Reduced Graphene-Oxide-Encapsulated MoS$_2$/Carbon Nanofiber Composite Electrode for High-Performance Na-Ion Batteries

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Abstract: Sodium-ion batteries (SIBs) have been increasingly studied due to sodium (Na) being an inexpensive ionic resource (Na) and their battery chemistry being similar to that of current lithium-ion batteries (LIBs). However, SIBs have faced substantial challenges in developing high-performance anode materials that can reversibly store Na$^{+}$ in the host structure. To address these challenges, molybdenum sulfide (MoS$_2$)-based active materials have been considered as promising anodes, owing to the two-dimensional layered structure of MoS$_2$ for stably (de)inserting Na$^+$. Nevertheless, intrinsic issues of MoS$_2$—such as low electronic conductivity and the loss of active S elements after a conversion reaction—have limited the viability of MoS$_2$ in practical SIBs. Here, we report MoS$_2$ embedded in carbon nanofibers encapsulated with a reduced graphene oxide (MoS$_2$@CNFs@rGO) composite for SIB anodes. The MoS$_2$@CNFs@rGO delivered a high capacity of 345.8 mAh g$^{-1}$ at a current density of 100 mA g$^{-1}$ for 90 cycles. The CNFs and rGO were synergistically taken into account for providing rapid pathways for electrons and preventing the dissolution of S sources during repetitive conversion reactions. This work offers a new point of view to realize MoS$_2$-based anode materials in practical SIBs.

Keywords: molybdenum sulfides; carbon nanofibers; reduced graphene oxides; anodes; sodium-ion batteries

1. Introduction

A battery of things (BoT)—first mentioned by Tony Seba, the author of “Clean Disruption of Energy and Transportation”—has come for modern society, requiring battery-powered devices everywhere [1]. Current lithium-ion batteries (LIBs), with a high energy density of ~250 Wh kg$^{-1}$, have been considered to be promising energy storage systems combined with renewable energy technologies [2]. Despite the viability of LIBs, utilization of the state-of-the-art LIBs for an energy storage system (ESS) has been restricted due to finite reserves of Li$^+$ on earth, which would increase the price of Li sources used for large-scale applications [3]. Among alternatives to LIBs, sodium-ion batteries (SIBs) with a similar battery chemistry (redox potential of ~2.71 V vs. SHE) as LIBs have constituted an exciting avenue for advancing ESSs [4,5].

However, anode materials with low energy density have impeded the development of SIB technologies. To address this issue, many promising candidates (e.g., hard carbon, metal oxides/sulfides/selenides, etc.) with high capacities have been suggested so far [6–12]. However, carbonaceous materials show limited use due to their low specific capacity and...
less reversible capacity, and transition metal oxides (TMOs) need to be changed due to their low conductivity. As high-capacity anodes, sulfide-based materials such as FeS$_2$ and Sn$_2$S have been developed because transition metal sulfides (TMSs) have a higher electronic conductivity as well as an excellent ability to store Na$^+$ [11,12]. Among them, molybdenum sulfide (MoS$_2$)-based anode materials possessing large interlayer spaces (0.615 nm) between two-dimensional (2D) MoS$_2$ slabs could allow facile (de)insertion of Na$^+$ without few structural changes during conversion reactions (MoS$_2$ + 4Na$^+$ + 4e$^-$ → Mo$_4$(metallic) + 2Na$_2$S, a theoretical capacity of 670 mAh g$^{-1}$), leading to great electrochemical performance [13,14]. However, MoS$_2$ has an intrinsically low electronic conductivity, lowering the efficiency of (dis) charging SIB cells [15,16]. In addition, long channels of 2D MoS$_2$ interlayers are the bottleneck to Na$^+$ diffusion, degrading SIB performance toward Na$^+$ storage [17,18]. Furthermore, the dissolution of sulfur atoms contributes to a large loss in the overall mass after the conversion reactions, which is detrimental to achieving excellent battery performance. Therefore, we need to find a strategy to overcome the problems of MoS$_2$ mentioned above [19–21].

