High-performance Na₂Ti₂O₅ Nanowire Arrays Coated with VS₂ Nanosheets for Sodium-ion Storage

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Abstract

Na₂Ti₂O₅ (NTO) nanowire arrays coated with VS₂ nanosheets (NTO-VS₂) have been directly prepared on a current collector as a 3D anode for Na-ion batteries. Compared to graphite, the larger interlayer spacing of two dimensional VS₂ can offer facile intercalation of lithium and/or sodium ions. Aside from its natural metallic behavior, VS₂ also possesses a high theoretical capacity. The composite NTO-VS₂ nanowire arrays as an additive free 3D anode shows superior electrochemical performance compared to NTO. After 50 (C/10) and 100 (1C) cycles, the charge capacities of NTO-VS₂ are maintained, respectively, at 298 and 203 mA h g⁻¹, which are much higher than the values of 157 and 93 mA h g⁻¹ observed for the same cycled Na₂Ti₂O₅ electrode. The higher capacity, improved rate capability, and good stability of the composite NTO-VS₂ nanowire arrays are due to the structural stability of the Na₂Ti₂O₅ nanowire arrays and the higher capacity and conductivity of the two-dimensional VS₂ nanosheets.

Keywords: Sodium-ion batteries; sodium titanate; VS₂; nanosheets; nanowire array

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1. Introduction

As an energy storage device, Li-ion batteries (LIBs) have become indispensable in our modern life [1-4]. However, LIBs are encountering an inevitable challenge with respect to large-scale energy storage due to the restricted lithium resource and high cost [5, 6]. In this regard, Na-ion batteries (NIBs) are gaining increased attention for next-generation large-scale energy storage systems because, in contrast to lithium, sodium resources are practically inexhaustible and evenly distributed around the world. In addition, the standard oxidation potential of Na^+/Na (2.71 V *vs* SHE) is only slightly lower than that of Li^+/Li (3.05 V *vs* SHE), which makes it the most advantageous element for battery applications after lithium-ion batteries [7-10].

A variety of $\text{H/Li/Na}_x\text{TiO}_{2+x/2}$ compounds have been extensively studied as anode materials in energy-storage applications due to their low volume expansion and stable cycling [11-16]; however, there are only a few recent reports that describe their properties as Na^+ ion hosts. Among them, Meng et. al, and Palacín et. al. demonstrated that the layered oxide $\text{Na}_2\text{Ti}_3\text{O}_7$ could reversibly exchange Na-ions with the lowest voltage ever reported for an oxide insertion electrode [17-20]. The ultra-low voltage, long cycling performance, and intrinsic high reversibility of this material make it an attractive anode candidate for NIBs. However, all reported sodium titanates have spherical nanoparticles or random nanawires/nanotubes, which could potentially limit both electron and ion transport. Furthermore, recently reported sodium titanates in NIBs show relatively low capacities of $< 200 \text{ mA h g}^{-1}$ and poor rate capabilities due to their low electronic conductivity [11, 21, 22]. A possible

approach to enhance both their capacity and rate capability is to find suitable coating materials with high conductivity and capacity. As a result, well oriented sodium titanate grown directly onto a conductive substrate and coated with a high capacity and conductivity material could be highly desired for NIBs.

In addition to graphene, which has been widely studied in energy-storage devices as a representative of high-conductivity two-dimensional (2D) materials, other 2D inorganic materials – such as the 2D transition-metal disulfides (TMDs) VS_2 , WS_2 , and MoS_2 – have attracted extensive scientific attention for different applications. Similar to graphite, the atomic structure of this type of materials is characterized with a strong in-plane and a weak out-of-plane bonding [23-26]. Moreover, these 2D TMDs have a larger interlayer spacing than graphite, which can offer the intercalation of lithium or/and sodium ions [27-29]. Very recently, synthesis of vanadium disulfide (VS_2) with a few layers of nanosheets has been achieved experimentally and found to possess superior metallic quality than MoS_2 . They also demonstrate exceptionally high capacitance [28]. Aside from its intrinsically metallic behavior, VS_2 monolayer also has a higher theoretical capacity of 466 mA h g^{-1} for lithium storage and a lower or similar lithium diffusion barrier compared to MoS_2 and graphite, which makes it a highly attractive anode candidate for energy storage [29]. VS_2 was first reported as a cathode with the Na system in the 1980s, and it intercalated up to one Na per VS_2 during first discharge as a cathode [30, 31].

