

Metallic few-layered 1T-VS₂ nanosheets for enhanced sodium storage

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Abstract: Metallic few-layered 1T phase vanadium disulfide nanosheets have been employed for boosting sodium ion batteries. It can deliver a capacity of 241 mAh·g⁻¹ at 100 mA·g⁻¹ after 200 cycles. Such long-term stability is attributed to the facile ion diffusion and electron transport resulting from the well-designed two-dimensional (2D) electron-electron correlations among V atoms in the 1T phase and optimized in-planar electric transport. Our results highlight the phase engineering into electrode design for energy storage.

Key words: metallic 1T phase; vanadium disulfide; ultrathin nanosheet; sodium ion batteries

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1. Introduction

Lithium ion batteries have played important roles in our daily life, but suffered from problems like limited lithium resource and environment friendless, etc.^[1]. Due to the merits of sodium, including similar electrochemical activities, abundance, sodium ion batteries (SIBs) stand out for energy storage recently^[2]. When looking for suitable electrode materials, there is the challenge with the large ionic radius of Na⁺, which endows more difficult Na⁺ intercalation/extraction into the hosts.

Vanadium disulfide (VS₂) is a layered material consisting of V atomic layers sandwiched between the two S atomic layers. The weak interlayer van der Waals interactions allow facile Na⁺ intercalation and diffusion between strong interlayer covalent layers without any obvious change in volume. VS₂ is known to be stable in both H and 1T polytypes^[3]. Due to the distinct 2D electron-electron correlations among V atoms in the 1T phase, 1T-VS₂ is not only favorable for the metallic nature with superior in-plane electronic conductivities, but also carrier diffusion kinetics. In view of these merits, 1T VS₂ with high electric conductivity would be of significance for sodium ion batteries and deep insights into atomic packing features and electrochemical performances.

Herein, owing to the two-dimensional features and distinct electronic structure, metallic few-layered 1T-VS₂ nanosheets exhibit long-term stable sodium storage. The capacities after 200 cycles deliver 241.3 mAh·g⁻¹ at 100 mA·g⁻¹. Metallic 1T-VS₂ nanosheets stands out with satisfied electrochemical performance among all the intercalation-based pure VS₂ anodes in SIBs.

2. Materials and methods

Precursor-VS₂ was synthesized by a facile solvothermal method. In a typical synthesis, 1 mmol NH₄VO₃ (99.0%, Macklin) powder in 30 mL NMP (99.0%, Aladdin) and 5 mmol C₃H₇NO₂S (97%, Aladdin) were mixed and transferred into a 45 mL Teflon-lined stainless-steel autoclave and heated to 200 °C for 24 h. The product was collected by centrifugation, and then lyophilized. 1T-VS₂ was obtained by annealing the above precursors at 400 °C under Ar for 2 h.

X-ray diffraction (XRD) was conducted by a Bruker D8 X-ray diffractor with Cu radiation ($\lambda = 0.15406$ nm). A Sirion field-emission scanning electron microscope (SEM), Talos F200X transmission electron microscope (TEM) (accelerating voltage = 200 kV) was used to observe the morphology and structure. X-ray photoelectron spectroscopy (XPS) spectra were obtained using a Thermo Scientific Alpha spectrometer. Raman spectra were detected via a Lab RAM HR 532 nm laser spectrometer (HORIBA Scientific).

The sodium storage was measured using CR2032 coin cells assembled in an argon-filled glove box (H₂O and O₂ levels < 0.1 ppm). The working electrode was composed of 60 wt% active materials, 20 wt% Super P and 20 wt% polyvinylidene fluoride (PVDF) binder. The mixed slurry was coated in Cu foil and vacuum-dried at 80 °C for 12 h. The mass loading of 1T-VS₂ averaged about 0.8–1.0 mg·cm⁻². The electrolyte was 1 M NaCF₃SO₃ in methoxymethane (DME). Glass-fiber filter (Whatman GF/B) was served as the separators and sodium plates were served as the counter electrodes for half cells. Cyclic voltammetry (CV) was performed on a CHI760E electrochemical workstation at a scan rate of 0.1 mV·s⁻¹. All cells were tested in the voltage window from 1.0 to 3.0 V at room temperature.

