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## Free-standing hierarchically sandwich-type tungsten disulfide nanotubes/graphene anode for lithium-ion batteries

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**ABSTRACT:** Transition metal dichalcogenides (TMD), analogue of graphene, could form various dimensionalities. Similar to carbon, one dimensional (1D) nanotube of TMD materials has wide application in hydrogen storage, Li-ion batteries and supercapacitors due to their unique structure and properties. Here we demonstrate the feasibility of tungsten disulfide nanotubes (WS<sub>2</sub>-NTs)/graphene (GS) sandwich-type architecture as anode for lithium-ion batteries for the first time. The graphene based hierarchical architecture plays vital roles in achieving fast electron/ion transfer, thus leading to good electrochemical performance. When evaluated as anode, WS<sub>2</sub>-NTs/GS hybrid could maintain a capacity of 318.6 mA/g over 500 cycles at a current density of 1A/g. Besides, the hybrid anode does not require any additional polymeric binder, conductive additives or a separate metal current-collector. The relatively high density of this hybrid is beneficial for high capacity per unit volume. Those characteristics make it a potential anode material for light and high performance lithium-ion batteries.

**KEYWORDS:** Lithium-ion batteries, anode material, graphene, tungsten disulfide nanotube, sandwich-type structure, electro-chemical performance

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4 Rechargeable lithium ion batteries (LIBs) have long been considered as the  
5 most effective energy-storage technology and dominated portable electronic market  
6 for over two decades.<sup>1,2</sup> Based on the intercalation mechanism, state-of-the-art Li-ion  
7 technology can exhibit a theoretical specific energy of ~400 Wh/kg, such as  
8 LiCoO<sub>2</sub>/graphite system.<sup>3</sup> However, it is urgent to explore new chemistries and  
9 materials that can significantly increase the cell energy density, considering the future  
10 demand for electronic vehicles and large-scale energy storage plants.<sup>4,5</sup>

11 Graphite, a widely used anode material for the current LIBs, has a theoretical  
12 capacity of only 372 mAh/g, given a fully intercalated LiC<sub>6</sub> compound, which is one  
13 of the limiting factors for achieving high energy density of the cell<sup>6</sup>. In order to  
14 overcome such technical bottleneck, considerable effort has been devoted to design  
15 and synthesise new anode materials with higher theoretical specific capacity, such as  
16 transition metal oxides (SnO<sub>2</sub>, Co<sub>3</sub>O<sub>4</sub>, Fe<sub>3</sub>O<sub>4</sub>), Sn and Si<sup>7</sup>. However, all these materials  
17 suffer from severe volume variation during charge-discharge cycling, which results in  
18 serious pulverisation of the electrodes, and thus, rapid capacity degradation. For  
19 instance, Si has a high specific capacity of 4200 mAh/g if fully lithiated to Li<sub>4.4</sub>Si,  
20 however, it also shows a large volume expansion up to 400%. Such volume expansion  
21 causes huge mechanical stress of the electrode, and therefore, severely limits the  
22 lifetime of Si anode. Although various strategies have been proposed to enhance the  
23 structural stability of Si-based materials, including carbon or polymer coating<sup>8, 9</sup>,  
24 nano-structuring<sup>10-12</sup> and hierarchical hybridization,<sup>13-15</sup> it is still very challenge to  
25 overcome the issue of the inherent volume change of these materials during cycling.

26 Transition metal dichalcogenides (TMD) MX<sub>2</sub> (M=Mo, Ti, V, and W, X=S or  
27 Se)<sup>16, 17</sup> with the similar feature of layered structure as graphite could have great  
28 potential for alternative anode materials. In general, MX<sub>2</sub> has strong covalent bonds  
29 within layers and weak Van der Waals forces between layers, which provide ideal  
30 space for intercalation of lithium ions. For instance, MoS<sub>2</sub> has much larger spacing  
31 between neighboring layers (0.615 nm) than that of graphite (0.335 nm) and weak van  
32 der Waals forces between the layers, which, in principal, may make the Li<sup>+</sup> diffuse  
33 easier. However, certain electrochemical properties of MX<sub>2</sub> can only be achieved in  
34 their 1-D or 2-D nanostructured crystals because of the relatively high resistance for  
35 Li-ion transport in their bulk form. In addition, the electron conductivity of this type  
36 of materials is still too low, which could lead to rapid capacity fading and poor rate  
37 performance when using as the anode material in a Li-ion cell. A widely used  
38 approach to overcome this problem is to design and optimize nanocomposites for  
39 good electrical conductivity, since nanostructured TMD likely allows to increase Li-  
40 ion intercalation/de-intercalation due to the high surface area and shorter diffusion  
41 path for Li-ion transport.

42 Among these TMD compound, MoS<sub>2</sub>, as the most studied TMD for Li<sup>+</sup> storage  
43 today, has received considerable attention as a possible anode candidate for Li-ion  
44 cells. For instance, MoS<sub>2</sub>-C nanotube<sup>18</sup> and graphene/MoS<sub>2</sub> nano-flake<sup>19</sup> have been  
45 reported with significant improvement in cycle life and rate performance by taking  
46 advantages of the large electrolyte-electrode interface and reduced ion diffuse  
47 pathway. On the other hand, WS<sub>2</sub> with higher intrinsic electrical conductivity than  
48 MoS<sub>2</sub><sup>20</sup>, which is not studied in detail yet, could be a more suitable candidate as the  
49 anode material for Li-ion cells.

50 Herein, we propose a conceptually new approach to design and fabricate a novel  
51 three dimensional WS<sub>2</sub> nanotubes/graphene (WS<sub>2</sub>-NTs/GS) hybrid with unique  
52 sandwich-type architecture via a simple one-pot hydrothermal reaction. As shown in  
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3 Figure 1, WS<sub>2</sub>-NTs/GS hybrid was easily prepared by dispersion WS<sub>2</sub>-NTs into  
4 homogenous graphene oxide (GO) solution and subsequent hydrothermal reaction at  
5 controlled PH value for conversion of GO to GS<sup>21</sup>. GS could curl and cross-link to  
6 form 3D network during dehydration due to the combination of hydrophobic nature  
7 and  $\pi$ - $\pi$  interactions<sup>22</sup> while WS<sub>2</sub>-NT was embedded into the galleries of GS. More  
8 importantly, controlling PH of solution by adding appropriate amount of ammonia  
9 could further enhance those assemble in a compact manner.<sup>23</sup> The procedure is  
10 detailed in the experimental section of the Supporting Information. The unique hybrid  
11 could benefit from the synergistic effects of its each component. Specifically, the  
12 imbedded WS<sub>2</sub>-NTs could effectively prevent GS from complete restacking, thus  
13 affording pores and channel for ion diffusion. Meanwhile, the good electrical and  
14 mechanical properties of GS could not only enhance the anode conductivity, but also  
15 accommodate the volume change of anode during cycling. As a result, WS<sub>2</sub>-NTs/GS  
16 hybrid exhibited improved cycling stability and rate capability compared with that of  
17 WS<sub>2</sub>-NTs.  
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21 X-ray diffraction (XRD) patterns of WS<sub>2</sub>-NTs and WS<sub>2</sub>-NTs/GS are shown in  
22 Figure 2A. The analysis of WS<sub>2</sub>-NTs hybrid spectrum shows highly crystalline  
23 hexagonal structure (JCPDS No. 84-1398). For WS<sub>2</sub>-NTs/GS hybrid, all the  
24 diffraction peaks are consistent with that of WS<sub>2</sub>-NTs except for an additional small  
25 and broad peak appearing at  $2\theta$  of 24~26° (inset). Such peak originates from the (002)  
26 plane of GS, indicating a disordered stack of graphene sheet. These results suggest  
27 that the attachment of WS<sub>2</sub>-NTs on GS does not influence its crystallinity and no new  
28 phases are generated.  
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31 To further elucidate the effect of the deposition of WS<sub>2</sub>-NTs on the  
32 microstructure of graphene, Raman spectroscopy was carried out to characterize the  
33 carbon lattice in the WS<sub>2</sub>-NTs/GS hybrid (Figure 2B). The Raman spectrum of pure  
34 graphene (GS) showed a pattern of partially graphitized carbon. The peak at ~1350  
35 cm<sup>-1</sup> (D band) is assigned to defects and disorder in the graphene layer while peaks at  
36 ~1593 cm<sup>-1</sup> (G band) is related to the coplanar vibration of sp<sup>2</sup>-bonded carbon atoms  
37 in GS. Interestingly, the intensity of the D band in the WS<sub>2</sub>-NTs/GS hybrid is higher  
38 than that of the pure GS, indicating a more disordered stack of graphene layer in the  
39 hybrid. To some extents, it reveals that the WS<sub>2</sub>-NTs were embedded into the  
40 interlayer galleries of GS and prevent it from restacking. It should also be noted that  
41 the characteristic Raman scattering peaks for WS<sub>2</sub>-NTs are mainly observed below  
42 1000 cm<sup>-1</sup>, which is consistent with the crystalline nature of WS<sub>2</sub>-NTs in the hybrid.<sup>24</sup>  
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45 To determine the chemical composition of WS<sub>2</sub>-NTs/GS hybrid, X-ray  
46 photoelectron spectroscopy (XPS) analyses were conducted. According to the broad  
47 XPS scan spectrum in the region of 0-1100 eV (Figure 3A), four elements including  
48 W, S, C, O are detected and their atomic concentration is 7.55%-W, 13.54%-S,  
49 66.91%-C, 12.00%-O, respectively. The calculated atomic ratio of S to W is ~1.8,  
50 closed to the theoretically predicted value for WS<sub>2</sub>. The W<sub>4f</sub>XPS spectra of the hybrid  
