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In Situ Growth of W$_2$C/WS$_2$ with Carbon-Nanotube Networks for Lithium-Ion Storage

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Abstract: The combination of W$_2$C and WS$_2$ has emerged as a promising anode material for lithium-ion batteries. W$_2$C possesses high conductivity but the W$_2$C/WS$_2$-alloy nanoflowers show unstable performance because of the lack of contact with the leaves of the nanoflower. In this study, carbon nanotubes (CNTs) were employed as conductive networks for in situ growth of W$_2$C/WS$_2$ alloys. The analysis of X-ray diffraction patterns and scanning/transmission electron microscopy showed that the presence of CNTs affected the growth of the alloys, encouraging the formation of a stacking layer with a lattice spacing of ~7.2 Å. Therefore, this self-adjustment in the structure facilitated the insertion/desertion of lithium ions into the active materials. The bare W$_2$C/WS$_2$-alloy anode showed inferior performance, with a capacity retention of ~300 mAh g$^{-1}$ after 100 cycles. In contrast, the WCNT01 anode delivered a highly stable capacity of ~650 mAh g$^{-1}$ after 100 cycles. The calculation based on impedance spectra suggested that the presence of CNTs improved the lithium-ion diffusion coefficient to 50 times that of bare nanoflowers. These results suggest the effectiveness of small quantities of CNTs on the in situ growth of sulfides/carbide alloys: CNTs create networks for the insertion/desertion of lithium ions and improve the cyclic performance of metal-sulfide-based lithium-ion batteries.

Keywords: WS$_2$; W$_2$C; hydrothermal method; carbon nanotubes; lithium-ion batteries

1. Introduction

The rise of graphene, transition-metal chalcogenides (TMCs), transition-metal oxides, and layered-structure transition-metal carbides/nitrides (MXenes) shows the significance and potential of 2D-layered nanomaterials, which can be applied in various fields such as displays, energy storage, energy conversion, and electronic devices [1–18]. TMC materials possess high theoretical lithium-storage capacity (~670 mAh g$^{-1}$ with MoS$_2$ and 433 mAh g$^{-1}$ with WS$_2$). However, the practical showed that a high abnormal capacity was recorded, which can contribute by conversion reaction, the derived solid electrolyte interface (SEI)-layer formation, or the high lithiation process in the interfacial lithium-storage spaces [19–21]. For example, Feng et al. fabricated WS$_2$ nanoflakes for lithium-ion batteries (LIBs), which delivered a high initial discharge capacity of ~1700 mAh g$^{-1}$ at a current of 47.5 mA g$^{-1}$ [22]. Liu et al. synthesized mesoporous WS$_2$, showing a high initial discharge capacity of ~1300 mAh g$^{-1}$ [23]. However, the TMCs anode material with the conversion reaction could be significantly degraded due to the dissolution of the sulfur into electrolyte, creating a gel-like polymeric layer [24]. Recently, the combination of TMCs with MXenes has received significant attention owing to the tunable bandgap of TMCs, active edge of chalcogenide atoms with high conductivity of MXenes, high stability, and active edge of metal atoms [25–28]. For example, Zhao et al. developed vertical MoS$_2$/Mo$_2$C nanosheets on carbon paper, which maximized the active sites of the active edges and resulted in high electrocatalytic performance in the hydrogen-evolution reaction [29]. Cheng et al. used guar gum as the carbon source for nanoflower MoS$_2$/Mo$_2$C as an efficient sustainable
electrocatalyst for the production of hydrogen gas [30]. Faizan et al. fabricated Mo$_2$C stacked with MoS$_2$ nanosheets for lithium-storage applications. Li et al. [31] modified the surface of WS$_2$/W$_2$C materials with N and S, which improved their electrochemical catalytic properties [28]. Nguyen et al. controlled the growth of W$_2$C/WS$_2$ nanoflowers via a hydrothermal method for use as stable anode materials in lithium-ion batteries (LIBs) [32,33]. The carbide MXenes possess high conductivity and stability; however, they are not highly active materials by themselves [6–10]. Their lithium-storage capability is low, and thus they could only be employed as additive materials [34–37]. Meanwhile, carbon nanotubes (CNTs) possess high conductivity and light weight and are popular network materials for enhancing connectivity in electronic applications [38,39]. Therefore, CNTs and derived carbon materials have been widely used as skeleton or network of the active materials for LIBs. For example, Lu et al. used a CNT/MoS$_2$ composite as a binder-free anode material showing high performance in LIBs [40]. Chen et al. developed a FeS$_2$/CNT composite material with a neural-network-like structure, which delivered a superior rate and high cycling performance in sodium-ion batteries [41]. The use of TMCs, MXenes, and CNTs in a system could combine their advantage such as physical, chemical stability, high conductivity, and high capability for lithium-storage applications.