In this work, $\text{Na}_2\text{Ti}_2\text{O}_5$ (NTO) nanowire arrays coated with VS_2 nanosheets (NTO- VS_2) were successfully prepared on flexible Ti foil as an additive-free 3D

anode for NIBs. The as-prepared, well-ordered arrays grown directly onto a current collecting substrate is particularly interesting owing to their vectorial ion and electron transport properties.

2. Experimental

Electrode Preparation: NTO-VS₂ composite nanowire array electrodes were prepared via a two-step hydrothermal method. First, Na₂Ti₂O₅·H₂O nanowire arrays on Ti foil (30 μm thick) were prepared as reported previously [3, 13, 14]. Then the prepared Na₂Ti₂O₅·H₂O nanowire arrays on Ti foil were heated at 300 °C for 3h to obtain the pristine anode Na₂Ti₂O₅ (NTO). The pristine NTO was then put into 50 mL of water containing 0.4 g NH₄VO₃, 0.8 g thioacetamide (TAA), and 0.1 M NaOH for a second hydrothermal reaction at 160 °C for 20 h. Afterwards, the formed NTO-VS₂ composite nanowire arrays were washed with deionized water and ethanol and thoroughly dried in air. The weight percent of VS₂ in the NTO-VS₂ electrodes is around 25 wt. %.

Materials Characterization: The phase purity and crystal structure of the obtained materials were studied with X-ray diffraction (XRD, Miniflex 600) with Cu Kα radiation from 10 to 80° 2-theta at a scan rate of 0.02° s⁻¹. BET (AutoSorb iQ2, Quantachrome Instruments), field emission scanning electron microscopy (FE-SEM, Quanta 650), scanning transmission electron microscopy (STEM, S5500), and transmission electron microscopy (TEM, JEOL 2010F) were used to examine the surface area, morphology, crystalline structure, and elemental distribution of the

samples. EDS was used to investigate the elements of Ti, Na, V, and S spectra in NTO and NTO-VS₂ nanowires.

Evaluation of Electrochemical Behavior: The electrochemical characterizations were performed with 2032-type coin cells with two-electrodes, assembled in an Ar-filled dry glove box with the NTO-based nanowire arrays (NTO and NTO-VS₂)/Ti-foil as the working electrode and Na metal as the counter electrode. 1M NaClO₄ in ethylene carbonate (EC)/propylene carbonate (PC) (1/1 by volume) with 3% fluorinated ethylene carbonate (FEC) was used as an electrolyte and glass fiber was used as the separator. The discharge-charge cycling was performed between 0.01 and 2.5 V at room temperature at different C-rates of C/10 to 20 C with an Arbin Instruments cycler (1 C = 200 mA g⁻¹). Electrochemical impedance spectroscopy (EIS) was carried out in the frequency range of 1 MHz to 100 mHz on an electrochemical workstation with an impedance analyzer (SI 1260/SI 1287, Solartron), with an amplitude of the alternating voltage of 5 mV. Cyclic voltammetry (CV) testing was performed on a VoltaLab PGZ 402 (Radiometer Analytical) electrochemical workstation with a scan rate of 0.1 mV s⁻¹. The loading of active materials is around 1–1.5 mg/cm²