51 exhibits peaks observed at 33.5 eV and 31.3 eV, corresponding to the W<sub>4f5/2</sub> and W<sub>4f7/2</sub>  
52 characteristic peaks of WS<sub>2</sub>-NTs (Figure 3B). As for the peak at 36.9 eV, we assign it  
53 to the W-O bond, indicating a low surface oxidation<sup>25</sup>. The presence of WS<sub>2</sub>-NTs can  
54 be further confirmed by the two distinct S<sub>2p</sub> peaks at 161.9 eV and 163.2 eV, which  
55 correspond to the S<sub>2p3/2</sub> and S<sub>2p1/2</sub> components of WS<sub>2</sub>-NTs (Figure 3C). Besides, C1s  
56 (284.5eV) and O1s (530eV) peaks are mainly attributed to the carbon and oxygen  
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3 atom in GS. The deconvolution of the C1s peaks is displayed in Figure 3D. Peaks  
4 centred at 286.1, 287.9 eV are attributed to the residual C-O and C=O groups,  
5 respectively. Compared with the case of GO<sup>26</sup>, the peak intensities of most oxygen  
6 containing groups decrease remarkably, indicating the restoration of sp<sup>2</sup> hybridized  
7 carbon network. Meanwhile, the O/C ratio was 1:5.6 for the hybrid, which was also  
8 consistent with the reduction degree of GO by dehydration mechanism<sup>27</sup>.  
9 Accordingly, we can conclude that the hybrid consists of GS and WS<sub>2</sub>-NTs, whose  
10 content are about 35.4 wt % and 64.6 wt%, respectively.  
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13 The morphology and structure of the WS<sub>2</sub>-NTs/GS hybrid were characterized by  
14 SEM and TEM. The SEM image (Figure 4A) of WS<sub>2</sub>-NTs exhibits a uniform one  
15 dimensional (1D) structure with diameter of around 60 nm and length of about 5  $\mu$ m.  
16 Like carbon nanotubes, such straight structure could easily form bundles, which  
17 provide extra lithium intercalation between inter-tubular sites. Figure 4B shows the  
18 electron diffraction pattern of two parallel WS<sub>2</sub>-NTs. The {10 $\bar{1}$ 0} spots appear to be  
19 arranged in a double-hexagonal pattern, corresponding to in plane diffractions in each  
20 tube<sup>28</sup>. The HR-TEM image (Figure 4C) of individual WS<sub>2</sub>-NTs clearly displays the  
21 hollow interior and multi-walls. Compared with straight WS<sub>2</sub>-NTs, WS<sub>2</sub>-NTs/GS  
22 hybrid display a three dimensional (3D) sandwich-like architecture that individual  
23 WS<sub>2</sub> nanotubes are homogeneously incorporated into the interlayer galleries of  
24 graphene sheets (Figure 4D). From the magnified SEM (inset), we can see that thin  
25 graphene could easily wrap around WS<sub>2</sub>-NTs due to its flexibility. The  
26 microstructure of WS<sub>2</sub>-NTs/GS hybrid was further analyzed by HR-TEM (Figure 4D  
27 and 4E). It is clear that WS<sub>2</sub>-NTs bundles were well dispersed in graphene matrices.  
28 According to the cross-sectional images, there are about five layer graphene sheets  
29 wrapping around the edges of WS<sub>2</sub>-NTs, which have a d-spacing of approximately  
30 0.62 nm twice than that of GS (~0.34 nm). Figure 4G shows the photograph of the  
31 black cylinder of the assembled WS<sub>2</sub>-NTs/GS hybrid, which can be cut and  
32 compressed into circular pellet with a diameter of 11 mm for direct use as anode in  
33 standard CR 2025 coin cell.  
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38 To investigate the anode performance of the WS<sub>2</sub>-NTs/GS hybrid,  
39 electrochemical characterization was conducted based on two-electrode coin-type  
40 cells (CR 2025) with Li metal as the counter-electrode. Figure 5A shows cyclic  
41 voltammograms (CV) of the WS<sub>2</sub>-NTs/GS hybrid anode for the initial three cycles  
42 between 0.01 and 3.00 V at a scan rate of 0.1 mV/s. In the first cycles, two small  
43 cathodic peaks at 1.6 V and 1.5 V are observed, which correspond to the lithium  
44 insertion to WS<sub>2</sub> to form Li<sub>x</sub>WS<sub>2</sub>. The following sharp overlap peak at 0.75 V could  
45 be attributed to the subsequent conversion reaction of Li with WS<sub>2</sub> and the formation  
46 of a solid electrolyte interlayer (SEI)<sup>29, 30</sup>. The starting cathodic peak at 0.5 V is  
47 related to the insertion of Li<sup>+</sup> into graphene, which is also electroactive for lithium  
48 storage<sup>31</sup>. During the anodic scan, three oxidation peaks at 1.0, 1.6, 2.2 V are  
49 observed, corresponding to the reverse extraction of Li<sup>+</sup> from graphene and Li<sub>x</sub>WS<sub>2</sub>  
50 host, respectively. From the second cycle onward, the cathodic peak at 0.75 V  
51 disappears while the original cathodic peaks at 1.6 V and 1.5 V shift to 2.1 V and 1.8  
52 V, indicating improved reversibility of lithiation and delithiation with cycling. In  
53 addition, no obvious changes are observed for the redox peaks, implying that the  