The geometry optimizations and density of states (DOS) calculations were performed by the spin-polarized density functional theory (DFT) method, as implemented in the Vienna *ab initio* simulation package (VASP) code with the projector augmented wave (PAW) method. The VS₂ monolayer

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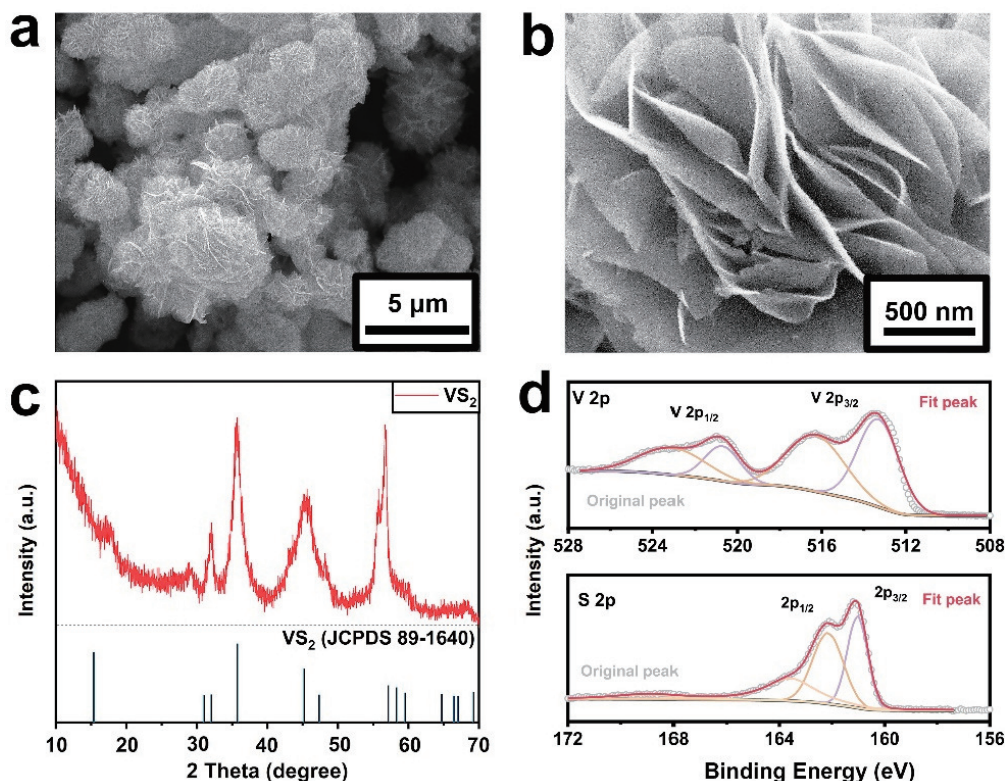


Fig. 1. (Color online) Characterizations of few-layered VS_2 . (a, b) SEM images. (c) XRD pattern and the standard pattern. (d) XPS spectra.