3. Results and discussion

To determine the phase structure of the nanowire array products on titanium foils, X-ray diffraction (XRD) measurements were conducted with the samples removed from the Ti substrate as well as with nanowire arrays on Ti substrate (**Figure 1** and Figure S1). Compared to the JCPDS (No. 47-0124) card, the significant enhancement

of the (020) diffraction peak in the $\text{Na}_2\text{Ti}_2\text{O}_5$ (NTO) pattern indicates that the growth of the $\text{Na}_2\text{Ti}_2\text{O}_5$ nanowires is along the [010] direction [32]. Following the hydrothermal step involving the reaction with NH_4VO_3 and thioacetamide for VS_2 nanosheet coating onto NTO nanowires (NTO- VS_2), the diffraction peaks appearing at 15.5, 35.3, 45.1, 54.5 and 65.7 degrees 2-theta due to (001), (011), (003), (110), and (004) diffraction planes could all be indexed to the VS_2 phase with $a = b = 3.22$ and $c = 5.75$ Å (JCPDS card no. 89-1640) [28].

The SEM images of the ordered nanowire array samples are shown in **Figure 2a** and b. The length of both the as-prepared NTO and NTO- VS_2 nanowires determined from SEM are 12 ± 0.5 μm. The different steps of layer formation can also be demonstrated by the changing color of the nanowire films (inset), which changes from white (NTO) to black (NTO- VS_2). The rough surface of the NTO- VS_2 nanowire after further reaction processing with NH_4VO_3 and thioacetamide could be further verified by the scan transmission electron microscopy (STEM) images shown in Figure 2c and 2d. The mean diameter of the NTO and NTO- VS_2 nanowire determined from STEM images are, respectively, 85 ± 5 nm and 100 ± 5 nm. In addition, the Brunauer-Emmett-Teller (BET) surface area of NTO- VS_2 nanowires increases from $28.5 \text{ m}^2 \text{ g}^{-1}$ for NTO nanowires to $43.6 \text{ m}^2 \text{ g}^{-1}$ (Figure S2). The energy dispersive X-ray spectroscopy (EDS) mapping images of a single hybrid NTO- VS_2 nanowire are shown in Figure 2e-h. The distribution of V and S elements clearly encase the location of Ti and Na, indicating that VS_2 is successfully formed on the surface of the

NTO nanowires during the following hydrothermal step. For a comparison, the EDS mapping images of a single NTO nanowire are shown Figure S3.

Further morphological and structural characterizations of the prepared nanowire materials were performed with transmission electron microscopy (TEM) as seen in **Figure 3**. Figure 3a shows the typical pristine NTO nanowire with a diameter of around 85 nm. It is apparent that the prepared nanowire sample possesses a single-crystalline, one-dimensional structure oriented in the [100] direction according to the SAED (Figure S4). This structure can significantly increase the capabilities of electron and Na-ion diffusion in the electrodes. The measured inter-planar spacing of 0.36 and 0.80 nm in Figure 3b are in excellent agreement with the d-spacing of the (110) and (200) planes of layered $\text{Na}_2\text{Ti}_2\text{O}_5$ [33]. Compared with pristine NTO nanowires, the composite NTO- VS_2 nanowires after a second step of hydrothermal reaction have a rougher surface due to the VS_2 nano-sheets coating process, with a diameter of around 100 nm (Figure 3c). The co-existing SAED pattern of the composite sample shown in Figure 3d also confirm the formation of dual phase NTO- VS_2 nanowire, where the observed (101) plane and (310) plane are, respectively, mapped to VS_2 and layered $\text{Na}_2\text{Ti}_2\text{O}_5$. The lower magnification of NTO- VS_2 nanowire shown in Figure 3e indicates that several layers are uniformly coated onto the NTO nanowire. Furthermore, a well-crystallized structure with lattice fringes of about 0.36 and 0.27 nm can be clearly seen in Figure 3f, which correspond to the (101) and (100) inter-planar spacing of VS_2 and layered $\text{Na}_2\text{Ti}_2\text{O}_5$, respectively.