54 anode exhibits good electrochemical stability. For comparison, the CV of just WS<sub>2</sub>-  
55 NTs is shown in Figure S1. It can be seen that the electrochemical behavior of WS<sub>2</sub>-  
56 NTs is almost the same with that of WS<sub>2</sub>-NTs/GS hybrid except the absence of redox  
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3 related to the insertion/extraction of  $\text{Li}^+$  into/from GS.  
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5 Figure 5B shows the galvanostatic charge/discharge profiles of the  $\text{WS}_2$ -NTs/  
6 GS hybrid anode in the 1st, 2nd, 10th and 50th at a current density of 0.1 A/g. The  
7 hybrid anode delivers an initial capacity of 996.4 mAh/g and a corresponding charge  
8 capacity of 697.7 mAh/g with a first-cycle Coulombic efficiency of  $\sim 70.0\%$ . The  
9 large discharge capacity is attributed to the formation of SEI layer and the irreversible  
10 conversion reaction between Li and  $\text{WS}_2$ , which are consistent with the above CV  
11 analysis. After the initial capacity loss, a high capacity retention upon cycling are  
12 observed and the pattern of discharge and charge plateaus remains unchanged. A  
13 capacity of 500.2 mAh/g is achieved after 50 cycles. For comparison, pure  $\text{WS}_2$ -NTs  
14 were tested under the same current density as that for the  $\text{WS}_2$ -NTs/GS hybrid anode  
15 (Figure S2). The first discharge and charge capacities for  $\text{WS}_2$ -NTs anode are 768.5  
16 and 660.8 mAh/g, respectively. And serious capacity decay is observed with cycling,  
17 accompanied with the gradual disappearance of discharge plateaus at  $\sim 2.0$  V. After 50  
18 cycles, the capacity of  $\text{WS}_2$ -NTs anode dramatically decreases to 202.8 mAh/g.  
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21 Figure 5C reveals tenth-cycle discharge capacities of around 692.6, 574.8, 546.2,  
22 393.5 mAh/g at current density of 0.1, 0.2, 0.5, 1.0 A/g, respectively. Besides, the  
23 specific capacity of  $\text{WS}_2$ -NTs/GS hybrid anode could recover to 487.9 mAh/g when  
24 the current density is returned to 0.1 A/g. More importantly, the galvanostatic  
25 measurements for the  $\text{WS}_2$ -NTs/GS hybrid anode at increasing rate (inset) show the  
26 same pattern of discharge and charge plateaus, indicating good rate performance and  
27 rate tolerance. In contrast, pure  $\text{WS}_2$ -NTs anode exhibits poor capacities and rate  
28 capabilities. Even when the current density reduced, the capacity cannot recover its  
29 initial level. This difference supports that the 3D hierarchical structure could  
30 successfully enhance electronic/ionic transport within the anode, resulting improved  
31 electrochemical kinetics, which is further evidenced by the results of EIS (Figure 5D)  
32 that the charge-transfer resistance ( $R_{ct}$ ) values of  $\text{WS}_2$ -NTs/GS hybrid anode is found  
33 to be 37.5  $\Omega$ , which is lower than that of  $\text{WS}_2$ -NTs (52.6  $\Omega$ ).  
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37 Figure 5E compares the long cycle performance of  $\text{WS}_2$ -NTs and  $\text{WS}_2$ -NTs/GS  
38 hybrid anode at high current density of 1 A/g. In the case of  $\text{WS}_2$ -NTs/GS hybrid  
39 anode, the initial capacity is as high as 886.1 mAh/g and it still maintains a capacity  
40 of 318.6 mAh/g after 500 cycles. In contrast, much more capacity decay is observed  
41 for  $\text{WS}_2$ -NTs. The specific capacity dramatically decreases from 695.4 mAh/g to  
42 171.9 mAh/g after 500 cycles. The good cycle performance of  $\text{WS}_2$ -NTs/GS hybrid  
43 anode benefits from the following factors: (1) the incorporation of GS significantly  
44 enhances the conductivity of anode; (2) the hybrid 3D architecture consisting of  
45 layered  $\text{WS}_2$ -NTs and GS affords pores and large electrolyte/electrode interface, thus  
46 providing channels for Li-ion diffusion and reactive sites for Li-ion intercalation; (3)  
47 the flexible GS could effectively accommodate the volume change during cycling.  
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50 In summary, we have demonstrated the feasibility of  $\text{WS}_2$  nanotube/graphene  
51 sandwich-type architecture for good electrochemical performance. To the best of our  
52 knowledge, it is the first time for reporting such a conceptual design. Compared with  
53 pure  $\text{WS}_2$ -NTs, the hybrid anode exhibits much improved cycling stability and rate  
54 capability without additional polymeric binder, conductive additives or a separate  
55 metal current-collector. More importantly, the relatively high density of this hybrid is  
56 beneficial for high capacity per unit volume, which offsets its poor operating potential and  
57 thus makes it a promising anode material for light and high performance lithium-ion  
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batteries.