In this study, W$_2$C/WS$_2$-alloy nanoflowers were fabricated with a small quantity of CNTs as a connective network using a hydrothermal method. The presence of a CNT network is not only effective for the formation of alloy flowers but also improves the electrochemical performance of the as-prepared anode materials in lithium storage. The structural changes and stable performance of W$_2$C/WS$_2$ in a CNT network (WCNT) were investigated and discussed.

2. Materials and Methods
2.1. Chemical Materials
Thioacetamide (TAA, C$_3$H$_5$NS, 99%), WCl$_6$ powder (99.9%), multiwalled CNTs (>90%), and polyvinylidene fluoride (PVDF, M$_W$ ~ 534,000) were purchased from Sigma-Aldrich Inc. (St. Louis, MO, USA). Super-P amorphous carbon black (C, approximately 40 nm, 99.99%) and absolute ethanol were purchased from Alpha Aesar, Inc. (Ward Hill, MA, USA). All materials were used as received. WCl$_6$ was stored in an Ar-filled glove box.

2.2. Synthesis of WCNT
The WCNT was prepared using a modified procedure for W$_2$C/WS$_2$ nanoflower synthesis [33]. CNTs were dispersed in ethanol using sonication. Then, 0.6 g WCl$_6$ was added to 4 mL of the CNT solution with an adjusted weight ratio of CNT: WCl$_6$ of 5, 10, and 15%. TAA (1.2 g) was dispersed in a separate vessel containing 4 mL of absolute ethanol. The TAA solution was then quickly mixed with the WCl$_6$/CNT solution and stirred for 5 min. Then, 10 mL of deionized (DI) water was added to the solution, and the mixture was transferred into a 40 mL polypropylene-lined autoclave and heated at 250 °C for 12 h. The obtained powder was washed four times with ethanol and DI water and dried in a vacuum oven at 60 °C. The samples with different quantities of CNTs (5, 10, and 15%) were marked as WCNT01/02/03, respectively.

2.3. Material Characterization
The structures of W$_2$C/WS$_2$ and WCNT samples were determined using X-ray diffraction (XRD, D/MAX-2200 Rigaku, Tokyo, Japan) over the 2θ range of 10–70° and transmission electron microscopy (TEM, TECNAI G2F30, FEI Corp., Hilsboro, OR, USA). Their morphologies were analyzed using field emission scanning electron microscopy (FESEM, SIGMA HD, Carl Zeiss, Jena, Germany) at an accelerating voltage of 5 kV. Thermogravimetric analysis (TGA) was measured using a thermal analyzer (Q600 SDT, TA Instruments, New Castle, DE, USA).
2.4. Electrochemical Measurements

The W$_2$C/WS$_2$ and WCNT anode materials were evaluated by assembling half-cell LIBs using a coin-type cell (CR 2032, Rotech Inc., Gwangju, Korea) with a lithium reference electrode. The active materials were mixed with carbon super P and PVDF (weight ratio of 70:15:15) in a n-methyl-2-pyrrolidone solution to form a slurry, which was then coated on copper foil using a doctor blade. The working electrodes were dried in a vacuum oven at 70 °C for 24 h to remove the solvent. The anodes were punched into 12 mm circular disks. The loading mass of the active materials was ~1.0–1.3 mg. LIBs were assembled in an Ar-filled glove box using 1 M LiPF$_6$ in ethylene carbonate/diethylene carbonate (EC:DEC = 1:1 by volume) as the electrolyte. Cyclic voltammetry (CV) tests and electrochemical impedance spectroscopy (EIS) were performed using a battery-cycle tester (WBCS3000, WonAtech, Seocho-gu, Seoul, Korea) over the voltage range of 0.01–3.00 V vs. Li/Li$^+$ and frequency range from 100 kHz to 0.1 Hz, respectively. The cycling stabilities were measured over the voltage range of 0.01–3.00 V using a ZIVE MP1 (WonAtech, Seocho-gu, Seoul, Korea).

