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VS_2 Nanosheets: A Potential Anode Materiral for Li-ion Batteriers

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Abstract: The flower-like VS_2 nanosheets were synthesized by a one-step solvothermal method. The X-ray diffraction, Raman, SEM, and TEM studies showed the growth mechanism of VS_2 flowers in detail. These experimental results indicate that the reaction temperature and time have the direct effect on the formation of VS_2 nanosheets. As anode material for Li-ion batteries, the VS_2 nanosheets exhibit an initial discharge and charge capacity are 195.4 and 90.6 mAh/g at current density of 200 mA/g. High Coulombic efficiency over 98% and improved rate capacity are achieved for the VS_2 nanosheets. All results suggest that the VS_2 nanosheets can be utilized as a promising anode material for Li-ion batteries with high power density and fast charge/discharge rates.

Key words: VS_2; nanosheets; Li- ions batteries; anode materials

The lack of electrical energy has become an urgent problem with the rapidly growing of the global economy and population. Meanwhile, most of electrical energy is from fossil fuels, harmful gases are produced during the combustion of fossil fuels, which cause serious pollution and affect people's health. So the renewable energy and the safe and reliable energy storage systems are urgently needed. Rechargeable lithium-ion battery, as an energy storage system, has been extensively studied and widely used in electric vehicles, portable electronic devices, and implantable medical devices[1-4]. However, the relative small specific capacity and low cycling life seriously hinder the development of lithium-ion battery. So it is urgent to develop advanced electrode materials with large specific capacity, high-rate capability, high cycling life, and safety[2, 5-6]. Recently, layered transition-metal sulfides, such as MoS_2[7-8], WS_2[9-10] and VS_2[11-12], are considered as the promising electrode materials due to their outstanding electronic behavior, large surface area and high chemical tolerance.

Vanadium disulfide (VS_2), as a typical layered transition-metal sulfide, is a hexagonal crystal with layered, graphite-like structure; this structure is stacked by S-V-S layers and the layers are connected by Van der Waals forces[13]. VS_2 have been used in moisture responsiveness[14], supercapacitors[15], catalysis[16], FET[17], and Li-ion batteries[11-12, 18] due to its unique physical, chemical, electronical, optical, mechanical and magnetic properties. This layered structure enables the convenient intercalation and exfoliation of Li^+ ions. In addition, the application of VS_2 nanostructures or VS_x nanocomposite in Li^+ ions battery has been reported[12, 18]. In recent years, many different methods have been developed to prepare VS_2 nanostructures, such as hydrothermal[15, 19-20], the sulfidization of VO_x precursor[16, 21], the exfoliation of bulk VS_2[14-15]. However, the preparation of VS_2 nanostructures with high quality is still a great challenge. In this paper, we present a simple hydrothermal route for the preparation of the VS_2 nanosheets and we also studied the affect of the reaction temperature and time to the final sample morphology. In addition, we investigated the application of VS_2 nanosheets in Li^+ ions battery.

1 Experimental

1.1 Synthesis of flower-like VS_2 nanostructures

All of the chemical reagents used in this experiment are of analytical grade and used without further purification. The VS_2 nanosheet was synthesized by a simple hydrothermal method. In a typical VS_2 nanosheet synthesis, 2 mmol of ammonium vanadate (NH_4VO_3) was added to 18 mL solution which contained 15 mL deionized water and 3 mL ammonia. With vigorous stirring, the ammonium vanadate was completely dissolved. After that, 10 mmol thioacetamide (CH_3CSNH_2) was added to the above solution under magnetic stirring. The final homogeneous solution was trans-

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ferred into a Teflon-lined stainless-steel autoclave with a capacity of 25 mL, which was sealed and kept at certain reaction temperature (140℃, 160℃, and 180℃) for different time (10 h, 15 h, and 20 h) and then cooled to room temperature under ambient conditions. After the autoclave was cooled to room temperature, the black products were washed for several times with ethanol and distilled water, followed by drying at 80℃ for 10 h in vacuum.