## ASSOCIATED CONTENT

### Supporting Information

Detail of experimental and additional figures depicting experiment results. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Author Contribution

||R.C. and T.Z. contributed equally to this work.

### Notes

The authors declare no competing financial interest.

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3 Figure Captions:

4 Figure 1. Schematic illustration of the fabrication of 3D hierarchically structured  
5 WS<sub>2</sub>-NT/GS hybrid.  
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7 Figure 2. (A) XRD patterns of WS<sub>2</sub>-NTs and WS<sub>2</sub>-NTs/GS hybrid; (B) Raman spectra  
8 of WS<sub>2</sub>-NTs/GS hybrid with those of WS<sub>2</sub>-NT and GS.  
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10 Figure 3. XPS spectra of WS<sub>2</sub>-NTs/GS hybrid: (A) broad scan spectrum; (B) W4f; (C)  
11 S2p; (D) C1s.

12 Figure 4. (A) and (D) SEM images of WS<sub>2</sub>-NTs and WS<sub>2</sub>-NTs/GS hybrid; (B) and (C)  
13 HR-TEM images of WS<sub>2</sub>-NTs; (E) and (F) HR-TEM images of WS<sub>2</sub>-NTs/GS hybrid;  
14 (G) photography of WS<sub>2</sub>-NTs/GS hybrid and schematic illustration of the fabrication  
15 WS<sub>2</sub>-NTs/GS anode in standard CR 2025 coin cell.  
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18 Figure 5. (A) Cyclic voltammetry of the WS<sub>2</sub>-NTs/GS hybrid anode over a voltage  
19 range of 0.01–3.00 V at a scanning rate of 0.1 mV/s; (B) Discharge/charge voltage  
20 profiles of WS<sub>2</sub>-NTs/GS hybrid anode at a current density of 100 mA/g; (C) rate  
21 capabilities of WS<sub>2</sub>-NTs/GS hybrid and WS<sub>2</sub>-NTs anode, inset: discharge/charge  
22 voltage profiles of WS<sub>2</sub>-NTs/GS hybrid at current density of 0.1, 0.2, 0.5, 1 A/g; (D)  
23 Nyquist plots of the WS<sub>2</sub>-NTs/GS hybrid and WS<sub>2</sub>-NTs anode at open potential before  
24 cycling; (E) Cycling stability of WS<sub>2</sub>-NTs/GS hybrid and WS<sub>2</sub>-NTs anode at 1 A /g  
25 for 500 cycles.  
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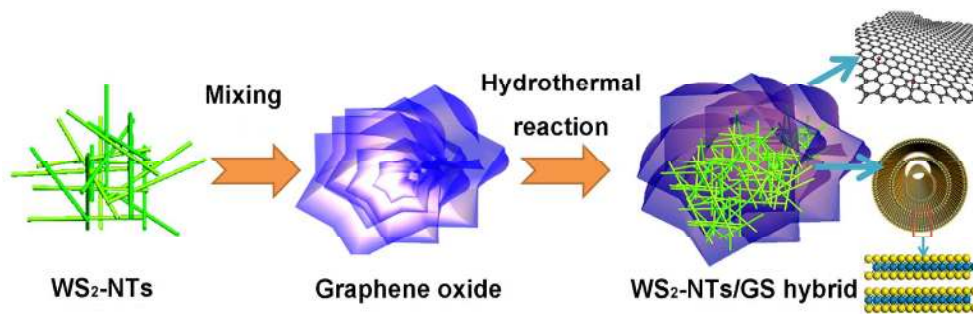


Figure 1. Schematic illustration of the fabrication of 3D hierarchically structured WS<sub>2</sub>-NT/GS hybrid.