3. Results

The morphologies of the W$_2$C/WS$_2$ nanoflowers and the WCNT samples are shown in Figure 1. The sizes of nanoflowers range from 100 to 300 nm with many leaves, which consist of 2D nanosheets, as shown in Figure 1a. The presence of CNTs in the samples reduced the number of leaves. All the alloy nanoflowers were wrapped in theCNT network. In addition, at a low concentration of CNTs in the WCNT01 sample, the W$_2$C/WS$_2$ nanoflowers grew to a larger size of ~300–400 nm, as illustrated in Figure 1b. At above 10% of CNTs, the size of nanoflowers decreased to 200–300 nm, as shown in Figure 1c,d. At lower quantity of CNTs (2 and 3 wt%), the separate growth of W$_2$C/WS$_2$ nanoflowers was found (data not shown), indicating the nonuniformity. Therefore, the minimum content for the effective coverage of W$_2$C/WS$_2$ was 5 wt% CNTs. It is noteworthy that the presence of CNTs could act as a seed point for growth of W$_2$C/WS$_2$ nanoflowers. In the bare W$_2$C/WS$_2$ nanoflower, their leaves were bended around a center. In WCNT samples, the leaf surface was flat, resulting in an increase in the flower size. However, the increased quantity of CNTs could occupy more spaces in solution, which could limit the growth of W$_2$C/WS$_2$ flower leaves. Moreover, the high concentration of CNTs could lead to the aggregation in the prepared solution. Therefore, the increased quantity of CNTs in the samples led to the size reduction and the absence of nanoflowers in the frame network. Moreover, the separate growth of W$_2$C/WS$_2$ was observed as a result of CNT aggregation, as shown in Figure S1.

Figure 2a shows the XRD patterns and TEM/HR-TEM images of the W$_2$C/WS$_2$ alloy flowers and WCNT samples. The XRD patterns of the W$_2$C/WS$_2$ alloys were confirmed by the standard W$_2$C and WS$_2$ peaks, as reported in previous studies [28,42,43]. The (001) and (100) peaks of W$_2$C are clearly observed. The (002) peak of WS$_2$ overlapped with the stacking layer peak at ~12.6°, whereas the (004), (103), and (006) planes were clearly observed. The (002) peak of the CNTs was not clear until 15% CNT content was used in the samples. The WCNT03 sample showed a low-intensity peak at that position. Furthermore, the high crystallinity of W$_2$C and WS$_2$ and their large sizes also contributed to the high peak intensity, leading to decreased CNT peaks. In addition, the samples with CNTs showed significantly improved peaks for the stacking layer at 2θ = 12.6°. According to Bragg’s law, $d = \lambda/2\sin \theta$ (where $d$ is the lattice spacing, $\lambda$ is the incident X-ray wavelength, and $\theta$ is the diffraction angle); the average lattice spacing was ~7.2 Å. This lattice spacing is large compared to the ionic radius of Li$^+$, which is 0.76 Å, therefore, this spacing could provide a facile path for lithium ions to easily insert/desert into the material structures. The TEM images in Figure 2b–d also confirm the formation of W$_2$C/WS$_2$ on CNTs network, with the lattice spacing of the stacking layer in the range of 0.62–0.84 nm, which is consistent with the XRD results. Therefore, the presence of CNTs not only created a frame network but also facilitated the growth of W$_2$C/WS$_2$ alloys, forming average lattice spacing of ~7.2 Å, which is promising for metal-ion-storage applications. The TEM images with energy dispersive
x-ray elemental mapping also confirmed the presence of W, S, C atoms on the W₂C/WS₂ and CNT structure in Figure S2. The TGA curves of bare W₂C/WS₂ and WCNT01 samples were presented in Figure S3. The mass of bare W₂C/WS₂ and WCNT01 sample reduced to ~90% and ~80% after the measurement. It is noted that both W₂C/WS₂ and CNTs were oxidized during the measurement. Therefore, the different mass percentage after the measurement is proportional to the mass change from CNTs. The amounts of W₂C/WS₂ and CNTs in WCNT01 were calculated to be 90 and 10 wt%, respectively. The increased quantity of CNTs could reduce the nanoflowers’ size, leading to an increase in surface area and an improvement in the electrochemical performance of anode materials.