1.2 Characterization of the sample

The phase composition and crystallographic structure of the as-prepared samples were examined by X-ray diffraction (XRD) technique with Cu Kα irradiation. The sizes and morphologies of the products were investigated using a field emission scanning electron microscope (FESEM; S-4800, Hitachi, Minato-ku, Tokyo, Japan). The structure details of the nanosheet were examined by transmission electron microscopy (TEM) and high- resolution transmission electron microscopy (HRTEM, JEOL, JEM 2100F).

1.3 Electrochemical tests

Electrochemical properties of the sample were evaluated using CR2025-type coin cells assembled in an argon filled glove box. The working electrodes were prepared by slurry onto a Ni foam current collector. The electrode slurry was made by mixing 75wt% active materials, 15wt% acetylene black, and 10wt% polyvinylidene fluorides (PVDF) dissolved in N-methyl-2-pyrrolidinone. The coated electrodes were dried at 120℃ for 12 h in vacuum and then pressed. Li foil served as the counter electrode and reference electrode, and a polypropylene microporous sheet (Celgard-2300) as a separator. The electrolyte solution was a 1.0 mol/L $LiPF_6$ solution in a mixture of ethylene carbonate/dimethyl carbonate (EC/DMC) (1:1 in volume).

2 Results and discussion

The composition and structures of the synthesized samples were examined by X-ray diffraction powder pattern (XRD), and the XRD patterns of samples were shown in Fig. 1(a). Sample S1, S2, S3, S4, and S5 were prepared by solvothermal method at 140℃ for 15 h, 160℃ for 15 h, 180℃ for 10 h, 180℃ for 15 h, and 180℃ for 20 h, respectively. The XRD pattern in Figure 1a S4 shows the crystalline of the as-prepared product obtained by solvothermal treatment at 180 ℃ for 15 h. All the observed diffraction peaks in the pattern are well indexed to the hexagonal VS_2 (JCPDS-36-1139; a=b=0.3218 nm and c=0.5755 nm), and no secondary phases are found. The Raman spectrum of the sample S4 in the range of 100–1100 cm^{-1} are shown in Fig. 1(b). Six strong peaks positioned at 140.4, 192.0, 282.0, 406.6, 687.8, 993.2 cm^{-1} are observed. In addition, these peaks are sharp and their intensity is strong which indicates the sample is in a high crystalline state. Meanwhile, two weak peaks positioned at 473, 524 cm^{-1} are also detected. The Raman spectrum analysis supports the results of the XRD.

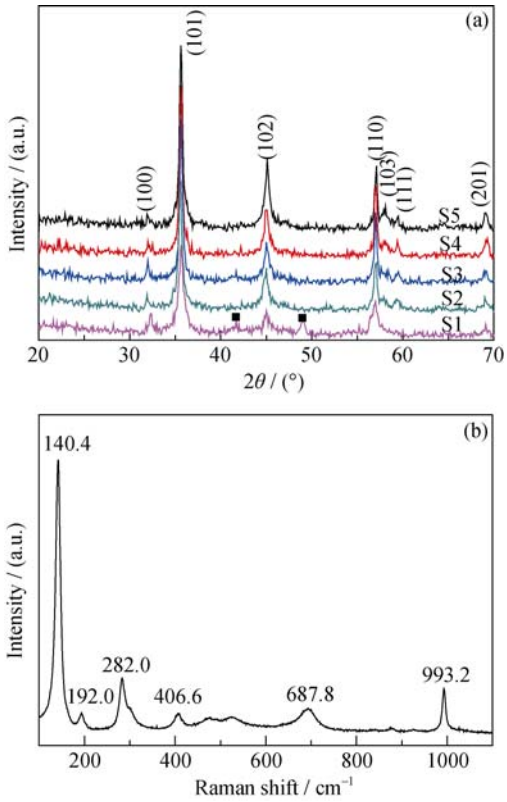

Fig. 1 Powder X-ray diffraction patterns of samples (a) and Raman spectrum of sample S4 (b)

Figure 2 (c and d) show the morphology and size of the as-synthesized product obtained by solvothermal treatment at 180℃ for 15 h. We can see that the samples are composed of uniform flower-like VS_2 nanostructures which stacked by a great quantity of nanosheets. The dimension of single nanoflowers can reach about 5–10 μm, and the average thickness of nanosheet is about 500 nm.

