In-situ Grown Hierarchical MoS\(_2\) Nanoflakes on Three-Dimensional Carbon Fiber Papers as Free-Standing Anodes for Lithium-Ion Battery

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Received: 17 April 2019 / Accepted: 28 June 2019 / Published: 31 July 2019

Owing to the high capacity of MoS\(_2\), it’s considered to be a next-generation lithium ion batteries (LIB) anode material. However, the weak electron transfer limits its application. Herein, hierarchical MoS\(_2@\)CFP composite materials based on in-situ grown hierarchical MoS\(_2\) nanoflakes on three-dimensional carbon fiber paper (CFP) is prepared. The hierarchical MoS\(_2@\)CFP composites serve as self-supporting electrodes and show potential for improved battery performance. The 1st discharge capacity reached 1332 mAh/g and still reached 703 mAh/g after 100 cycles at a current density of 0.1 A/g. The superior performance of the MoS\(_2@\)CFP composites was mainly attributed to the combination of a high capacity ability of MoS\(_2\) and the high electron transport capability of carbon fibers. In addition, this synthetic strategy provides a certain idea for the synthesis of other layered composite materials.

**Keywords:** MoS\(_2\) nanoflakes, carbon fiber papers, lithium-ion battery, in-situ growth

1. INTRODUCTION

LIBs are considered to be the power source for vehicles for the next generation in recent decades [1, 2]. However, the new LIB anode needs to be developed due to the shortcomings of traditional commercial anodes, such as the low capacity of commercial graphite anodes, and the volume change of commercial silicon anodes when used [3-5]. It is hoped to find a safe, environmentally friendly and natural resource-rich anode with high capacity. Recently, transition metal dichalcogenides (TMDCs) has
received extensive attention owing to the special bidimensional structure [6-9]. The interlayer space between hierarchical structures of TMDs allows small ions to be inserted/extracted, such as lithium ion, sodium ion and potassium ion [10-12]. Therefore, the TMDs are considered as ideal anode materials [2].

MoS₂, typical TMDs’ representative and has been extensive researched and applied in electrocatalysis, photocatalysis, and membrane separation [13-18], etc. The theoretical lithium storage of molybdenum disulfide up to 670 mAh/g, higher than commercial graphite anode (373 mAh/g). In addition, the MoS₂ anodes have little effect on the volume change when it is used. It is because the interlayer spacing of layered MoS₂ is 6.15 Å and can be expanded to 15 Å because of insertion of the remaining \( \text{Li}^+ \). However, some MoS₂’ shortcomings such as weak electron conduction capability, low rate capability and poor cycling stability, limiting its practical application. In order to overcome these obstacles, researchers have explored many ways to increase the capacity of MoS₂ electrodes by combining with different carbon nanomaterials. For example, Chen fabricated MoS₂/ agraphitic carbon composites anode by solvothermal method [19]. Furthermore, Chen and his co-workers fabricated superior performance MoS₂/graphene nanoflake anode by in-situ solution phase reduced method [20]. Similarly, Mai’s group reported in-suit growth MoS₂ on reduced graphene oxide (rGO) composites and obtained MoS₂/rGO hybrids anode with excellent performance [21]. Lu and co-workers employed inserting \( \text{Li}^+ \) into bulk MoS₂ and obtained exfoliation of \( \text{Li}_x\text{MoS}_2 \), then coated with dopamine (DOPA) on the single-layer MoS₂ surface and calcinated (DOPA)ₓMoS₂ under nitrogen to obtain MoS₂/N-doped graphene, which shows a superior performance for \( \text{Li}^+ \) storage [22]. Mahanty’s group mixed MoS₂ with multiwalled carbon nanotube (MWCNTs) and performed multiple milling, then got the MoS₂/MWCNTs hybrids anode, providing a new idea for the preparation of MoS₂/carbon composites [23]. Wang’s group went a step further, reported a mixture of MoS₂ and single-carbon nanotubes (SCNTs) by dispersed MoS₂ and SCNTs in N-cyclohexyl-2-pyrrolidone (CHP) and used point probe sonication to blended materials to the composites in CHP, then the MoS₂/SCNTs composites was obtained by filtration through a nitrocellulose membrane under vacuum, which displayed an excellent electrochemical performance [24]. Recently, Chen fabricated a 3D layered MoS₂ nanosheets/carbon nanofiber via sample dip process, then obtained MoS₂/ACF hybrids anodes with a superior performance for \( \text{Li}^+ \) storage and good discharging/charging cycling stability [25].

