Supporting Information

Design and Understanding of Core/Branch Structured VS$_2$ Nanosheets @ CNT as High-Performance Anode Material for Lithium-Ion Batteries

Xing Li†,1, Jiatian Fu†,1, Yuping Sun†,1, Mei Sun2, Shaobo Cheng3, Kaijian Chen1, Xigui Yang1, Qing Lou1, Tingting Xu1, Yuanyuan Shang1, Junmin Xu*,1, Qing Chen*,2, Chongxin Shan*,1

1 Key Laboratory of Material Physics, Ministry of Education, School of Physics and Engineering, Zhengzhou University, Zhengzhou, 450052, China
2 Key Laboratory for the Physics and Chemistry of Nanodevices and Department of Electronics, Peking University, Beijing 100871, China
3 Condensed Matter Physics and Materials Science, Brookhaven National Laboratory, Upton, NY 11973, USA

†These authors contributed equally to the work.

*Corresponding Author: cxshan@zzu.edu.cn; qingchen@pku.edu.cn; junminxu@zzu.edu.cn.

1 Estimation of the weight ratio of VS$_2$ in the composite

According to our SEM images in Figure 1(a-b), each single-walled CNT is surrounded by many thin VS$_2$ thin flakes, thus the weight ratio of CNT in the composite is quite small and can be neglected. To provide a reference for the weight ratio of VS$_2$ in the VS$_2$@CNT composite, we directly grown VS$_2$ nanosheet on the high purified single walled CNTs (HP-SWCNT, XFNANO Materials Tech Co., Ltd) with the same method. The corresponding thermogravimetric (TGA) curves for pure HP-SWCNT and VS$_2$@HP-SWCNT are shown in Figure S1. For pure HP-SWCNT, the weight loss between 500-600 is attributed to the decomposition of HP-SWCNT and the residual weight percent is $W_{HP-SWCNT} = 9.4\%$. For the VS$_2$@HP-SWCNT composite, a continuous weight loss observed below
160°C is due to desorption of water molecules on and within the surface layers. The weight loss caused
by the oxidation of VS₂ occurred in the temperature range of 160-500°C. The weight loss between
500-800 is attributed to the decomposition of HP-SWCNTs and the oxidation of V⁴⁺ to relatively
greater and stable V⁵⁺.¹ The residual weight percent in VS₂@HP-SWCNT is \( W_{\text{VS}_2@\text{HP-SWCNT}} = 75.8\% \). Therefore, the weight ratio of VS₂ (\( X_{\text{VS}_2} \)) and HP-SWCNT (\( 1 - X_{\text{VS}_2} \)) can be calculated based on the
following equation:²,³

\[
\frac{M_{\text{v}_2\text{o}_5}}{2M_{\text{vs}_2}} \times X_{\text{VS}_2} + W_{\text{HP-SWCNT}}(1 - X_{\text{VS}_2}) = W_{\text{VS}_2@\text{HP-SWCNT}}
\]

\( M_{\text{v}_2\text{o}_5} \) and \( M_{\text{vs}_2} \) are the molecular weight of V₂O₅ and VS₂. The weight ratio of VS₂ in the composite
is estimated to be 95.2%.

![Figure S1. TGA data of (b) pure HP-SWCNT and (c) VS₂@HP-SWCNT.](image)

2. CV curves of the CNT film

To distinguish the contributions of CNT film and VS₂ NS to the acquired CV profiles in Figure
2, a LIB with grown CNT film electrode is also fabricated. Figure S2 (a) shows the comparison of
the CV curves of CNT film electrode and VS₂ NS@CNT electrode at scan rate of 0.1 mV/s. Two
peaks at 1V and 0.8V with lower intensity are observed during the initial cathodic sweep of the CNT
film electrode, while no obvious peaks are observed during the following anodic sweep. Figure S1
(b) shows the CV curves of the CNT film electrode in the first three cycles. It should be noted that no
obvious reduction/oxidation peaks are observed in the 2nd and 3rd cycles. Since the CNT films in these
two electrode materials are synthesized with the same, the two pairs reduction/oxidation peaks located
at 0.7 V/1.7 V and 2.0 V/2.3 V in the VS\textsubscript{2} NS@CNT electrode are resulting from VS\textsubscript{2} NS (Figure 2(a)).

**Figure S2.** (a) Comparison of the CV profiles of CNT film electrode and VS\textsubscript{2} NS@CNT electrode. (b) First three cycles of the CV profiles of the CNT film electrode.

3. **Morphology of VS\textsubscript{2} after the 1\textsuperscript{st} cycling process**

As shown in Figure S3, the morphology of VS\textsubscript{2} flakes after the 1\textsuperscript{st} cycling process were broken into several pieces by cracks and more active sites are exposed for the following cycling processes.

**Figure S3.** SEM images showing the morphology of VS\textsubscript{2} flakes after the 1\textsuperscript{st} cycling process.

4. **Morphology Evolution of VS\textsubscript{2} NS@CNT**

The morphology evolution of VS\textsubscript{2} NS is in-situ investigated by the SEM. Figure S4(a) shows the experimental setup, where the VS\textsubscript{2}@CNT, LiO\textsubscript{2} and Li metal act as anode, electrolyte and cathode, respectively. The lithiation process is initiated by applying a -2V voltage on the VS\textsubscript{2}@CNT and the current is limited to 100nA. As indicated by the red arrows, volume expansions are clearly
observed in the interior region of the VS$_2$ NS (Figure S4 (b) and (c)).

**Figure S4.** (a) Experimental setup for the in-situ SEM investigation on the discharging/charging processes. SEM images of the red framed region in (a) after (b) 0s and (c) 2362s lithiation process.

5. **Microstructural analysis of the lithiated/delithiated VS$_2$ NS**

The FFT patterns of the triangular shaped NS and the crystalline matrix in Figure S5(a) are shown respectively in Figure S5(b) and Figure S5(c). According to our analysis, the triangular shaped NS and the crystalline matrix is indexed to Li$_2$S.

**Figure S5.** Microstructural analysis of the lithiated VS$_2$ NS. (a) HRTEM image of the lithiated VS$_2$. The FFT patterns of the region marked by the blue frame (b) and red frame (c) in (a).

Figure S6 shows the enlarged view of the VS$_2$ nanosheet (Figure 6) before and after delithiation, from which we can see that the crystalline Li$_2$S crystal gradually disappear and the particle size of V is decreased during this process.
Figure S6. Particle size comparison of V before (a) and after (b) delithiation process.

References: