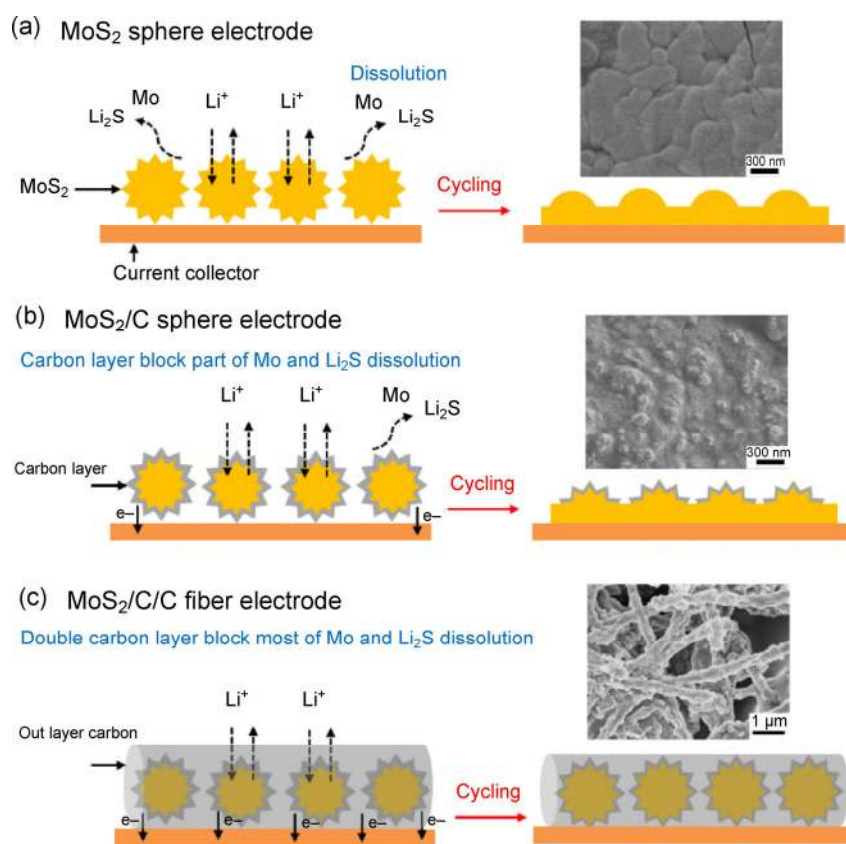
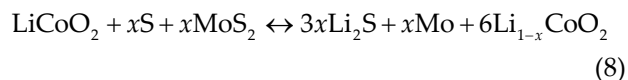


Figure 4 Schematic illustrating the lithiation process and the electrode structure fading and SEM images after 150 cycles of (a) pure MoS₂ sphere, (b) MoS₂/C spheres, and (c) MoS₂/C/C fiber.

the lithiation process and electrode structure evolution after long-term cycling. As demonstrated in the schematic and shown in SEM images, the pure MoS₂ spheres electrode showed serious structure fading and formed into continuous film after long-term cycling because of direct exposure of MoS₂ to the electrolyte [15, 27]. This could lead to the profound decomposition of MoS₂ nanospheres and the dissolution of metallic Mo and Li₂S. The MoS₂/C electrode also exhibited obvious structure change, but part of the nanosphere structures was still observed at the up surface of the electrode, due to the thin layer of carbon coating protection [34]. After coating with outer layer carbon fiber, the double-layer carbon coating could limit the volume change of the whole electrode and the dissolution of metallic Mo and sulfides during the lithiation/delithiation cycles. Thus, even after long-term cycling, the MoS₂/C/C fiber electrodes could still maintain the original fibrous network structure, which further explains why this double-layer carbon-coated MoS₂ material could

display such an enhanced rate performance, high reversible capacity, and long-term cycle life [50].

To further demonstrate the promising properties of MoS₂/C/C fiber as the anode material of Li-ion batteries, we fabricated a full cell with a LiCoO₂ electrode as the cathode. Figure 5(a) indicates the working potential of LiCoO₂ is 3.0–4.2 V, while MoS₂/C/C shows a working potential of 0.0–3.0 V, which shows the great potential of these materials to form high performance full batteries and be used as the next general lithium-ion battery. Figure 5(b) exhibits the charge and discharge voltage profiles of the full battery, which show a potential from 0 to 4.2 V, a capacity of 155 mAh/g at 0.1 A/g, and close to the theoretical capacity of LiCoO₂. The total electrochemical reactions of the full cell can be explained by Eq. (8)