The electrochemical performances of the as-prepared NTO and NTO-VS₂ nanowire array anodes were evaluated in half-cells utilizing metallic sodium film as the counter electrode. To understand the various plateaus for the NTO based electrodes, cyclic voltammetry (CV) studies were applied to both the NTO and NTO-VS₂ electrodes. **Figure 4a-b** shows the first three CV curves of both nanowire electrodes at a scan rate of 0.1 mV s⁻¹. The CV profiles of the NTO nanowire electrode (Figure 4a) show two pairs of cathodic/anodic peaks at around 0.63 / 0.31 V and 1.08 / 0.96 V that are contributed by the layered Na₂Ti₂O₅. The plateau at around 0.7 V is consistent with the irreversible decomposition of the electrolyte and formation of a solid film at the surface of the electrode, resulting in a large polarization during the first discharge [19, 34]. Referring to Figure 4b, another pair of cathodic/anodic peaks at 1.53 / 1.25 V can be found in the CV curve, which could be attributed to the Na-intercalation/de-intercalation processes of VS₂. The cathodic/anodic peaks at 1.08 / 0.96 V contributed by the layered sodium titanium oxides may overlap with the Na-intercalation/deintercalation processes of VS₂, limiting their visibility. Consequently, we propose a possible sodium-storage mechanism in the NTO-VS₂ composite electrode at the initial discharge as follows [19, 30, 35]:

The initial three discharge-charge cycle profiles for the prepared NTO and NTO-VS₂ nanowire electrodes with a current rate of C/10 (1 C = 200 mA h g⁻¹) are shown in Figure 4c and 4d, respectively. The initial discharge capacities were 426 mA

h g⁻¹ for NTO and 575 mA h g⁻¹ for the NTO-VS₂ composite electrodes. The increased initial discharge capacity of NTO-VS₂ is due to the capacity contribution of the coated higher capacity VS₂ nanosheets and the larger surface area of VS₂ resulting in more irreversible capacity. A large irreversible loss in the 1st cycle can be observed in both nanowire electrodes, though it is particularly large in the composite NTO-VS₂ electrode. This loss is mainly due to (i) irreversible intercalation of Na⁺ ions into Na₂Ti₂O₅, (ii) irreversible conversion of VS₂ by Na⁺ ions, and (iii) formation of a solid-electrolyte interface (SEI) layer on VS₂ by electrolyte decomposition [19, 34, 36]. It is also noted that after the first three cycles, the NTO-VS₂ electrode shows good capacity retention, indicating that this VS₂ modification method is an effective technique to simultaneously improve the specific capacity and reversibility of the NTO nanowire electrodes. The superior cyclability of the composite NTO-VS₂ electrode is further demonstrated by the long cycling shown in Figure 5.

Figure 5a and **5b** compares the cycling performance of these two electrodes at, respectively, C/10 and 1C rates in the voltage range of 0.01 – 2.5 V. As shown in Figure 5a and b, composite NTO-VS₂ electrode display a much higher capacity and good cycling performance with a high coulombic efficiency of around 99.8% after 100 cycles (Figure S5a) compared to that of the pristine NTO electrode. After 50 (C/10) and 100 (1C) cycles, the respective charge capacity of NTO-VS₂ is maintained at 298 and 203 mA h g⁻¹, which is much higher than the values of 157 and 93 mA h g⁻¹ observed for similarly cycled NTO. For further comparison, pure VS₂ was also prepared and applied in NIBs (Figure S6 and S7). The morphology of pure VS₂

powder consists of aggregated nanoparticles instead of the nanosheet coating on NTO nanowires. Compared to the NTO and NTO-VS₂ electrodes, the VS₂ electrode shows much lower capacity retention with only 3.6% of the reversible capacity at C/10 rate and 3.8% at 1C rate after 50 cycles, indicating that the Na₂Ti₂O₅ nanowire structure and uniform VS₂ nanosheet coating play a vital role in cycling stability.