In this work, we successfully fabricated interlayer-enlarged MoS$_2$ nanoflakes, which were doubly covered with carbon nanofibers (CNFs), and reduced graphene oxide (rGO) (MoS$_2$@CNFs@rGO). The MoS$_2$ nanoflakes were first confined in the CNFs by thermolysis, subsequently encapsulated by the rGO via electrostatic interaction and reduction processes. The interlayers of MoS$_2$ nanoflakes in the CNFs were expanded during the thermolysis at 800 $^\circ$C under the H$_2$ atmosphere. Moreover, the synergy of CNFs and rGO not only increase the electronic conductivity of the composite but also prevent the loss of S, enabling the SIB cells to be operated reversibly with a high capacity of 345.8 mA g$^{-1}$ for 90 cycles at a high current density of 100 mA g$^{-1}$. With the support of experimental and analytical studies, the underlying reaction mechanism of MoS$_2$@CNFs@rGO was investigated and proposed.

2. Materials and Methods

2.1. Experimental

Firstly, the MoS$_2$@CNFs were synthesized by electrospinning and a thermolysis process [17]. For the electrospinning, a solution containing 15 wt % of ammonium tetrathiomolybdate ((NH$_4$)$_2$MoS$_4$, ATTM, Alfa Aesar, Ward Hill, MA, USA) and 15 wt % of poly(styrene-acrylonitrile, SAN, Mw = 1,300,000) dissolved in 10 mL of N,N-dimethylformamide (DMF, Sigma-Aldrich, Burlington, MA, USA), was prepared on the hot plate by stirring the solution at 70 $^\circ$C for 12 h. The solution was electrospun by applying a high voltage of 15 kV using an electrospinning machine (NanoNC, Seoul, South Korea). After the electrospinning, the electrospun NFs were thermally treated under H$_2$/Ar (4/96, v/v) surroundings at 450 $^\circ$C for 2 h and under a pure Ar (99.999%) atmosphere at 800 $^\circ$C for 6 h, respectively [17,22]. These processes were performed to make the MoS$_2$@CNFs. For wrapping the entire surfaces of MoS$_2$@rGO with the rGO, the Ti-O-Ti-O atomic layers (sub-nm) were coated on the MoS$_2$@rGO by using atomic layer deposition (ALD); this forms hydroxyl groups (OH-) of the atomic layers on MoS$_2$@rGO for rGO wrapping [7,23]. Then, poly(allylamine hydrochloride, Mw = 900,000, Sigma-Aldrich) was utilized as a surface modifier to form an amine group (NH$_2$-) on the surface, inducing a positively charged surface, i.e., -NH$_3^+$-grafted MoS$_2$@CNFs, in an aqueous solution. The MoS$_2$@rGO was added to the PAH solution. After stirring for 2 h, the PAH-modified MoS$_2$@rGO was rinsed three times with distilled water and dried at 60 $^\circ$C in a vacuum oven overnight. Lastly, the modified sample was encapsulated with rGO according to the method in the same manner of our previous works [7,24], resulting in MoS$_2$@CNFs@rGO.

2.2. Materials Characterization

Nova 230 (field-emission scanning electron microscope (FE-SEM), FEI, Hillsboro, OR, USA) was employed to obtain FE-SEM images. The crystal structure of MoS$_2$@CNFs@rGO was investigated by X-ray diffraction (XRD) patterns using D/Max-2500, with RIGAKU Corp. (Tokyo, Japan) with Cu K$\alpha$ ($\lambda = 1.54$ Å) between 10$^\circ$ and 80$^\circ$ at a scan rate of
0.066° s⁻¹. Both internal and external morphologies of MoS2@CNFs@rGO and the distribution of elemental were analyzed by a high-resolution transmission electron microscope (HR-TEM) operating at 300 kV and a scanning TEM (STEM) using a Tecnai F30 S-Twin (FEI, Hillsboro, OR, USA) equipped with energy-dispersive X-ray spectroscopy (EDX). The chemical states of MoS2@CNFs@rGO were investigated by X-ray photoelectron spectroscopy (XPS, K-alpha, Thermo VG Scientific, Waltham, MA, USA). In addition, the dominant vibration modes in the MoS2@CNFs@rGO were investigated using Raman spectroscopy (ARAMIS, Horiba Jobin Yvon, Montpellier, France) with a 514 nm laser source.