Figure 1. FESEM images of (a) W₂C/WS₂ (b) WCNT01, (c) WCNT02, and (d) WCNT03 samples.

To further confirm the structure of W₂C/WS₂ on CNTs, Figure 3a shows the Raman spectra of W₂C/WS₂ nanoflowers and WCNT01 samples. The optical phonon modes (E₁2g and A₁g) of WS₂ were well-recorded at ~350 and 415 cm⁻¹ [44]. The tungsten-carbide vibration modes were also detected at ~700 and ~800 cm⁻¹ [10]. The W₂C/WS₂ alloys showed a low intensity of carbon sp3 and sp2 peaks, corresponding to the D and G band, respectively. These peaks are highly increased in the WCNT01 sample, indicating the presence of the CNT structure [45,46]. The XPS spectra of WCNT01 material are shown in Figure 3b–d. The W⁴⁺ peaks can be deconvoluted to the W–C binding and W–S binding, corresponding to the doublets with W 4f⁷/₂ at 32.2 and 33.0 eV, respectively. Moreover, small W⁶⁺ peaks were observed, which could be due to the oxidation on the surface during sample preparation. Sulfur atoms show a doublet of S 2p₃/₂ and 2p₁/₂ peaks at 161.7 and 163.0 eV, respectively, indicating the S–W binding. A small peak at 169.5 eV was observed due to the surface oxidation of the material. The C 1s spectrum could be deconvoluted into six peaks at 284.1, 284.6, 285.5, 286.5, 287.2, and 290.6 eV, which correspond to the C–W, C=σ, C–C, C–O, C=O, and O–C=O binding, respectively. These results are consistent with binding energy of CNT and carbide compounds, indicating the formation of W₂C/WS₂ on CNTs [30,45,47].
Figure 2. (a) XRD patterns of W2C/WS2 and WCNT01/02/03; (b) TEM images and (c,d) high-resolution TEM (HR-TEM) images of WCNT01.

Figure 3. (a) Raman spectra of bare W2C/WS2 and WCNT01 samples. High-resolution XPS spectra of (b) W 4f, (c) S 2p, and (d) C 1s of WCNT01 sample.
To reveal the effectiveness of CNTs in W<sub>2</sub>C/WS<sub>2</sub> materials, CV of bare and CNT-frame-networked samples was performed (Figure 4). The electrochemical process can be summarized in the following equations:

\[
WS_2 + xLi^+ + xe^- \rightarrow Li_xWS_2 \tag{1}
\]

\[
W_2C + yLi^+ + ye^- \rightarrow Li_yW_2C \tag{2}
\]

\[
Li^+ + e^- + \text{electrolyte} \rightarrow \text{SEI} \tag{3}
\]

\[
Li_xWS_2 + (4-x)Li^+ + (4-x)e^- \rightarrow 2Li_2S + W \tag{4}
\]

\[
2Li_2S \rightarrow 4Li^+ + 4e^- + 2S \tag{5}
\]