Figure 3(a) is a typical transmission electron microscopy (TEM) image of the as-synthesized product obtained by solvothermal treatment at 180℃ for 15 h, which indicates the sheetlike structure. The HRTEM image of VS_2 nanosheet is shown in Fig. 3(b). The clear lattice fringes show that the VS_2 nanosheets have a well-defined crystal structure. Meanwhile, the lattice spacing along two different directions is 0.251 nm and 0.278 nm, which are corresponding to the (101) and (100) planes, respectively. The selected-area electron diffraction (SAED) (Fig. 3(c)) taken from a nanosheet shows a spot pattern that is consistent with a high quality single crystal with hexagonal structure.

In order to investigate the growth process of flower-like

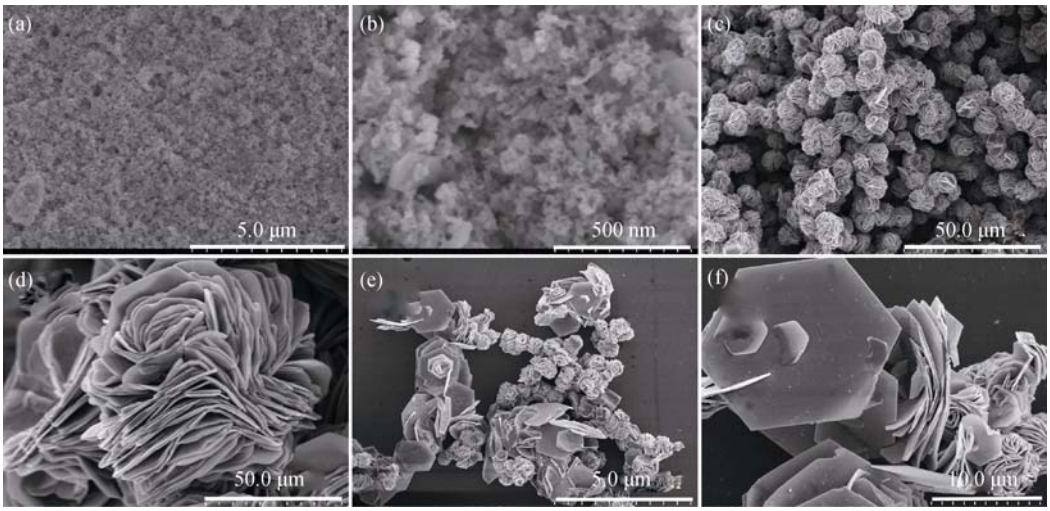

Fig. 2 SEM and FESEM images of samples prepared at 180℃ for 10 h (a, b), 15 h (c, d) and 20 h (e, f)