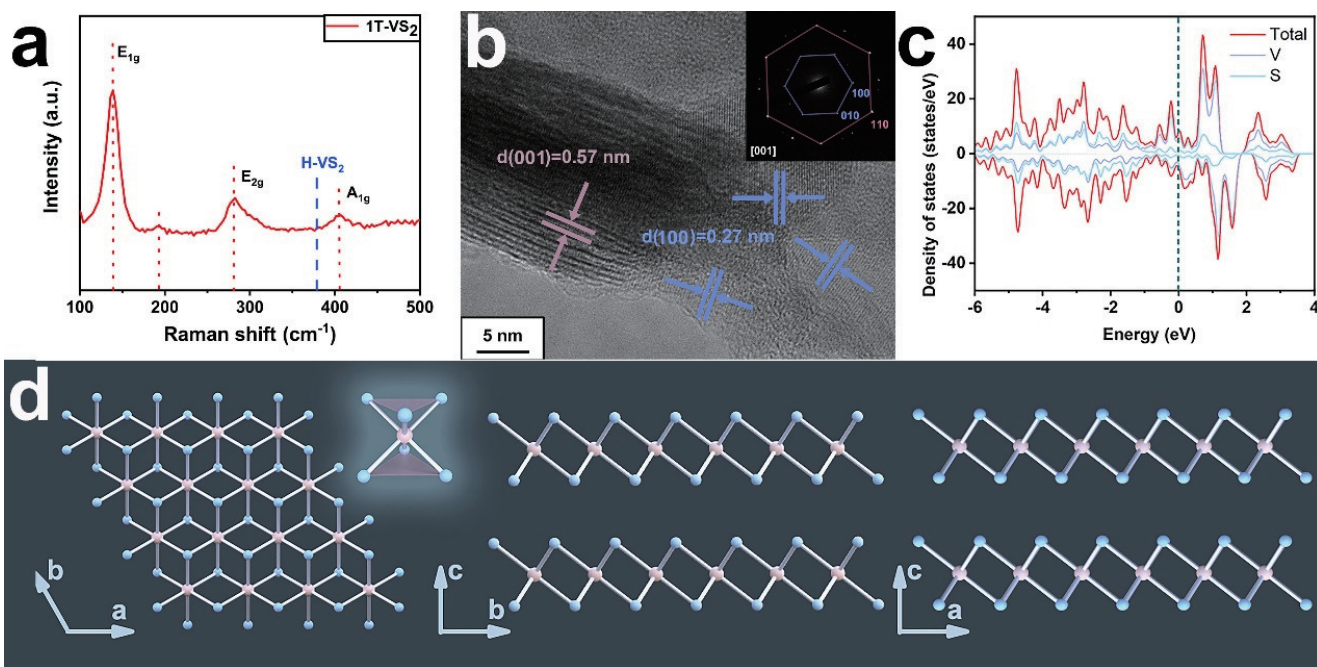


Fig. 2. (Color online) (a) Raman spectrum, (b) HRTEM images with SAED, (c) DOS diagram, and (d) VS_2 structure along different directions.

was modelled by building a $3 \times 3 \times 1$ supercell and a vacuum space in the z -direction was set to 15 \AA . The cut-off energy was set to 450 eV and force on each atom was converged 0.02 eV/\AA . The Brillouin zones were represented with a $6 \times 6 \times 1$ k -point grid for DOS calculations^[4].

3. Result and discussion

Metallic 1T-VS_2 was achieved via a facile solvothermal approach and post-annealing. Their SEM image in Fig. 1(a) shows homogeneous stacked nanosheets of the lateral size

around 1000 nm with an overall flower morphology. The magnified image in Fig. 1(b) reveals the thickness of $\sim 10 \text{ nm}$. The XRD pattern in Fig. 1(c) can be indexed as hexagonal 1T-VS_2 (JCPDS 89-1640, $P\text{-}3m1$), indicating high crystallinity and phase purity. The location of the (001) peak represents a layer spacing of 5.7 \AA along the stacking of (001) planes. XPS measurement was used to detect the chemical states of VS_2 . In Fig. 1(d), typical peaks of the V 2p spectrum (516 and 524 eV) belong to V $2p_{1/2}$ and V $2p_{3/2}$ spin-orbits, proving the existence of V^{4+} and V^{2+} ^[5]. The XPS spectrum for S 2p levels