2.3. Electrochemical Evaluation

All the electrodes were prepared by casting a slurry, including active materials (80%), a conducting agent (Super-P, Sigma-Aldrich, Burlington, MA, USA) (10%), and a polyvinylidene fluoride (PVDF, Mw ~534,000, Sigma-Aldrich, Burlington, MA, USA) binder (10%); the slurry was mixed together using an agate mortar and cast on a copper foil as a current collector. After casting, the electrode was dried in a vacuum oven for 12 h. The mass loading of the MoS2@CNFs@rGO was approximately 1.0 ± 0.1 mg cm⁻². Half-cell (2032 type-coin cell) assembly was done in an Ar-filled glovebox (water content < 0.1 ppm). Na metal was used as a counter electrode, and a Whatman glass microfilter was employed as a separator for SIB cell tests. The used SIB electrolyte was 1 M NaClO₄ in propylene carbonate (PC) with 5 wt % of FEC. The assembled coin cells for Na storage were cycled at a current density of 100~20,000 mA g⁻¹ between 0.005 and 3.0 V using a battery tester (WBCS3000 device by WonATech, Seoul, South Korea).

3. Results

3.1. Materials Characterization

The synthetic procedures to prepare the MoS2 nanoflakes confined in CNFs wrapped with the rGO net (MoS2@CNFs@rGO) are schematically illustrated in Figure 1. The MoS2-nanoflake-embedded carbon nanofibers (MoS2@CNFs) were prepared by thermal treatment using ammonium tetrathiomolybdate ([NH₄]₂MoS₄) and poly(styrene-acrylonitrile) (SAN) as precursors through the electrospinning method (Figure 1a). First, the ([NH₄]₂MoS₄) was decomposed into MoS₂ at 450 °C in the presence of reducing (H₂) gas [25,26]. Then, carbonization and crystallization steps for MoS₂ are performed through heat treatment at 800 °C under an inert gas environment. The reactions that occur during the heat treatment process are as follows.

\[
\text{([NH}_4\text{]}_2\text{MoS}_4 \rightarrow \text{MoS}_3 + 2\text{NH}_3 \uparrow + \text{H}_2\text{S} \uparrow \quad (1)}
\]

\[
\text{MoS}_3 \rightarrow \text{MoS}_2 + \text{S} \quad (2)
\]

\[
\text{([NH}_4\text{]}_2\text{MoS}_4 + \text{H}_2 \rightarrow \text{MoS}_2 + 2\text{NH}_3 \uparrow + 2\text{H}_2\text{S} \uparrow \quad (3)}
\]

Figure 1. Schematic illustration for preparation of MoS2@CNFs@rGO. (a) Fabrication of MoS2@CNFs synthesized by thermolysis after electrospinning. (b) Electrostatic interaction between PAH-modified MoS2@CNFs and GO. (c) The final product of rGO-wrapped MoS2@CNFs achieved after hydrazine reduction.
For rGO coating on the MoS$_2$@CNFs, the surface of MoS$_2$@CNFs was modified using poly(allylamine hydrochloride) (PAH) [7,23,24]. Firstly, the MoS$_2$@CNFs were dipped in PAH solution; the surface functional group changed from the hydroxy surface group to the amine group (-NH$_2$) (see the details in the Materials and Methods section). The PAH-modified MoS$_2$@CNFs have positively charged amine functional groups (NH$_3^+$) exposed on the surface. On the other hand, the GO has functional groups of the carboxyl group (-COOH) and hydroxy group (-OH), attributed to the negative charge of GO in the aqueous solution. The GO flakes were quickly attracted to the surface of PAH-modified MoS$_2$@CNFs due to the electrostatic self-assembly (Figure 1b). Then, the GO was chemically reduced by hydrazine treatment, which rendered the strong chemical bond between the amine functional group and oxygen group with the ring-opening reaction. Finally, the GO changed to rGO, covering the entire surface of MoS$_2$@CNFs (Figure 1c).