To examine the effect of VS₂ coating on rate capability, both the nanowire electrodes were assessed by discharge/charge at different C rates ranging from C/10 to 20C, and then back to C/10 rate as shown in Figure 5c. Due to the presence of VS₂ in the NTO-VS₂ electrode, the composite nanowire electrode exhibits higher capacity, with discharge capacities of 292, 233, 210, 161, 124, 95 and 75 mA h g⁻¹, respectively, at C/10, C/2, 1C, 2C, 5C, 10C and 20C rates. Meanwhile, the pristine NTO nanowire electrode maintains discharge capacities of only 180, 132, 166, 101, 76, 52 and 27 mA h g⁻¹, respectively, at C/10, C/2, 1C, 2C, 5C, 10C and 20C rates. After measuring at high rates, the NTO-VS₂ composite anode is still able to provide a capacity of 282 mA h g⁻¹ when the current rate was set back to C/10, corresponding to an initial capacity retention of 96.5%. Besides the unique 1D structure, in which each nanowire is anchored to the current-collector that can provide fast Na⁺ and electron transport throughout the electrode, the superior electrochemical performance of the composite electrode may result from the superior transport and physical advantages of the 3D composite nanowire array structure such as (i) higher theoretical capacity of the VS₂ active material compared to Na₂Ti₂O₅ and (ii) high electronic conductivity of the VS₂ nanosheets coated onto the NTO nanowires in the NTO-VS₂ nanowires. The Nyquist

plots of NTO and NTO-VS₂ electrodes depict a semicircle at high-medium frequency and an inclined line at low frequency, which correspond, respectively, to film resistance/charge transfer and diffusion resistance (Figure 5d). The smaller semicircle (over all electrode resistance including film and charge-transfer resistance) of the NTO-VS₂ electrode suggests that after the VS₂ modification, the composite nanowire arrays have not only a lower film resistance but also a lower charge-transfer resistance and undergo a fast faradic reaction, which support the enhanced high-rate performance of the NTO-VS₂ anode compared to the pristine NTO electrode (Figure 5c).

The morphological evolutions of NTO-based nanowire electrodes after 100 discharge/charge cycles are shown in **Figure 6**, Figure S8, and Figure S9. Compared with the NTO-based nanowire before cycling (Figure 3), only a small volume expansion was observed in both cycled nanowires (diameter changed), but both electrodes maintain the nanowire morphology and their array structure. Furthermore, the distribution of V and S elements by EDS mapping clearly encase the location of Ti and Na, indicating that VS₂ is still located on the surface of the NTO nanowires even after 100 cycles. This low volume expansion characteristic and structural maintenance are important for its stable cycling.

4. Conclusions

In summary, Na₂Ti₂O₅ nanowire arrays (NTO) and VS₂ modified NTO nanowire arrays (NTO-VS₂) have been prepared and applied as an additive-free 3D anode in NIBs. The unique NTO-VS₂ composite nanowire array electrode obtained effectively

couples the electrochemical functionality of the individual components including the excellent stability and low voltage of NTO and the high capacity and rate capability (high electronic/ionic) of VS_2 . Notably, after modification with VS_2 , these unique 3D nanowire array anodes demonstrate superior electrochemical performance including high charge/discharge capacities, improved capability, and exemplary cycling performance. Further studies on VS_2 and/or VS_2 composite materials may accelerate the development of 2D transition-metal sulfides in lithium and sodium energy storage, considering its outstanding performance.