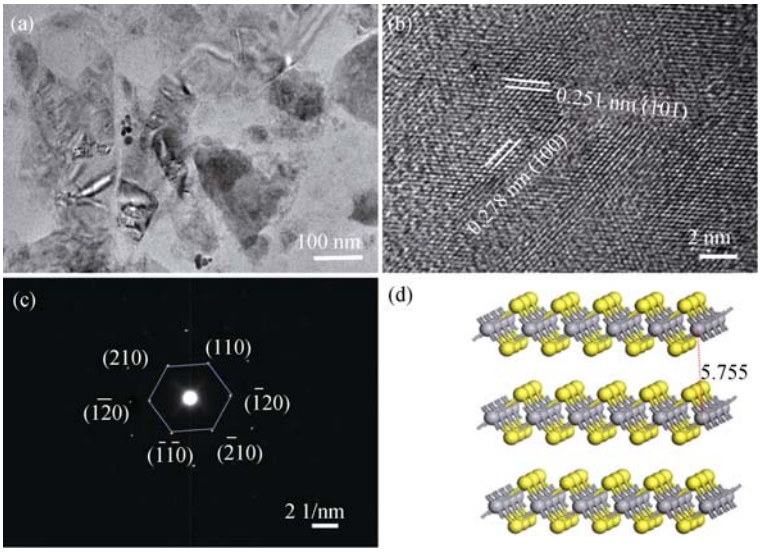

Fig. 3 TEM image of ultrathin (a), HRTEM image (b), SE-AD pattern (c), and the unit cell and side view of VS_2 nanosheets (d) thicknesses is about 500 nm.

VS_2 nanostuctures assembled by nanosheets, experiments were designed at different reaction times. When the solvothermal treatment was conducted for 10 h, a large number of nanoparticles which assembled by small size sheet-like structure were observed (Fig. 2 (a) and (b)). The XRD pattern in Fig. 1(a)S3 shows that the VS_2 crystalline phase formed. When the aging time was prolonged to 15 h, the uniform VS_2 nanoflowers were produced. The XRD pattern in Fig. 1(a)S4 and the Raman spectrum of sample S4 shows the as-prepared product obtained by solvothermal treatment at 180℃ for 15 h has good crystallization behaviour. This can be also confirmed by the HRTEM and SEAD of this sample. However, when the aging time increased to 20 h, large size hexagonal shape samples are observed (Fig. 2(e) and (f)). The width of a single VS_2 hexagonal microsheet is about 10um, and the Meantime, the impact of the reaction temperature was critical to the growth and morphology of the VS_2 nanostructures. The impact of the reaction temperature in the synthesis of the VS_2 nanostructures was also studied. Figure 4 shows the impact of reaction temperature on the shape and size of the VS_2. At 140℃ for 15 h, the products are composed of some diamond-like particles and some random particles (Fig. 4 (a) and (b)). In the meantime, the XRD pattern (Fig. 1(a)S1) shows that other peaks except VS_2 are also observed. When the reaction temperature was increased to 160℃, sheet-like particles appeared in the products, but the quality of this sheets is not good (Fig. 4(c) and (d)). The results of XRD (Fig. 1(a)S2) of this sample show it is composed by pure VS_2. At 180℃ with the same reaction conditions, the sample is composed by uniform VS_2 nanoflowers (Fig. 2(c) and (d)). All of this confirms that that the reaction temperature and time plays a key role in the he growth and morphology of the VS_2 nanostructures.

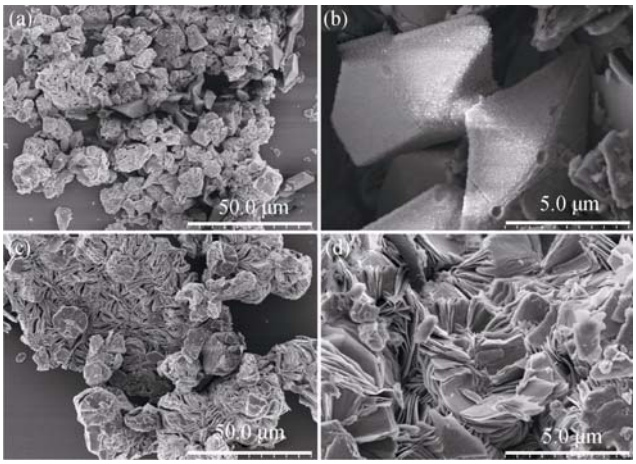

Fig. 4 SEM images of samples prepared at 140℃ (a, b) and 160℃ (c, d)