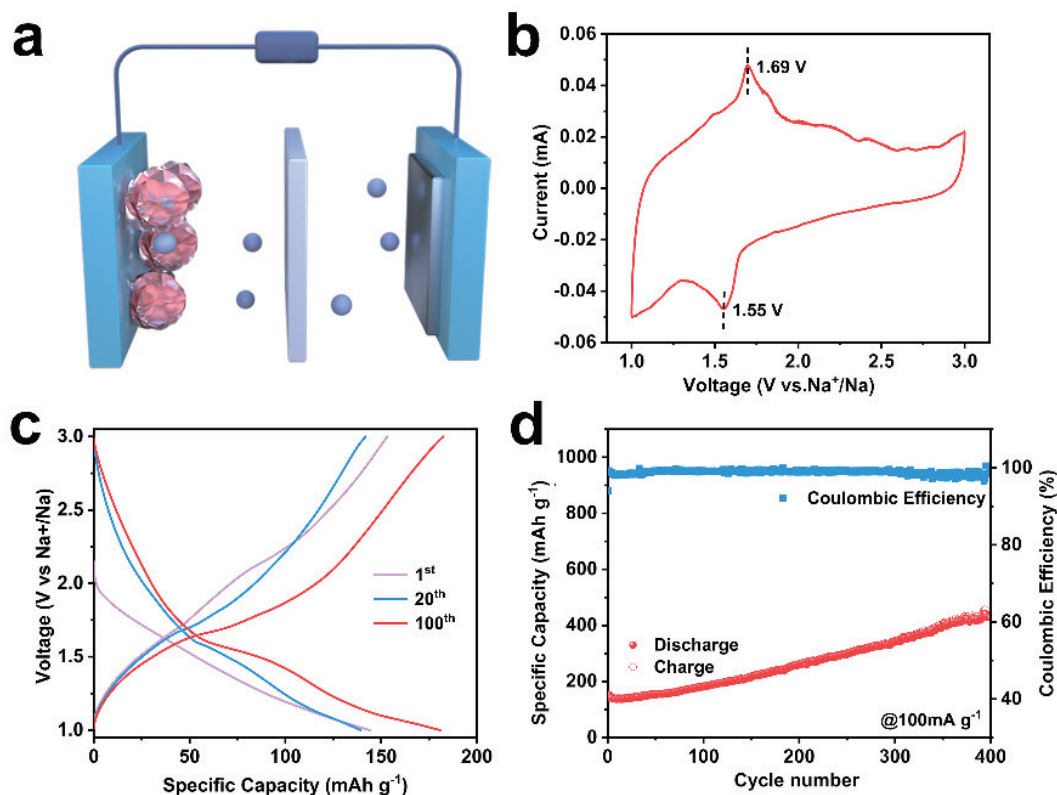


Fig. 3. (Color online) (a) Detailed schemes of 1T-VS₂-based sodium-ion battery. (b) CV curves for the 3rd cycle at 0.1 mV·s⁻¹. (c) The galvanostatic discharge/charge profiles of 1st, 20th and 100th at 100 mA·g⁻¹. (d) Cycling retentions at 100 mA·g⁻¹.

of S 2p_{1/2} and S 2p_{3/2} conform to the couple of doublet peaks around 162 and 161 eV. Raman spectrum in Fig. 2(a) further verify the metallic state of VS₂. Six peaks located at 138.9, 193.0, 282.2, and 405.7 cm⁻¹ confirm 1T-VS₂ (standard peaks with red lines) rather than H-VS₂ (standard peaks in blue lines)^{6, 7}. Fig. S1 shows the valence band XPS spectrum, which also indicates the high electrical conductivity of 1T-VS₂.