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References

- [1] J. M. Tarascon, M. Armand, *Nature*, 414 (2001) 359-367.
- [2] P. G. Bruce, B. Scrosati, J.M. Tarascon, *Angew Chem. Int. Ed.*, 47 (2008) 2930-2946.
- [3] J. Y. Liao, D. Higgins, G. Lui, V. Chabot, X. C. Xiao, Z. W. Chen, *Nano Lett.*, 13 (2013) 5467-5473.
- [4] J. Y. Liao, A. Manthiram, *Adv. Energy Mater.*, 4 (2014) 1-8.
- [5] H. L. Pan, Y.S. Hu, L. Q. Chen, *Energy Environ. Sci.*, 6 (2013) 2338-2360.
- [6] S. W. Kim, D. H. Seo, X. H. Ma, G. Ceder, K. Kang, *Adv. Energy Mater.*, 2 (2012) 710-721.
- [7] I. T. Kim, E. Allcorn, A. Manthiram, *Phys. Chem. Chem. Phys.*, 16 (2014) 12884-12889.
- [8] I. T. Kim, E. Allcorn, A. Manthiram, *Energy Technol-Ger.*, 1 (2013) 319-326.
- [9] S. Li, Y. F. Dong, L. Xu, X. Xu, L. He, L.Q. Mai, *Adv. Mater.*, 26 (2014) 3545-3553.
- [10] Y. Park, D. S. Shin, S.H. Woo, N.S. Choi, K.H. Shin, S.M. Oh, K.T. Lee, S.Y. Hong, *Adv. Mater.*, 24 (2012) 3562-3567.
- [11] H. L. Pan, X. Lu, X. Q. Yu, Y. S. Hu, H. Li, X. Q. Yang, L. Q. Chen, *Adv. Energy Mater.*, 3 (2013) 1186-1194.
- [12] L. F. Shen, E. Uchaker, X. G. Zhang, G. Z. Cao, *Adv. Mater.*, 24 (2012) 6502-6506.

- [13] J. Y. Liao, V. Chabot, M. Gu, C. M. Wang, X. C. Xiao, Z. W. Chen, *Nano Energy*, 9 (2014) 383-391.
- [14] J. Y. Liao, X. C. Xiao, D. Higgins, G. Lui, Z.W. Chen, *Acs Appl. Mater. Interfaces*, 6 (2014) 568-574.
- [15] J. Y. Liao, X. C. Xiao, D. Higgins, D.G . Lee, F. Hassan, Z.W. Chen, *Electrochim. Acta*, 108 (2013) 104-111.
- [16] M. Shirpour, J. Cabana, M. Doeff, *Energy Environ Sci.*, 6 (2013) 2538-2547.
- [17] Y. Sun, L. Zhao, H.L. Pan, X. Lu, L. Gu, Y.S. Hu, H. Li, M. Armand, Y. Ikuhara, L.Q. Chen, X.J. Huang, *Nat. Commun.*, 4 (2013) 1870-1879.
- [18] P. J. P. Naeyaert, M. Avdeev, N. Sharma, H. Ben Yahia, C.D. Ling, *Chem. Mater.*, 26 (2014) 7067-7072.
- [19] P. Senguttuvan, G. Rousse, V. Seznec, J.M. Tarascon, M.R. Palacin, *Chem. Mater.*, 23 (2011) 4109-4111.
- [20] J. Xu, C. Z. Ma, M. Balasubramanian, Y. S. Meng, *Chem. Commun.*, 50 (2014) 12564-12567.
- [21] X. N. Luan, Y. Wang, *J. Mater. Sci. Technol.*, 30 (2014) 839-846.
- [22] K. Q. Wu, X. T. Lin, L. Y. Shao, M. Shui, N. B. Long, Y. L. Ren, J. Shu, *J. Power Sources*, 259 (2014) 177-182.
- [23] J. N. Coleman, M. Lotya, A. O'Neill, S.D. Bergin, P.J. King, U. Khan, K. Young, A. Gaucher, S. De, R. J. Smith, I. V. Shvets, S.K. Arora, G. Stanton, H. Y. Kim, K. Lee, G. T. Kim, G. S. Duesberg, T. Hallam, J. J. Boland, J. J. Wang, J. F. Donegan, J. C. Grunlan, G. Moriarty, A. Shmeliov, R. J. Nicholls,