In the first cycle of the bare W<sub>2</sub>C/WS<sub>2</sub> anode, the cathodic scan showed the insertion of lithium ions into the layered structure of W<sub>2</sub>C and WS<sub>2</sub> at ~1.5 V (Equations (1) and (2)). The solid-electrolyte-interface (SEI) layer formed at ~0.6 V (Equation (3)) [48,49]. The peak at ~0.3 V is related to the deep insertion of Li<sup>+</sup> ions described by Equation (4) [50]. Meanwhile, from the second cycle onward, the cathodic scan demonstrated three major peaks at ~2.0, 1.3, and 0.9 V. As per the previous report, the dissolution of the S atom generated a gel-like SEI layer, which led to the shift of the cathodic peak to ~2.0 V [24]. The peaks at 1.3 and 0.9 V are related to the insertion of Li ions into WS<sub>2</sub> and W<sub>2</sub>C [33]. In the anodic scan, \(Li_2S\) decomposes at ~2.3 V, as shown in Equation (5), and the oxidation of \(W\) to \(W^{4+}\) occurs at 1.9 V [23]. The anodic peak at 1.2 V may correspond to the desertion of Li<sup>+</sup> ions from \(Li_yW_2C\) as the reverse reaction of Equation (2). The presence of the
CNT network increased conductivity and prevented coverage of the gel-like SEI layer. Therefore, the WCNT01 and WCNT02 samples showed cathodic peaks of ~1.6 V and 0.25 V, which are lower than 2.0 V and 0.3 V, as demonstrated by the bare W2C/WS2 anode. The decomposition peak of Li2S also shifted to ~2.5 V. Interestingly, the intensity of SEI formation peaks of the WCNT01/02 anodes at ~0.5–0.7 V dramatically decreased in comparison to that of the bare anode. At a CNT content above 15%, the WCNT03 anode showed a similar behavior to the bare W2C/WS2 anode, in which the cathodic peak at 2.0 V (Equation (1)) and the peak at ~0.5 V for SEI-layer formation (Equation (3)) appeared again with high intensity. This is attributed to the nonuniform W2C/WS2 on the CNTs, which originated from the aggregation of CNTs at high concentrations in the prepared mixture before the hydrothermal process. Thus, a low quantity of CNTs (below 10%) could enhance the electrochemical performance by preventing the coverage of the gel-like SEI layer.

The initial voltage profiles of the as-prepared anodes are shown in Figure 5. The WCNT01/02/03 samples showed a low open potential of ~1.1 V in comparison to the W2C/WS2 sample, which could be attributed to the contact of W2C/WS2 with CNTs. This behavior was also observed in MoS2 and WS2 grown with graphene or CNTs, as discussed in several reports [45,51–53]. The initial discharge capacity of the W2C/WS2 sample was in the range of 1000–1100 mAh g−1. The voltage profiles of the bare W2C/WS2 alloy anode showed the discharge plateau at ~1.4 V and charge plateau at ~2.3 V. However, these plateaus gradually decreased after the first cycle. In contrast, the plateaus of the WCNT01/02/03 anodes were much more stable, demonstrating a similar flat form during the first three cycles. This indicates that the CNT network optimized the electrochemical reaction, resulting in a stable flat form of the voltage profiles.

![Figure 5. Initial voltage profiles of the (a) W2C/WS2 alloys, (b) WCNT01, (c) WCNT02, and (d) WCNT03 anodes.](image-url)

The long-term cyclic stability of these four anodes was further evaluated, as illustrated in Figure 6a–d. The bare W2C/WS2 anode exhibited fast degradation for the first 20 cycles,
and only approximately 40% of the initial capacity remained (~400 mAh g⁻¹); then, it gradually degraded to ~28% of the initial capacity (~300 mAh g⁻¹) after 100 cycles, as shown in Figure 6a. Meanwhile, the WCNT01 electrode underwent a fast degradation in only the first five cycles, and the capacity then slowly degraded to 650 mAh g⁻¹ (67% of the initial capacity) after 100 cycles. Both the WCNT02 and WCNT03 anodes showed a fast reduction in capacity for the first ten cycles, followed by a slow reduction to 420 and 410 mAh g⁻¹, respectively. These results indicate that a high concentration of CNTs is not necessary and even reduces the overall capacity owing to the lower contribution of the lithium-ion host. Therefore, it was confirmed that only 5% CNTs in the alloys were sufficient to connect the network of W₂C/WS₂, prevent fast degradation, and stabilize the capacity. The rate performances of bare W₂C/WS₂ and WCNT01 anodes are shown in Figure S4. The bare W₂C/WS₂ anode shows a low performance at 1.0 A, which delivered a low capacity ~ 110 mAh g⁻¹ and low recovered capacity ~79% when reducing the current rate from 1.0 to 0.1 A g⁻¹. on the other hand, the WCNT01 anode with CNT networks could remain at a capacity of ~250 mAh g⁻¹ at 1.0 A g⁻¹ and recovered ~92% capacity when reducing the current rate to 0.1 A. Moreover, the WCNT01 anode shows a trend to recover 100% capacity when increasing the number of cycles at 0.1 A g⁻¹. Furthermore, the capacity of the composite anode continuously degrades with the increase in cycles. This could be due to the main two reasons: First, the lithium-counter electrode could be degraded due to the imperfect recovery of Li and the SEI-layer formation on the surface [54–56]. Second, it could be due to the degradation of active materials. The CNT network can prevent the formation of a gel-like polymeric layer. However, the sulfur atom could be slowly dissolved into electrolyte during cycling, as discussed for bare WS₂ materials. Due to the conversion type of anode materials, the WS₂ will be converted to W-Li alloys and Li₂S when inserting the Li ions. Therefore, it is believed that the cycling process could slightly change the morphologies and material types. However, with the stability of CNT networks, it can prevent these changes with a slow rate.