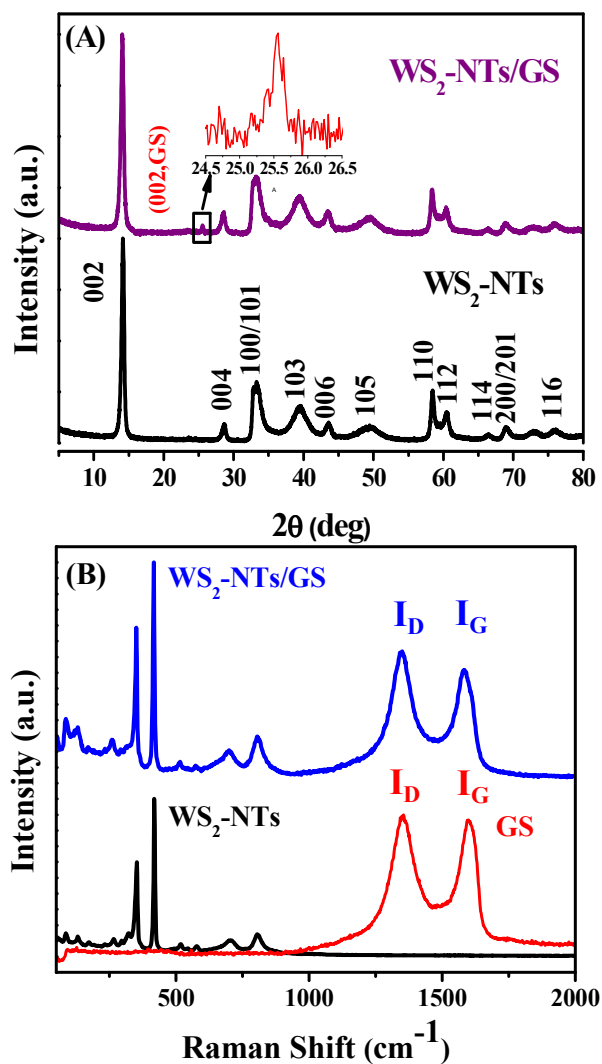


Figure 2. (A) XRD patterns of WS<sub>2</sub>-NTs and WS<sub>2</sub>-NTs/GS hybrid; (B) Raman spectra of WS<sub>2</sub>-NTs/GS hybrid with those of WS<sub>2</sub>-NT and GS.