The morphology of synthesized MoS$_2$@CNFs is shown in Figure 2a,b, demonstrating that the nanocomposite possessed one-dimensional (1D) NF networks, with the diameter of each fiber at about 200 nm and several microsized pores among the NFs. These pores facilitate electrolyte penetration to enhance electrochemical performance. The morphological change of MoS$_2$@CNFs@rGO was confirmed through SEM images (Figure 2c,d).

It is confirmed that rGO flakes were covered on the NF surfaces while the 1D architecture of MoS$_2$@CNFs was maintained. To verify the internal structure and phase of the MoS$_2$@CNFs and MoS$_2$@CNFs@rGO, transmission electron microscopy (TEM) analysis was conducted. For the MoS$_2$@CNFs, few-layer MoS$_2$ flakes were uniformly distributed into CNFs (Figure 3a).
After the graphene wrapping process, the rGO flakes substantially covered the MoS$_2$@CNFs without any aggregations. Individual NFs were wrapped by stacked rGO flakes with a thickness of approximately 3 nm (Figure 3b,c). We expected that the favorable influx of Na$^+$ into MoS$_2$@CNFs would be possible through the thin rGO layer, and the electrically conductive rGO would enhance the electrical efficiency of the battery cell by facilitating the electron transport. Figure 3d shows a high-resolution TEM (HR-TEM) image of MoS$_2$@CNFs@rGO. The lattice fringe of the MoS$_2$ in the MoS$_2$@CNFs@rGO is approximately 0.660 nm, indicating that the multilayer MoS$_2$ nanoflakes had enlarged interlayer spacing compared to the general interlayer spacing (~0.615 nm) of multilayer MoS$_2$ [27,28]. The enlarged interlayers can be attributed to the CNFs suppressing the crystallization of MoS$_2$ during thermolysis. In addition, the wide interlayer distance might allow Na$^+$ to diffuse rapidly, promoting Na$^+$ flux in the whole electrode. The homogeneous distribution of elements—such as C (yellow), Mo (red), and S (green)—in the MoS$_2$@CNFs@rGO was investigated by energy-dispersive spectroscopy (EDS) mapping images from a scanning TEM (Figure 3e). The elements were well-distributed in the 1D NF composite, which can be supported by the qualitative data in Figure S1.

To further consider the crystal structure and phase information of the MoS$_2$@CNFs@rGO, Figure 4 exhibits the X-ray diffraction (XRD) patterns of MoS$_2$@CNFs and MoS$_2$@CNFs@rGO. At 14.2°, 33.3°, and 59.1°, the XRD peaks correspond to planes (002), (100), and (110) of the MoS$_2$ phase (JCPDS #37-1492), respectively [29]. Through the graphene wrapping process, no peak shifts were observed for MoS$_2$@CNFs@rGO. Furthermore, as a result of XPS analysis, the chemical states of Mo and C of MoS$_2$@CNFs@rGO showed insignificant change despite the chemical reduction reaction. (Figure S2). Figure 5 compares the Raman spectra of MoS$_2$@CNFs and MoS$_2$@CNFs and shows the vibrational modes, the fingerprint
of the chemical state of the MoS$_2$ phase. MoS$_2$@CNFs and MoS$_2$@CNFs@rGO represent two peaks at 379.1 and 402.7 cm$^{-1}$ due to in-plane E$_{1g}^{12g}$ and out-of-plane A$_{1g}$ vibration modes [30]. Several studies exhibited that the relative intensity of these two peaks suggests the characteristics of MoS$_2$ crystals, given dimensions and edge profiles. Generally, the intensity of the A$_{1g}$ mode is greater than that of the E$_{1g}^{12g}$ mode when the MoS$_2$ flakes have an edge-end structure. There is no difference between the E$_{1g}^{12g}$ and A$_{1g}$ mode peaks for MoS$_2$@CNFs and MoS$_2$@CNFs@rGO, indicating that the MoS$_2$ nanoflakes in the CNFs maintain their structures without damage during the fabrication process. Furthermore, introducing the rGO layer increases the intensity of the D and G bands, which indicates the carbon structure (Figure 5b and Figure S3) [31,32]. The integrated area ratio of sp$^3$ to sp$^2$ (Asp$^3$/Asp$^2$) has been proven to provide useful information concerning the nature of carbon [32]. The low ratio of Asp$^3$/Asp$^2$ indicates the presence of a large amount of sp$^2$ carbon. The Asp$^3$/Asp$^2$ were 1.31 for MoS$_2$@CNFs and 1.15 for MoS$_2$@CNFs@rGO, respectively. It means that the amount of sp$^2$-type carbon increased after rGO wrapping and the reduced graphene oxide layers are well-introduced in the MoS$_2$@CNFs@rGO sample.