According to the synthesis process and above experimental results, the formation and growth mechanism of products are proposed. The reaction temperature and time play the important roles in the formation of seed nuclei. During the hydrothermal process, hydrolysis and dissociation of thioacetamide and Na_3VO_4 occur. The sulfur generated from the dissociated thioacetamide promotes the formation of pristine VS_2 sheets. The formation of the flowerlike morphology of VS_2 probably involves two steps: an initial nucleating stage and a crystal growth stage involving an Ostwald ripening process, which is known for the growth of flowerlike metal sulfide structures[17]. In the initial stage, various functional groups present in the reaction vessel, such as $–NH_2$, –COOH, and –SH, react with V^{4+} ions to form V–S complexes, which then decompose to form VS_2 nuclei for later growth. In the second stage, the flowerlike structures would form as a result of the Ostwald ripening, weakly stack together and self-assembly of the VS_2 sheets (Fig. 3(d)).

To evaluate the lithium storage properties of the VS_2 nanosheets, electrochemical measurements were carried out based on a coin-type half cell configuration at room temperature. To understand the electrochemical reaction in charge and discharge processes, the cycle voltammogram of the VS_2 nanosheets is initially measured. Figure 5(a) exhibits the voltage profiles of the VS_2 sample in the 1st, 2nd, 3rd, 10th, 20th cycles at a current density of 200 mA/g. In the first charge curve, there is a voltage plateau at 2.1 V. During the first discharge process, a voltage plateau appears at 1.1V. The voltage plateaus are attributed to the conversion reaction process:

$$x\mathrm{Li}^{+}+xe^{-}+\mathrm{VS}_2\leftrightarrow \mathrm{Li}_x\mathrm{VS}_2$$[11].

This is consistent with the deintercalation and intercalation of Li^+ ions from and into the layered-structure VS_2 nanosheets[22]. The first discharge and charge capacities are 195.4 and 90.6 mAh/g, respectively, corresponding to 46% Coulombic efficiency. It can be also learned that the Coulombic efficiency gradually increases along with cycling number, and keeps above 98% finally. This also can be learned from Fig. 5(b). The charge capacity after 20 cycles is 38 mAh/g, showing capacity retention of 87%. The theoretical capacity of VS_2 monolayer is 466 mAh/g if only mole of Li^+ is intercalated, which is larger than the results of our experiment. The first discharge capacity of the VS_2 nanosheets is above 195.4 mAh/g with a fast decrease to 115 mAh/g in the second cycle. This may be due to the difference of the thickness of VS_2 nanosheets, some of Li^+ are trapped in the layered nanosheets after the first discharge. So the thickness of VS_2 nanosheets has a direct affect in the charge capacity of this Li ion battery.

To further evaluate the electrochemical performance of VS_2 nanosheets, the rate cycling behavior of the VS_2 nanosheets was studied. Figure 5(c) shows the rate cycling behavior of the VS_2 nanosheets. It can be seen from Fig. 5(c), the discharge capacities remain stable and decreases regularly with the increase of the current density. After 10 cycles, a discharge capacity of 73 mAh/g is observed at 50 mA/g, and this value is slowly reduced to 50, 25, 20 and 16 mAh/g at 100, 200, 400 and 800 mAh/g, respectively. In the meantime, when the current changes from 800 mA/g to 50 mA/g, the specific capacity can almost return to the original value at once and does not ultimately change in the following cycles. The results indicate that the VS_2 nanosheets has high cycling stability. Base on our carefully investigation, there has been literature with respect to the individual VS_2 electrode for LIB, which showed the relatively low discharge capacity and coulombic efficiency[12]. The key parameters of present and previous work are summarized in Table 1.

3 Conclusions

In summary, the VS_2 nanosheets were synthesized by a simple one-step hydrothermal method. The formation of VS_2 nanosheets are investigated, which plays an important role and affected by the reaction temperature and time. The application of VS_2 nanosheets in Li-ions battery is also studied. It delivers an initial discharge capacity of 195.4 mAh/g at a current density of 200 mA/g. After being subjected over 50 cycles at different rates from 50 to 800 mA/g, the discharge capacity is retained when the current is back to 50 mA/g. This work might offer a new route to explore the applications of VS_2 nanosheets based composites in Li^+ ions batteries.