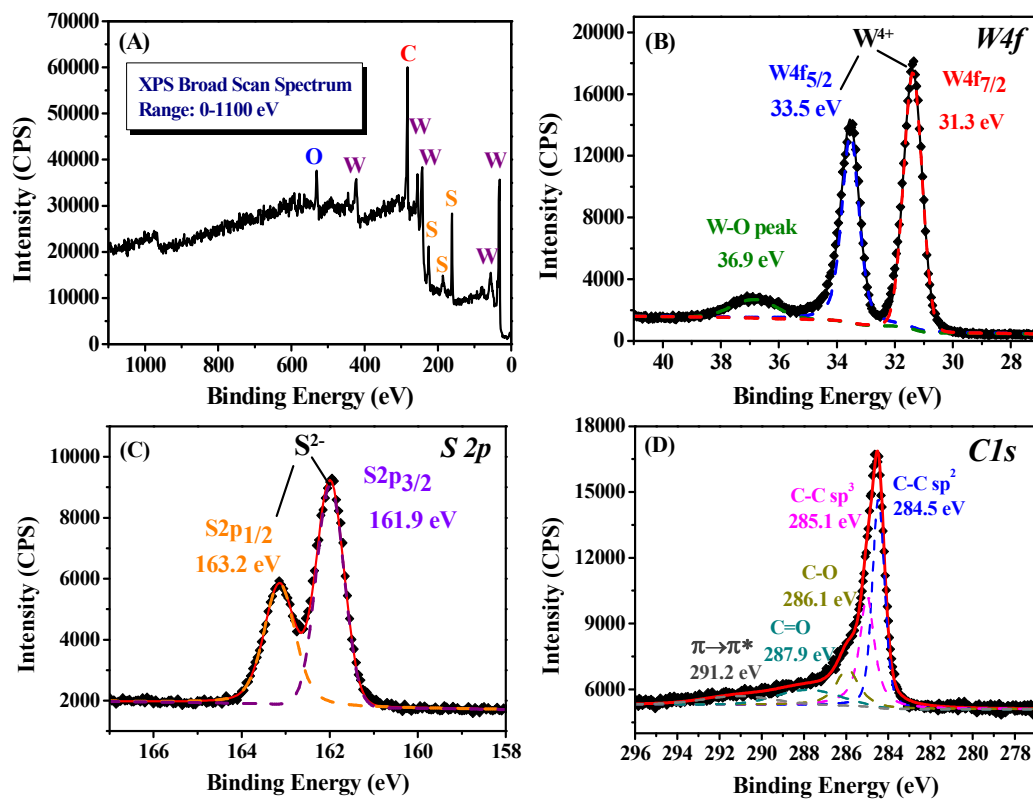
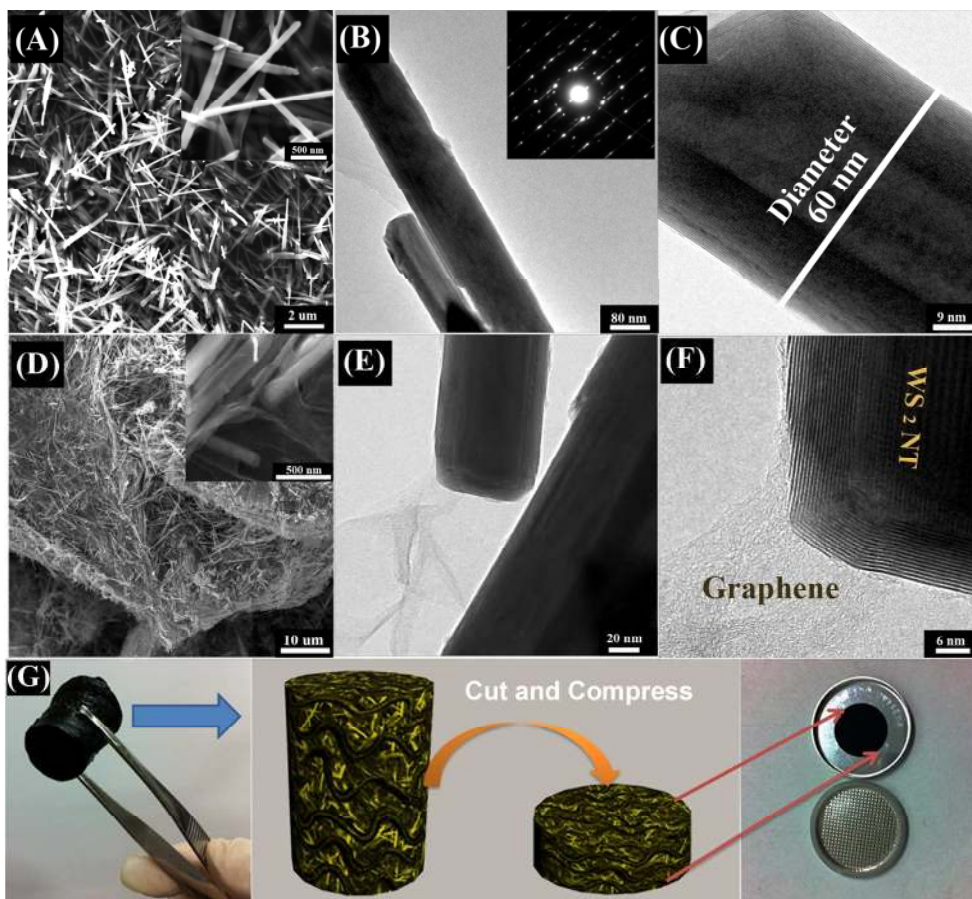


Figure 3. XPS spectra of WS<sub>2</sub>-NTs/GS hybrid: (A) broad scan spectrum; (B) W4f; (C) S2p; (D) C1s.



**Figure 4.** (A) and (D) SEM images of WS<sub>2</sub>-NTs and WS<sub>2</sub>-NTs/GS hybrid; (B) and (C) HR-TEM images of WS<sub>2</sub>-NTs; (E) and (F) HR-TEM images of WS<sub>2</sub>-NTs/GS hybrid; (G) photography of WS<sub>2</sub>-NTs/GS hybrid and schematic illustration of the fabrication WS<sub>2</sub>-NTs/GS anode in standard CR 2025 coin cell.