Herein, we demonstrate hydrothermal method to fabricate grown multilayer MoS₂ nanoflakes on the three-dimensional carbon fiber papers and then obtain the hierarchical MoS₂@CFP composite materials. As a composite material framework and a growth template of MoS₂, CFP has excellent electron and lithium ion transport properties and allows electrons to be transported along the path to MoS₂. The hierarchical MoS₂ structure stabilizes the lithium ion insertion/extraction process in the MoS₂ nanosheet, buffers the volume change of the MoS₂ nanosheet due to its interlayer space and improve the cycle performance. In addition, the MoS₂ possess high capacitance. The hierarchical MoS₂@CFP act as self-standing and free-binder anodes, displayed high reversible \( \text{Li}^+ \) storage capacity and excellent cycling stability.
2. EXPERIMENT

2.1 Chemicals

(NH4)6Mo7O24•4H2O and thiourea were purchased from Kelong Chemical Co. Ltd., Chengdu, China. The chemicals were used as received. Carbon fiber papers (CFP, TORAY, TGP-H-060, 20*20cm) were supplied by Saibo New Material Co., Ltd, Hefei, China. The water used in the experiment was deionized water.

2.2 Synthesis of MoS$_2$@CFP

Figure 1. Illustration of fabrication of as-designed electrode.

MoS$_2$ was grown in situ on CFP directly via hydrothermal method [26]. In brief, 0.1235 g (NH4)6Mo7O24•4H2O and 0.1064 g thiourea were dissolved in 70 mL deionized water and then aqueous solution was sonicated for 20 min. After that, aqueous solution and pre-treated CFP were poured in 100 mL autoclave, then treated at 200°C for 4 h. The autoclave was naturally cooled to room temperature. Then, the CFP wrapped with MoS$_2$ was taken out of the autoclave, cleaned with ethanol and then desiccated in vacuum oven at 40°C for 6 hours. Finally, MoS$_2$@CFP was annealed to obtained more complete lattice MoS$_2$ at 800°C with Ar/H$_2$ atmosphere for 2h.

2.3 Characterization

Composition test of the as-prepared MoS$_2$@CFP was using X-ray diffraction (XRD, PANalytical), with Cu Ka radiation at 40KV. Raman analysis was measured by Raman spectrometer (LabRAM HR800), with a laser excitation wavelength at 266 nm. Chemical state of the sample was characterized by an X-ray photoelectron spectrometer (XPS, AXIS SUPRA), with Al Ka. The sample’s morphology was obtained by the Scanning Electron Microscope (SEM, HITACHI) and Energy dispersive Spectroscopy (EDS) mapping scans. And the surface morphology was further characterized through transmission-electron microscopy (TEM, HITACHI).
2.4 Electrochemistry test

The electrochemical ability of as-designed electrode performed via coin cells test (CR-2032). A piece of MoS$_2$@CFP as work electrode, with lithium metal as both the counter and reference electrode and Celgard 2400 membrane as the separator, the electrolyte containing 1 mol/L LiPF$_6$ in a mixture of ethylene carbonate (EC), diethyl carbonate (DEC) and Ethyl methyl carbonate (EMC) ($V_{EC}/V_{DEC}/V_{EMC}$ = 1:1:1). The tested cells were assembled in an argon filled glovebox. The galvanostatic charged and discharged test of the cell recorded between 0.001 V and 3.0 V on a LAND CT2001A battery tester (Wuhan LAND electronics Co., Ltd, China). The other electrochemical tests are using CHI660D electrochemical workstation (CH Instruments, China). Impedance tests are using Electrochemical impedance spectroscopy (EIS).

3. RESULTS AND DISCUSSION

Fig. 1 synoptically declares the preparation of the in-suit grown hierarchical MoS$_2$ nanoflakes on the surface of CFP. It can be obtained that the petal-like structure, which shows the in suit anisotropic growth of the ultrathin hierarchical MoS$_2$ on the CFP surface.

Fig. 2a exhibits the XRD pattern of the samples. CFP has very strong peaks which is truncated for amplification of other peaks. CFP has very strong peaks which are truncated for amplification of other peaks. The peaks appearing in 26.2° and 54.8° can be indexed to highly carbonized carbon fiber [14]. The diffraction pattern of the in-situ grown MoS$_2$ has peaks at 14.2° and 34.6° are attributed to (002) and (101) planes of hexagonal MoS$_2$ [24]. The (002) diffraction is related to a d-spacing of 0.62 nm which is consistent with the TEM images.