- J. M. Perkins, E. M. Grievson, K. Theuwissen, D. W. McComb, P. D. Nellist, V. Nicolosi, *Science*, 331 (2011) 568-571.
- [24] B. Radisavljevic, A. Radenovic, J. Brivio, V. Giacometti, A. Kis, *Nat. Nanotechnol.*, 6 (2011) 147-150.
- [25] Y. J. Gong, J. H. Lin, X. L. Wang, G. Shi, S. D. Lei, Z. Lin, X. L. Zou, G. L. Ye, R. Vajtai, B. I. Yakobson, H. Terrones, M. Terrones, B. K. Tay, J. Lou, S. T. Pantelides, Z. Liu, W. Zhou, P. M. Ajayan, *Nat. Mater.*, 13 (2014) 1135-1142.
- [26] D. Q. Gao, Q. X. Xue, X. Z. Mao, W. X. Wang, Q. Xu, D.S. Xue, *J. Mater. Chem. C*, 1 (2013) 5909-5916.
- [27] H. S. S. R. Matte, A. Gomathi, A. K. Manna, D. J. Late, R. Datta, S. K. Pati, C. N. R. Rao, *Angew Chem. Int. Ed.*, 49 (2010) 4059-4062.
- [28] J. Feng, X. Sun, C. Z. Wu, L. L. Peng, C. W. Lin, S. L. Hu, J. L. Yang, Y. Xie, *J. Am. Chem. Soc.*, 133 (2011) 17832-17838.
- [29] Y. Jing, Z. Zhou, C. R. Cabrera, Z. F. Chen, *J. Phys. Chem. C*, 117 (2013) 25409-25413.
- [30] K. M. Abraham, L. Pitts and R. Schiff *J. Electrochem. Soc.*, 127(1980) 2545-2550.
- [31] J. Rouxel, *J. Solid State Chem.*, 17, (1976) 223-229.
- [32] J. Y. Liao, B. X. Lei, H. Y. Chen, D. B. Kuang, C. Y. Su, *Energy Environ. Sci.*, 5 (2012) 5750-5757.
- [33] B. Liu, J. E. Boercker, E. S. Aydil, *Nanotechnology*, 19 (2008) 505604.

- [34] M. Shirpour, J. Cabanaa, M. Doeffa, *Energy Environ. Sci.*, 6 (2013) 2538-2547.
- [35] X. Xu, S. Jeong, C. S. Rout, P. Oh, M. Ko, H. Kim, M. G. Kim, R. Cao, H. S. Shin, J. Cho, *J. Mater. Chem. A*, 2 (2014) 10847-10853.
- [36] L. David, R. Bhandavat, G. Singh, *A CS Nano*, 8 (2014) 1759-1770.

Figure Captions

Figure 1. X-ray diffraction patterns of pristine $\text{Na}_2\text{Ti}_2\text{O}_5$ (NTO) nanowire powder and NTO- VS_2 composite nanowire powder removed from the Ti substrate.

Figure 2. SEM images of (a, b) NTO and (c, d) NTO- VS_2 nanowires, and (e-h) corresponding EDS mapping images of single NTO- VS_2 nanowire.

Figure 3. TEM, HRTEM images, and SAED patterns of (a, b) NTO and (c-f) NTO- VS_2 nanowires.

Figure 4. CV plots (First three cycles) of (a) NTO and (b) NTO- VS_2 electrodes. First three discharge-charge curves of (c) NTO and (d) NTO- VS_2 electrodes.

Figure 5. Cycling performance comparison of NTO and NTO- VS_2 electrodes at different C-rates: (a) C/10 and (b) 1C rates; (c) rate performance at various current densities from C/10 to 20C rates of the NTO and NTO- VS_2 electrodes and (d) electrochemical impedance spectra (Nyquist plots) of NTO and NTO- VS_2 electrodes after first cycle.

Figure 6. SEM images of (a) NTO and (b) NTO- VS_2 nanowires after 100 cycles at 1C rate, and (c-f) corresponding EDS mapping images of single NTO- VS_2 nanowire.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Vitae

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Graphical Abstract

A core-shell $\text{Na}_2\text{Ti}_2\text{O}_5\text{--VS}_2$ (NTO- VS_2) nanowire array with a coating of VS_2 on $\text{Na}_2\text{Ti}_2\text{O}_5$ exhibits superior capacity and rate capability as an anode in sodium-ion batteries compared to the uncoated $\text{Na}_2\text{Ti}_2\text{O}_5$ (NTO) nanowire array.