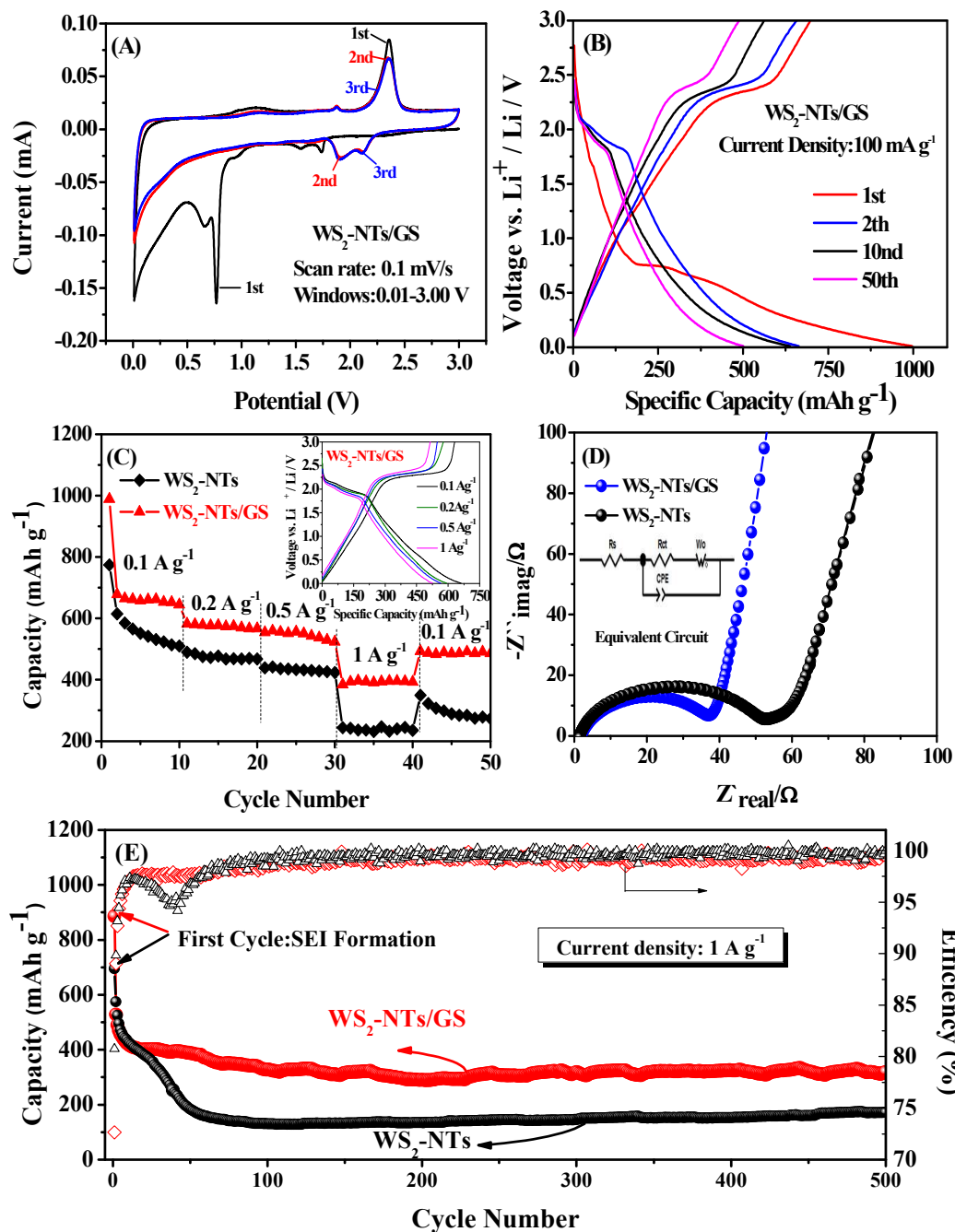
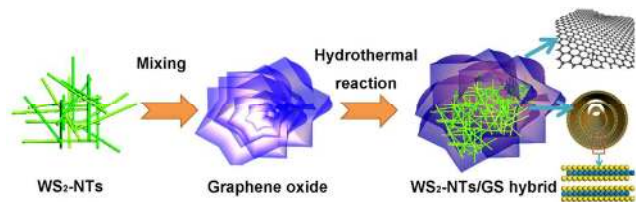


Figure 5 (A) Cyclic voltammety of the WS<sub>2</sub>-NTs/GS hybrid anode over a voltage range of 0.01–3.00 V at a scanning rate of 0.1 mV/s; (B) Discharge/charge voltage profiles of WS<sub>2</sub>-NTs/GS hybrid anode at a current density of 100 mA/g; (C) rate capabilities of WS<sub>2</sub>-NTs/GS hybrid and WS<sub>2</sub>-NTs anode, inset: discharge/charge voltage profiles of WS<sub>2</sub>-NTs/GS hybrid at current density of 0.1, 0.2, 0.5, 1 A/g; (D) Nyquist plots of the WS<sub>2</sub>-NTs/GS hybrid and WS<sub>2</sub>-NTs anode at open potential before cycling; (E) Cycling stability of WS<sub>2</sub>-NTs/GS hybrid and WS<sub>2</sub>-NTs anode at 1 A/g for 500 cycles.

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