The Raman analysis of MoS$_2$@CFP as displayed in Fig. 2b. The peaks at 378 and 402 cm$^{-1}$, corresponding to E$_{12g}$ and A$_{1g}$ modes of the hexagonal MoS$_2$, respectively [25]. The Raman shifts are from the first order Raman vibration modes with the S-Mo-S layer. Previous studies have shown that Raman chromatography can estimate layer number of hierarchical MoS$_2$ by two adjacent Raman shift peaks, and the gap value of MoS$_2$@CFP is 25 cm$^{-1}$, showing that MoS$_2$ maintains an ultra-thin state with only a few layers [27-29].

The XPS profiles of Mo and S as shown in Fig. 2c and 2d. Fig. 2c shows a high-resolution spectrum of Mo. The peaks at 229.0 and 232.0 eV can be attributed to the dual states of Mo$^{4+}$ 3d$_{3/2}$ and Mo$^{4+}$ 3d$_{5/2}$, the peaks have a separation energy close to 3.1 eV, which is characteristic of the Mo species. There is a weak peak about 236.0 eV, corresponding to Mo$^{6+}$, indicating that there is little Mo$^+$ oxidation. The peak at 226.0 eV corresponds to the S 2s component of MoS$_2$. The Peaks of 161.7 eV and 163.0 eV were observed in S 2p spectrum displayed in Fig. 2d, attributing to S$^{2-}$ 2p$_{3/2}$ and S$^{2-}$ 2p$_{1/2}$, respectively. In addition, the peak around 2.3 eV compared to the 2p$_{3/2}$ (164.1 eV) and 2p$_{1/2}$ (165.2 eV) peaks of element S, which is a typical 2p shift of S in MoS$_2$. [30, 31].
Figure 2. (a) XRD patterns of the samples; (b) Raman spectra of the samples; The XPS spectra of the samples, (c) the Mo 3d XPS spectrum and (d) S 2p XPS spectrum.

Figure 3. (a-b) SEM images of the original CFP; Figure 3(c-d) SEM images of the as-prepared MoS$_2$@CFP.
The morphology of the CFP and hierarchical MoS$_2$@CFP were obtained by investigated by SEM and TEM analyses. From the low-magnification Fig. 3a we can observe a single carbon nanofiber and the diameter of the single fiber is about 7 nm. High-magnification SEM images (Fig. 3b) shows the nanofiber’s smooth surface morphology. After CFP was surface-modified by MoS$_2$, the surface of the material becomes rougher as exhibited in Figure 3c. In addition, Fig. 3d shows the petal-like MoS$_2$ nanoflakes occupied the surface of the CFP. The hierarchical structure on the surface of the electrode facilitate the insertion and extraction of Li$^+$. 

EDS mapping images (Fig. 4) shows the distribution of elements for hierarchical MoS$_2$@CFP. The element distribution is evenly on the electrode surface (Fig. 4a), large number of homogeneous MoS$_2$ nanoflakes cover the surface of the carbon fiber. In such a nanomaterial structure, the good transmission performance of carbon fiber to electrons compensates for the poor conductivity of MoS$_2$, which is benefit for lithium battery performance.

![Figure 4](image)

**Figure 4.** (a) SEM image and the EDX mapping displays elements distribution of C (b), Mo (c) and S (d) of MoS$_2$@CFP.

TEM observed surface morphology of the molybdenum disulfide. The hierarchical nanostructure of MoS$_2$@CFP presented in the SEM images are difficult to observe clearly in the TEM images because the sample is dispersed in EtOH by ultrasound in TEM sample-fabrication process. TEM images shows the flower-like hierarchical MoS$_2$ nanoparticle (Fig. 5a) and the petal-like MoS$_2$ nanoflakes grew in
different directions, which all should be perpendicular to the surface of the CFP (Fig. 5b). In Fig. 5c, MoS$_2$ nanoflake’ thicknesses are only several nanometers. Moreover, the high resolution TEM image (Fig. 5d) further points out the clear interlayer structure of hierarchical MoS$_2$ that an interlayer spacing of 0.62 nm can be indexed to (002) planes and another interlayer distance of 0.27 nm can be attributed to (100) planes, which are consistent with the XRD analysis of the MoS$_2$ crystal.