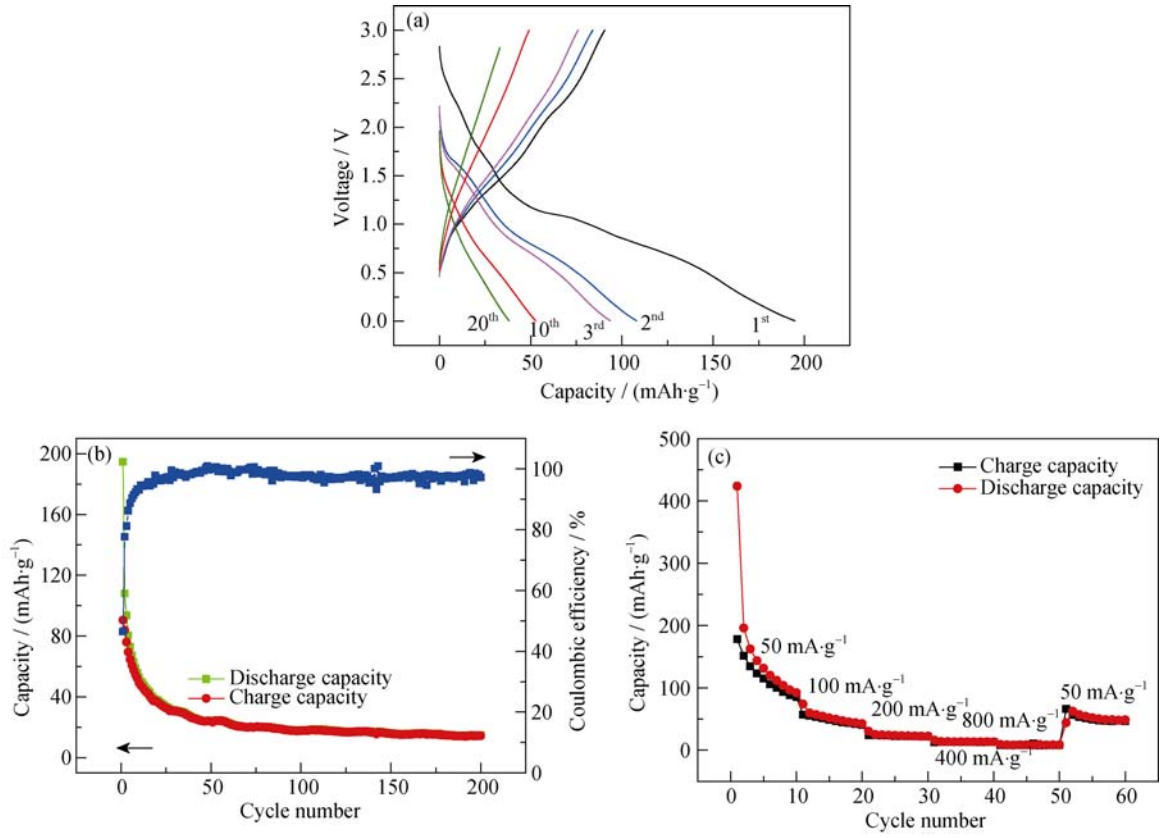

Fig. 5 Discharge and charge curves at a current density of 200 mA/g cycled between the voltage of 3.0–0.01 V *vs* Li/Li^+ (a), cycling performance of the prepared VS_2 nanosheets electrode at 200 mA/g (b), and rate capability of the VS_2 nanosheets electrode between 50 mA/g and 800 mA/g (c)

Table 1 Comparison of electrochemical performance data for various LIB electrode materials of base VS_2 and its hybrids

Sample	Voltage *vs* (Li/Li^+)/V	Theoretical specific capacity/ $(mAh·g^{-1})$	First discharge capacity/ $(mAh·g^{-1})$	Coulombic efficiency after (*x*) cycles/%	References
VS_2	2.43	466	86.0	–	[12]
PEDOT/ VS_2	2.68	–	130.0	–	[12]
PEDOT	2.80	–	78.0	–	[12]
VS_2 nanosheets	2.10	466	195.4	98(200)	This work

References:

[1] WANG X J, HOU Y Y, ZHU Y S. An aqueous rechargeable lithium battery using coated li metal as anode. *Scientific Reports*, 2013, **3:** 1401–1405.