![X-ray diffraction pattern of MoS$_2$@CNFs and MoS$_2$@CNFs@rGO.](image)

**Figure 4.** X-ray diffraction pattern of MoS$_2$@CNFs and MoS$_2$@CNFs@rGO.

![Raman shift spectra.](image)

**Figure 5.** Results of Raman analyses of MoS$_2$@CNFs and MoS$_2$@CNFs@rGO with different ranges: (a) 200–500 cm$^{-1}$, (b) 1000–2000 cm$^{-1}$.

| Samples | Carbon, C (wt%) | Sulfur, S (wt%) |
|---------|-----------------|----------------|
| MoS$_2$@CNFs | 23.6 | 29.8 |
| MoS$_2$@CNFs@rGO | 34.3 | 20.9 |

**Table 1.** Contents of the carbon and sulfur components of MoS$_2$@CNFs and MoS$_2$@CNFs@rGO.
To quantitatively identify the contents of rGO in MoS$_2$@CNFs@rGO, element analysis (EA) was carried out (Table 1). The MoS$_2$@CNFs contain 23.6 wt % of carbon and about 29.8 wt % of sulfur from MoS$_2$. After graphene wrapping, the amount of carbon (C) increased to 34.3 wt %, indicating that the sulfur (S) content was relatively decreased. Assuming that the ratio of CNF/MoS$_2$ is maintained after graphene wrapping, it is confirmed that the content of rGO accounts for about 17.7 wt % in the MoS$_2$@CNFs@rGO.

Since the 1D nanostructure of MoS$_2$@CNFs has a large surface area, a sufficient amount of rGO is required for the wrapping, even if it contains thin rGO layers. Therefore, the rGO should cover both the individual NFs and bundle of MoS$_2$@CNFs, increasing the electronic conductivity of the MoS$_2$@CNFs@rGO and preserving active materials, particularly S, during repetitive reactions [33,34].

Table 1. Contents of the carbon and sulfur components of MoS$_2$@CNFs and MoS$_2$@CNFs@rGO.

| Samples           | Carbon, C (wt %) | Sulfur, S (wt %) |
|-------------------|------------------|------------------|
| MoS$_2$@CNFs      | 23.6             | 29.8             |
| MoS$_2$@CNFs@rGO | 34.3             | 20.9             |

3.2. Electrochemical Measurement

In general, MoS$_2$ electrochemically reacts with Na$^+$ based on insertion and conversion reactions [35]. To testify to these electrochemical behaviors in the MoS$_2$@CNFs@rGO, the galvanostatic charge-discharge curves for the MoS$_2$@CNFs@rGO were obtained in a voltage window between 0.005–3.0 V (vs. Na/Na$^+$) at a current density of 100 mA g$^{-1}$ (Figure 6a). The initial discharge and charge capacities of MoS$_2$@CNFs@rGO are 1175 and 573 mAh g$^{-1}$, respectively, corresponding to a Coulombic efficiency (CE) of 48%. This capacity fading for the initial cycle is attributed to the generation of high irreversible capacitance stemming from the solid-electrolyte interphase (SEI) layers formed on the electrode with a large surface area. Nevertheless, in Figure S4, the initial CE of MoS$_2$@CNFs@rGO is higher than that of MoS$_2$@CNFs (44%). It appears that more SEI layers seem to form on the MoS$_2$@CNFs without the rGO coating layers while the rGO adequately stabilizes the SEI layers on the MoS$_2$@CNFs@rGO [36]. Moreover, rGO played a critical role in accelerating electron transport, which improved the initial CE of MoS$_2$@CNFs@rGO. It is confirmed that the MoS$_2$@CNFs@rGO has a voltage plateau at 1.4 V (vs. Na/Na$^+$) and a slope thereafter. This can be explained by a reaction caused by the insertion of Na$^+$ into MoS$_2$ (Equation (4)) and a subsequent conversion reaction (Equation (5)). Sodium polysulfide intermediate (Na$_x$S$_{2\text{−}x}$, where $x$ = 2 to 5) generated by the conversion reaction are easily dissolved in liquid electrolyte and move to the Na anode (“polysulfide shuttling”), leading to capacity loss and adverse effects on battery operation. The overall reaction can be represented as [37–39]:

$$\text{MoS}_2 + x \text{Na}^+ + x e^- \rightarrow \text{Na}_x\text{MoS}_2 \quad (x < 2) \quad (4)$$

$$\text{Na}_x\text{MoS}_2 + (4 - x) \text{Na}^+ \rightarrow 2 \text{Na}_2\text{S} + \text{Mo} \quad (5)$$

The voltage plateau generated at about 1.6 V in the charging process occurred due to the reduction of Na$_2$S to S. After the initial cycle, the SIB cell containing the MoS$_2$@CNFs@rGO electrode shows a highly reversible Na$^+$ storage ability. We evaluated the long-term stability of MoS$_2$@CNFs@rGO, as shown in Figure 6b. The MoS$_2$@CNFs@rGO delivered a high discharge capacity of 345.8 mAh g$^{-1}$ at the 90th cycle with a CE of 99.8%. In addition, the rate capability of MoS$_2$@CNFs@rGO was tested at various current densities between 0.1–20 A g$^{-1}$ (Figure 6c). At lower rates, the MoS$_2$@CNFs@rGO exhibited similar capacity retention to that of MoS$_2$@CNFs. On the other hand, the rate capability of MoS$_2$@CNFs@rGO was gradually improved at higher rates (>0.5 A g$^{-1}$). Moreover, the MoS$_2$@CNFs@rGO outperformed the MoS$_2$@CNFs even at a super-fast rate of 20 A g$^{-1}$. This outstanding ability to store Na$^+$ was also able to be used for Li$^+$ storage (Figure S5).
Sodium polysulfide intermediate (Na$_2$S$_x$, where $x$ = 2 to 5) generated by the conversion reaction are easily dissolved in liquid electrolyte and move to the Na anode (“polysulfide shuttling”), leading to capacity loss and adverse effects on battery operation. The overall reaction can be represented as [37–39]:

\[
\text{MoS}_2 + x \text{Na}^+ + x e^- \rightarrow \text{Na}_x\text{MoS}_2 \quad (x \leq 2)
\]

\[
\text{Na}_x\text{MoS}_2 + (4-x) \text{Na}^+ \rightarrow 2 \text{Na}_2\text{S} + \text{Mo}
\]

The voltage plateau generated at about 1.6 V in the charging process occurred due to the reduction of Na$_2$S to S. After the initial cycle, the SIB cell containing the MoS$_2$@CNFs@rGO electrode shows a highly reversible Na$^+$ storage ability. We evaluated the long-term stability of MoS$_2$@CNFs@rGO, as shown in Figure 6b. The MoS$_2$@CNFs@rGO delivered a high discharge capacity of 345.8 mAh g$^{-1}$ at the 90th cycle with a CE of 99.8%. In addition, the rate capability of MoS$_2$@CNFs@rGO was tested at various current densities between 0.1~20 A g$^{-1}$ (Figure 6c). At lower rates, the MoS$_2$@CNFs@rGO exhibited similar capacity retention to that of MoS$_2$@CNFs. On the other hand, the rate capability of MoS$_2$@CNFs@rGO was gradually improved at higher rates (>0.5 A g$^{-1}$). Moreover, the MoS$_2$@CNFs@rGO outperformed the MoS$_2$@CNFs even at a super-fast rate of 20 A g$^{-1}$. This outstanding ability to store Na$^+$ was also able to be used for Li$^+$ storage (Figure S5).

Figure 6. Electrochemical performances of MoS$_2$@CNFs@rGO. (a) Charge–discharge profile at 100 mA g$^{-1}$ between 0.005 V~3.0 V vs. Na/Na$^+$. (b) Cycling performance at 100 mA g$^{-1}$. (c) Rate capability with different current densities (0.1~20 A g$^{-1}$).

All things taken together, we elucidated the reaction mechanism of MoS$_2$@CNFs@rGO, based on the following factors: (I) MoS$_2$ nanoflakes with enlarged interlayer spacing and short lateral distance between each flake are beneficial for storing Na$^+$ in the CNFs. (II) The CNFs serve as a continuous passage for electrons and storage matrix for the active materials (Na$^+$ and S). (III) The rGO is synergistically advantageous in terms of fast kinetics. Eventually, it turns out that the MoS$_2$@CNFs@rGO synthesized by our fabrication approach enables the SIB cells to show remarkable performance toward Na$^+$ insertion and conversion reactions.

4. Conclusions

In summary, we report a straightforward approach to fabricate a composite consisting of MoS$_2$ nanoflakes confined in CNFs wrapped with a rGO net for SIB anodes. We effectively generated randomly distributed MoS$_2$ nanoflakes (a few layers) in the CNFs via thermolysis and wrapped the rGO onto the MoS$_2$@CNFs to enable the composite to be active for Na$^+$ storage. The MoS$_2$ nanoflakes possessing short lateral and expanded interlayer distances would be favorable for reversible insertion/desertion of Na$^+$. In addition, the strongly interconnected CNFs and rGO net promoted electron transfer through the whole electrode, rendering a high rate of capability and cyclability. Furthermore, the rGO would preclude the dissolution of S stemming from the conversion reactions at the outermost surfaces of the composite materials. The MoS$_2$@CNFs@rGO showed excellent cycle retention with a specific capacity of 345.8 mAh g$^{-1}$ at a current density of 100 mA g$^{-1}$ from
the initial cycle to the 90th cycle. We elucidated that in the MoS\textsubscript{2}-based anodes undergoing conversion reactions, caging the active materials in the electronically conductive scaffold is critical for improving electrochemical battery performance.

**Supplementary Materials:** The following are available online at https://www.mdpi.com/article/10.3390/nano11102691/s1. Figure S1: EDS spectrum of rGO@MoS\textsubscript{2}@CNFs, Figure S2: XPS analysis for MoS\textsubscript{2}@CNFs@rGO and MoS\textsubscript{2}@CNFs and for (a) C1s and (b) Mo 3d, Figure S3: Raman analysis for (a) MoS\textsubscript{2}@CNFs@rGO and (b) MoS\textsubscript{2}@CNFs with classified peaks (I, III: sp\textsuperscript{3} bonding, II, IV: sp\textsuperscript{2} bonding), Figure S4: Charge–discharge curves of MoS\textsubscript{2}@CNFs at a current density of 100 mA g\textsuperscript{−1}, Figure S5: Lithium-ion battery performance of MoS\textsubscript{2}@CNFs@rGO.

**Author Contributions:** Conceptualization, S.-H.C. and J.-W.J.; methodology, S.-H.C., J.-H.K. and I.-G.K.; validation, S.-H.C., I.-G.K. and J.-H.P.; formal analysis and investigation, S.-H.C. and J.-W.J.; writing—original draft preparation, S.-H.C., J.-H.K. and J.-W.J.; writing—review and editing as well as supervision, J.-W.J., H.-S.K. and I.-D.K.; project administration and funding acquisition, J.-W.J. All authors have read and agreed to the published version of the manuscript.

**Funding:** This work was supported by the 2021 Research Fund of the University of Ulsan.

**Institutional Review Board Statement:** Not applicable.

**Data Availability Statement:** Data are contained within the article.

**Acknowledgments:** This work was supported by the 2021 Research Fund of the University of Ulsan.

**Conflicts of Interest:** The authors declare no conflict of interest.

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