**Figure 6.** Cyclic performance of the (a) W₂C/WS₂ alloys, (b) WCNT01, (c) WCNT02, and (d) WCNT03 anodes under the current rate of 0.1 A g⁻¹.
Impedance measurements further confirmed the change in the electrical properties of the CNT networks in the W2C/WS2 materials, as shown in Figure 7a. The equivalent circuit was used with a modified Randle’s model, which contains a series resistance \( R_s \), charge-transfer resistance \( R_1 \), and SEI-layer resistance \( R_2 \) with a Warburg diffusion element and constant-phase elements Cpe1 and Cpe2. The extracted charge-transfer resistances of the bare W2C/WS2 and WCNT01/02/03 were 441.3, 125.9, 106.3, and 60.8 \( \Omega \), respectively. The enhancement in lithium diffusion can be estimated using the following equation [57–59]:

\[
D = \frac{R^2 T^2}{2 A^2 n^4 F^4 C^2 \sigma^2}
\]  

(6)

where \( R \) and \( F \) are the gas constant and Faraday constant, respectively, \( T \) is the absolute temperature, \( A \) is the effective area of the working electrode, \( n \) is the electronic transport ratio during the redox process, \( C \) is the molar density of Li\( ^+ \) in the electrode, and \( \sigma \) is the Warburg factor associated with the impedance of the cell, which can be obtained from the following equation [60]:

\[
Z' = R_s + R_1 + R_2 + \sigma \omega^{-1/2}
\]  

(7)

Figure 7. (a) Nyquist plots and (b) \( Z' \) vs. \( \omega^{-1/2} \) plots of the bare W2C/WS2 alloys and WCNT01/02/03 anodes.

Figure 7b shows the fitting line of \( Z' \) vs. \( \omega^{-1/2} \), in which the slopes of the lines of the bare W2C/WS2 and WCNT01/02/03 anodes are 1697.1, 389.9, 246.5, and 239.6, respectively. According to Equation (6), the diffusion coefficients of the lithium ions in WCNT01/02/03 are proportional to \( \sigma^{-1/2} \) and were approximately 19, 49, and 50 times higher than those of the bare W2C/WS2 anode, respectively. Even though the WCNT02/03 samples showed a great improvement in the lithium diffusion coefficient, their stability in terms of structure and electrochemical properties was not as suitable as that of the WCNT01 electrode. Therefore, WCNT01 is recommended as the best combination of CNTs with W2C/WS2 alloys for high-performance anodes in lithium-ion cells.

In order to investigate the lithium-storage mechanism, the CV curves at scan rates from 10 to 100 mV s\(^{-1}\), and the logarithm plot of peak currents with logarithm of scan rates are shown in Figure S5. The capacitive and diffusion contribution can be evaluated by the \( b \) factor in the following equation [61]:

\[
i = k \nu^b
\]  

(8)
where $i$ is the current density, $v$ is the scan rate, $k$ and $b$ are adjustable factors. When $b = 1$, the storage mechanism is capacitive; when $b = 0.5$, the storage mechanism is diffusion. By the logarithm of Equation (8), the $b$ factor can be obtained by plotting the fitting line of $\log(i)$ vs. $\log(v)$. The $b$ values are 0.9 and 0.52 with cathodic peak and anodic peak, respectively. In the cathodic process, the cell behavior can be considered as a capacitor, while in the anodic process, the diffusion-controlled process is major contributor to the current. Therefore, it is noted that the high reversible capacity of the WCNT01 anode was based on capacitive behavior.