Continuous lattice fringes (2.7 Å) in the HRTEM image belong to (100) planes of 1T-VS₂ in Fig. 2(b). The cross-section lattice fringes are 5.7 Å, consistent with the XRD analysis of the interlayer spacing along (001) planes. The SAED pattern (inset in Fig. 2(b)) of an independent nanosheet prove the single-crystalline feature of the hexagonal skeleton with {001} facets exposed. Considering the Gibbs-Thompson theory for crystal growth, the relative chemical potential depending on the surface-atom ratio is important to determine the growth rate⁸. Metallic 1T-VS₂ consists of [VS6] layers stacking along c-axis. The V atoms located in the octahedral centers of the offset S layers are highlighted in Fig. 2(d)⁹. [100] and [010] axes have equal chains of [VS6], and [001] axes have the lowest surface-atom ratio than other facets. So the exposure of {001} facets is finally able to be achieved. Interestingly, theoretical investigations confirm that the monolayer 1T-VS₂ is metallic according to the density of states (DOS), see Fig. 2(c). High local DOS values reside across the Fermi level, indicating the metallic nature and the potential for high 2D conductivity.

To quantify sodium storage ability, two-electrode coin cells were employed with VS₂ anodes as diagramed in Fig. 3(a). In order to avoid the conversion reaction of Na⁺ under the low potential window, the voltage range of 1–3 V

was selected here. Cyclic voltammetry (CV) measurements shown in Fig. 3(b) were used to illuminate the redox pairs. The peaks around 1.69 and 1.55 V belong to Na⁺ intercalation into the top sites of the V atoms and three S atoms and corresponding deintercalation. The overall reaction thus can be summarized like: $x\text{Na} + x\text{e}^- + \text{VS}_2 \rightarrow \text{Na}_x\text{VS}_2$. It confirms stable intercalation/extraction of Na⁺ and the electrochemical reversibility. The galvanostatic discharge/charge profiles (Fig. 3(c)) at 100 mA·g⁻¹ is similar with the trend of CV curves. Two plateaus can be clearly observed during the 1st, 20th, and 100th cycles. These features endow metallic 1T-VS₂ standing out among different SIBs anodes. Metallic 1T-VS₂ nanosheets delivered superior electrochemical properties at various current densities. After 200 cycles at 100 mA·g⁻¹, a capacity of 241.3 mA·h·g⁻¹ with ~100% coulombic efficiency was achieved, which was attributed to the solvent-induced activation of typical layered materials for SIBs (Fig. 3(d)).

Such superior sodium storage ability is attributed to two superiorities. First, strong electron-electron correlations among V atoms contribute to the metallic 1T phase. The metallic nature provides high 2D in-plane electric conductivities generate continuous conductive paths for electron transport. Second, {001} facets are mostly exposed with high specific surface areas, and thus Na⁺ diffusion through 2D permeable channels is facile due to the weak van der Waals interaction. Synergistics between the 2D nanosheets and phase engineering offer a reservoir for Na⁺ and electrolytes with shortened diffusion lengths. Sufficient space enables the alleviation of the volume expanding during the ion intercalation. The unique configuration inhibits the aggregation of nanosheets during long-term cycles. The optimization of ion and electron kinetics enables superior sodium storage within the electrode

matrix. It provides more insight into the design of electrode materials based on the intercalation mechanism.

4. Conclusions

Overall, metallic 1T-VS₂ nanosheets for reversible sodium storage are promising. Benefitting from 2D permeable channels and high conductivity scaffolds, resulting from the layered 1T phase with weak Van der Waals interlayer interactions, strong electron-electron correlations among V atoms, and the outward nanosheet features, metallic 1T-VS₂ nanosheets not only optimize the superiorities of intrinsic atomic packing for electron transport and ion diffusion, but also generate continuous conductive pathways during Na⁺ intercalation/extraction. The high conductivity along with the structural configuration contributes to the superior electrochemical performance at various current densities. The capacity of 1T-VS₂ can exceed 241.3 mAh·g⁻¹ after 200 cycles. It is rational to design electrodes from an intrinsic crystalline structure to maximize the potential of enhanced sodium storage.

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Appendix A. Supplementary materials

Supplementary materials to this article can be found online at <https://doi.org/10.1088/1674-4926/44/11/112701>.

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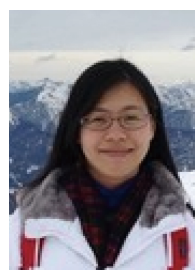
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