**Figure 5.** Nanostructure of the MoS$_2$@CFP. TEM images (a) and (b); HRTEM images (c) and (d).

The hierarchical MoS$_2$@CFP composite has a unique architecture combining one-dimensional carbon nanofibers with two-dimensional MoS$_2$ nanoflakes, which is potential for excellent lithium battery performance. Fig. 6a displays the first three times cyclic voltammograms curves of the electrode obtained at a scan rate of 0.2 mV/s between a voltage range of 0.001 V and 3.0 V vs. Li$^+$/Li. Displayed the CVs of the 1st lap is diverse from other circles. For the first cycle curve, a board peak located at 0.95 V is corresponding to phase transition from triggered phase to octahedral phase. Generally, a peak at around 0.95 V is related to the insertion of Li$^+$ into layers of MoS$_2$, forming Li$_x$MoS$_2$ and transforming MoS$_2$ from 2H to 1T [25, 32]. Another cathodic peak from the first cycle curve about 0.45 V due to Li$_x$MoS$_2$ is reduced to form Li$_2$S and Mo [32-34]. In addition, it is related to form solid electrolyte interface (SEI) due to the electrode material reacts with the electrolyte. At anodic sweeps, the oxidation-peak located at 1.75V, corresponding to Mo is oxidized to MoS$_2$. And the peak at around 2.42 V is attributed with the
Li$_2$S oxidation to S. Hence the electrode material would be divided into MoS$_2$, Mo, Li$_2$S and S after the cycles[20, 34-37].

Figure 6. (a) CV curves of the MoS$_2$@CFP electrode; (b) The galvanostatic charge-discharge (GCD) curves of the MoS$_2$@CFP electrode.

For subsequent cathodic scan, the shape of the redox potential is completely different from that observed at the 1st cycle. The minimum at 0.45 V evaporated, and correspondingly new peak at around 1.10 and 1.85 V appeared, which indicates a multistep Li$^+$-insertion mechanism. In addition, the peak about 1.85 V is associated with the conversion of elemental sulfur to polysulfide and then to Li$_2$S. The peak at around 1.10 V is related to the reaction of Li with Mo. According to recent reports, Li will form a coordination bond around Mo. The second and third cycles of CV curve are basically overlapping, proving a good reversibility of the MoS$_2$@CFP electrode [24, 34, 38].

Fig. 6b exhibits the GCD curves for the 1st, 2nd and 5th curve at a current density of 0.1 A/g between 0.001 V and 3.0 V. It can be obtained two clear terraces about 1.19 and 0.69 V during the initial discharge course, usually considered to be two lithiations and confirmed the insertion of ions. The Li$^+$ embed into the MoS$_2$ nanosheets and formed Li$_x$MoS$_2$. Another two plateaus located at 2.2-2.4 V suggests the reversible Li$^+$ extraction during the charge process. Furthermore, the peaks located near 2.29 V is also considered to be the Li$_2$S$^+$ oxidation [39, 40].
Figure 7. Cycling performance of the MoS$_2$@CFP at different current density: 0.1 A/g (a), 0.2 A/g (b) and 0.5 A/g (c); (d) Rate performance of the MoS$_2$@CFP 0.1 to 1.5 A/g.

As-prepared hierarchical electrode performs a good potential for application to electrode materials. Generally, the cycle performance and rate performance are used to indicate the lithium storage capacity. Fig. 7a, 7b and 7c separately show the charge (ion-extraction) and discharge (ion-insertion) curve of the MoS$_2$@CFP electrode for 100 cycles at the current density of 0.1 A/g, 0.2 A/g and 0.5 A/g. In the first cycle, the capacities are 1332, 1091 and 976 mAh/g at 0.1, 0.2 and 0.5 A/g. And after 100 cycles, the MoS$_2$@CFP electrode separately exhibits reversible discharge capacity of 703, 517 and 392 mAh/g at 0.1, 0.2 and 0.5 A/g. The hierarchical MoS$_2$@CFP composite shows an excellent cycling performance which compared with the normal CFP and MoS$_2$ electrodes. The comparison results of the as-prepared hierarchical MoS$_2$@CFP composite electrodes and the previously reported MoS$_2$ composite electrodes are shown in table S1. It can be observed that the performance of the prepared electrode is superior even compare with the previously reported MoS$_2$ composite electrodes.

Fig. 7d exhibits the rate performance at different current density from 0.1 to 1.5 A/g for the MoS$_2$@CFP electrode. The specific capacities are 1325, 976, 823, 734, 652, 595, 498, 431 and 337 mAh/g at different current density. And after cycles at different current density, the hierarchical MoS$_2$@CFP composite maintains capacity of 358 mAh/g. Furthermore, as-prepared MoS$_2$@CFP
The electrode also shows good capacity recovery after rate test. When the cycles returned to 0.1 A/g, the capacity is restored to 915 mAh/g after several cycling at current variation from 0.1 to 1.5 A/g.