The comparison of the research on WS$_2$-based materials for the LIB anode is shown in Table 1. It clearly illustrates that the bare 2D or oxygen-modified WS$_2$ have low electrochemical performances, which reveal their storage capability only for 20 cycles. The optimized compositions of WS$_2$ with other stable materials are required to enhance their cyclability and rate performance. Most compositions of WS$_2$ with graphene, carbon, or CNTs can form with some modifications such as N-doping or three-dimensional morphologies, where stable capacity can go up to ~960 mAh g$^{-1}$. In our study, the ternary compound with W$_2$C, WS$_2$, and CNTs for the LIB anode is not the best material but shows a comparative result. Moreover, the simple preparation method could be an advantage for the application in lithium storage. Therefore, it is noted that control of the flowers’ sizes and/or the compositions of functionalized CNTs and W$_2$C/WS$_2$ could be effective ways to further enhance their electrochemical performances for LIBs.

Table 1. Comparison of electrochemical performance of WS$_2$-based composite materials for lithium-ion batteries.

| Anode Materials          | Current Density (mA g$^{-1}$) | Initial Discharge Capacity (mAh g$^{-1}$) | Cycle Number | Specific Capacity (mAh g$^{-1}$) | References |
|--------------------------|-------------------------------|------------------------------------------|--------------|-----------------------------------|------------|
| WS$_2$ nanoflakes        | 47.5                          | ~1700                                    | 20           | ~700                              | [22]       |
| Oxygen-functionalized WS$_2$ | 50                            | ~920                                     | 20           | ~220                              | [62]       |
| Hierarchical WS$_2$ on 3D graphene | 100                          | ~800                                     | 100          | ~740                              | [63]       |
| Mesoporous WS$_2$        | 100                           | ~1300                                    | 100          | ~800                              | [23]       |
| N-graphene/WS$_2$        | 100                           | ~1300                                    | 100          | ~800                              | [64]       |
| N-carbon sphere/WS$_2$   | 100                           | ~735                                     | 100          | ~630                              | [65]       |
| N-graphene/WS$_2$        | 100                           | ~950                                     | 100          | ~960                              | [66]       |
| N-carbon/WS$_2$          | 100                           | ~1000                                    | 100          | ~640                              | [67]       |
| W$_2$C/WS$_2$/CNTs       | 100                           | ~1000                                    | 100          | ~650                              | This work  |

4. Conclusions

In this study, W$_2$C/WS$_2$ was synthesized in situ using CNT networks via a hydrothermal method. The presence of CNTs led to a decrease in the number of multi-edge nanoflowers with a size range of 200–400 nm. The CNT networks enhanced the conductivity of anode materials, which in turn reduced the cathodic peak intensity from 2.0 to ~1.6 V. The impedance spectra also suggest that the lithium-ion diffusion in the WCNT01/02/03 samples was 19, 49, and 50 times higher than that of the W$_2$C/WS$_2$ sample, respectively. WCNT01 anodes with 5% CNTs showed the best performance, with a capacity of 650 mAh g$^{-1}$ (67% of the initial value) remaining after 100 cycles. These results suggest that the utilization of CNT networks and a simple hydrothermal method can be appropriate for improving the overall stability of metal-sulfide anode materials.
Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/nano12061003/s1, Figure S1: SEM image of WCNT03 sample with and without CNT area, Figure S2: (a) TEM image, (b) Scanning TEM image and elemental mapped images (c) W-L, (d) S-K and (e) C-K of W2C/WS2 nanolayers on CNTs; Figure S3: TGA analysis of the synthesized W2C/WS2 and WCNT01 materials; Figure S4: Rate performance of (a) bare W2C/WS2 and (b) WCNT01 anodes at different current rate from 0.1 to 1.0 A g\(^{-1}\); Figure S5: (a) CV curves of WCNT01 anode at different scan rate from 20–100 mV s\(^{-1}\) and (b) plots of log(current) with log(scan-rate).

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