A red LED was lit up for more than 60 min by the assembled full battery (Fig. 5(c)), which indicates great

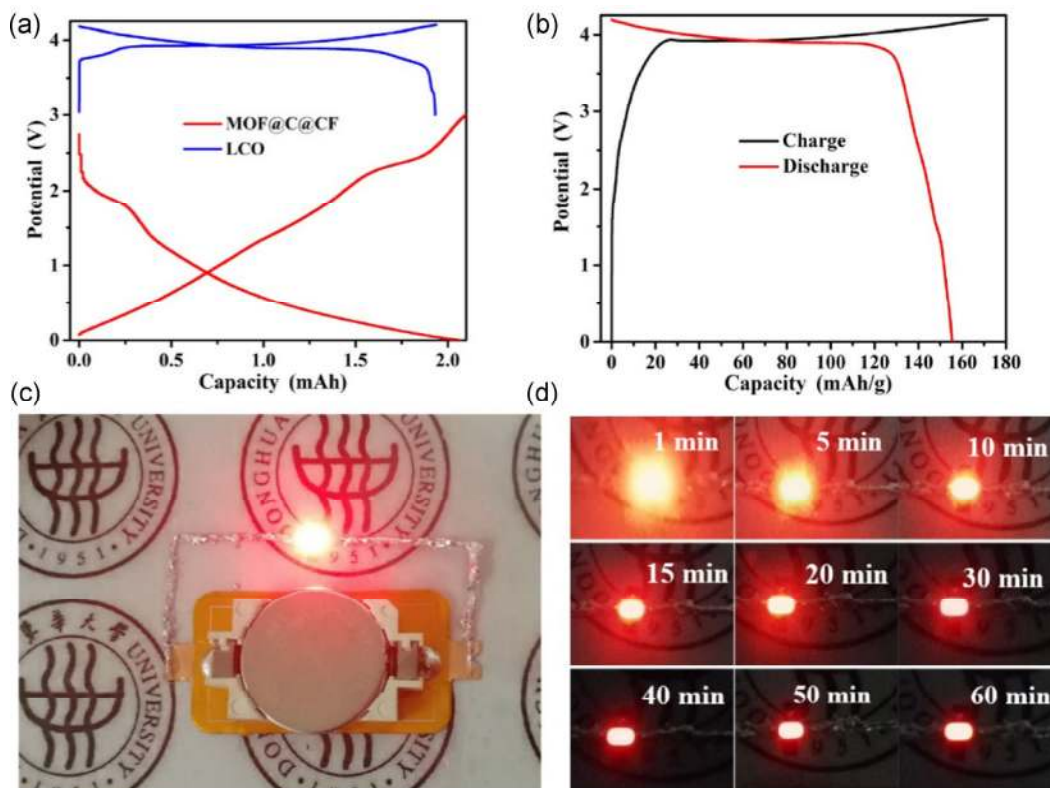


Figure 5 (a) Charge–discharge voltage profiles of MoS₂/C/C fiber and LiCoO₂ at 0.1 A/g. (b) Charge–discharge voltage profiles of a MoS₂/C/C//LiCoO₂ full battery at 0.1 A/g. (c) and (d) Red LEDs lit by the assembled full battery.

potential and practical application, and suggests the MoS₂/C/C fiber is a promising high-performance anode material. Figure S10 in the ESM shows the cycling performance of the MoS₂/C/C//LiCoO₂ full cell. The full cell retained 77% capacity after 80 cycles. After the initial 10 cycles, the capacity decreased to 107 mAh/g (83%) and the Coulombic efficiency stayed at 94%. However, the cell rapidly became more stable for the subsequent cycles, and achieved nearly 98% Coulombic efficiency for all following cycles.

4 Conclusions

In summary, we report a facile hydrothermal and subsequent electrospinning method to fabricate a double protective carbon layer coated MoS₂ fibrous electrode material, denoted as MoS₂/C/C fiber. Attributed to its intriguing double-layer carbon shell structure, the MoS₂/C/C fiber exhibits a series of remarkable electrochemical properties as the anode material of a Li-ion battery, such as a high first cycle specific capacity (1,275 mAh/g at 0.2 A/g), outstanding rate capability, and good capacity stability after long-term cycling (92.6% capacity retained after 800 cycles at 1 A/g). The high-energy storage performance of the MoS₂/C/C fiber material can be attributed to the design of the double carbon layer shell protection (inner amorphous carbon and outer carbon fiber). Furthermore, such a double-layer carbon coating strategy could prove useful in other areas of the energy storage field for improving rate capability and cycling stability.

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