EIS is used to explore the reason of prepared hierarchical MoS$_2$@CFP electrodes have such excellent performance and Li$^+$ storage and insertion dynamics. The Nyquist plots of electrodes before and after 100 cycles at a current density of 0.1 A/g are displayed in Fig. 8a. It can be obtained that the charge transfer resistance reduced after 100 cycles. The Nyquist plots are also fitted by the equivalent circuit model as displayed in Fig. 8b. The fitting parameters of the impedance are listed in Table 1. For the MoS$_2$/CFP electrode before cycles and after cycles, the $R_s$ value is dropped from 23.3 $\Omega$ to 22.5 $\Omega$; the $R_{ct}$ value is dropped from 547.9 $\Omega$ to 323.0 $\Omega$; and the $R_f$ value is 153.6 $\Omega$ after cycles. It is confirmed that the combination of MoS$_2$ and carbon fiber significantly enhances the electrical conductivity of MoS$_2$ and thus accelerates the transport of electrons during the insertion/extraction of lithium ions.

![Figure 8](image_url)  
**Figure 8.** (a) Nyquist plots of the electrode; (b) Equivalent circuit model corresponding to the Nyquist plots of electrode: (A) before, (B) after cycling.

<table>
<thead>
<tr>
<th>Electrode</th>
<th>$R_s$(Ω)</th>
<th>$R_{ct}$(Ω)</th>
<th>CPE1(μF)</th>
<th>$R_f$(Ω)</th>
<th>CPE2(μF)</th>
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<tbody>
<tr>
<td>MoS$_2$@CFP before cycling</td>
<td>23.3</td>
<td>547.9</td>
<td>32.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>MoS$_2$@CFP after cycling</td>
<td>22.5</td>
<td>323.0</td>
<td>2.43</td>
<td>153.6</td>
<td>24.7</td>
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</table>

4. CONCLUSION

In summary, the hierarchical MoS$_2$@CFP electrodes are fabricated by typical solvothermal method and then calcination in Ar/H$_2$ atmosphere at 800°C. The hierarchical MoS$_2$ in suit grew in nanoflakes on three-dimensional carbon fiber papers. Experimental results showed that the hierarchical MoS$_2$@CFP electrodes have high specific capacitance and excellent stability. The discharge capacity at 0.1 A/g achieved 1332 mAh/g in the 1st cycle and only attenuated to 703 mAh/g after 100 cycles. The three-dimensional CFP provides an electronic transmission path to MoS$_2$, and the hierarchical MoS$_2$ has
good Li-ions storage capacity. The synergistic effect of MoS$_2$ and CFP leads to excellent electrochemical performance of the hierarchical MoS$_2$@CFP electrode. The type of material should have good application potential in areas such as catalysis, supercapacitors, and membrane science.

SUPPORTING MATERIAL

**Figure 1s.** (a) Cycling performance of the MoS$_2$ electrode at a current density of 0.1 A/g; (b) The GCD curve of the MoS$_2$ electrode.

**Figure 2s.** (a) Cycling performance of the CFP electrode at a current density of 0.1 A/g; (b) The GCD curves of the CFP electrode.
Figure 3s. Photographic images of the CFP (a) and the hierarchical MoS\(_2\)@CFP (b).

Figure 4s. Water contact angle of the CFP (a, b and c) and the hierarchical MoS\(_2\)@CFP (d, e and f).

Figure 5s. Oil contact angle of the CFP (a, b and c) and the hierarchical MoS\(_2\)@CFP (d, e and f).
Table S1. Performance comparison of the as-prepared hierarchical MoS$_2$@CFP composite electrodes and the previously reported MoS$_2$ composite electrodes.

<table>
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<tr>
<th>Anode material</th>
<th>DCG performance of 1st cycle (current density: 0.1 A/g): mAh/g</th>
<th>DCG performance after 100 cycles (current density: 0.1 A/g): mAh/g</th>
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ACKNOWLEDGEMENTS
This work was financially supported by National Natural Science Foundation of China (No.51774245), Applied Basic Research Program of Science and Technology Department of Sichuan Province (No.2018JY0517), Sichuan Province sci-tech Supported project (2015RZ0023) and Youth science and technology creative group fund of Southwest Petroleum University (2015CXTD03).

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