[2] DUNN B, KAMATH H, TARASCON J. Electrical energy storage for the grid: a battery of choices. *Science*, 2011, **334:** 928–935.

[3] XI J Y, WU Z H, TENG X G, *et al*. Self-assembled polyelectrolyte multilayer modified Nafion membrane with suppressed vanadium ion crossover for vanadium redox flow batteries. *Journal of Materials Chemistry*, 2008, **18(11):** 1232–1238.

[4] YANG Z G, ZHANG J L, KINTNER-MEYER MICHAEL C W, *et al*. Electrochemical energy storage for green grid. *Chemical Reviews*, 2011, **111(5):** 3577–3613.

[5] ARMAND M, TARASCON J M. Building better batteries. *Nature*, 2008, **451:** 652–657.

[6] YUAN W W, ZHANG J, XIE D, *et al*. Porous CoO/C polyhedra as anode material for Li-ion batteries. *Electrochimica Acta*, 2013, **108:** 506–511.

[7] CHANG K, CHEN W. L-cysteine-assisted synthesis of layered mos_2/graphene composites with excellent electrochemical performances for lithium ion batteries. *ACS Nano*, 2011, **5:** 4720–4728.

[8] STEPHENSON T, LI Z, OLSEN B, *et al*. Lithium ion battery applications of molybdenum disulfide (MoS_2) nanocomposites. *Energy & Environmental Science*, 2014, **7(1):** 209–231.

[9] KARTICK B, SRIVASTAVA S K, MAHANTY S. Tungsten disulfide-multiwalled carbon nanotube hybrid anode for lithium-

ion battery. *Journal of Nanoscience and Nanotechnology*, 2014, **14(5):** 3758–3764.

[10] BHANDAVAT R, DAVID L, SINGH G. Synthesis of surface-functionalized ws_2 nanosheets and performance as Li-ion battery anodes. *Journal of Physical Chemistry Letters*, 2012, **3(11):** 1523–1530.

[11] JING Y, ZHOU Z, CABRERA C R, *et al*. Metallic VS_2 monolayer: a promising 2D anode material for lithium ion batteries. *Journal of Physical Chemistry C*, 2013, **117(48):** 25409–25413.

[12] MURUGAN A V, GOPINATH C S, VIJAYAMOHANAN K. Electrochemical studies of poly (3, 4-ethylenedioxythiophene) PEDOT/ VS_2 nanocomposite as a cathode material for re-chargeable lithium batteries. *Electrochemistry communications*, 2005, **7(2):** 213–218.

[13] MULAZZI M, CHAINANI A, KATAYAMA N, *et al*. Absence of nesting in the charge-density-wave system 1T-VS_2 as seen by photoelectron spectroscopy. *Physical Review B*, 2010, **82(7):** 075130–075135.

[14] FENG J, PENG L, WU C, *et al*. Giant moisture responsiveness of VS_2 ultrathin nanosheets for novel touchless positioning interface. *Advanced Materials*, 2012, **24(15):** 1969–1974.

[15] FENG J, SUN X, WU C, *et al*. Metallic few-layered VS_2 ultrathin nanosheets: high two-dimensional conductivity for in-plane supercapacitors. *Journal of the American Chemical Society*, 2011, **133(44):** 17832–17838.

[16] THERESE H A, ROCKER F, REIBER A, *et al*. VS_2 nanotubes containing organic-amine templates from the NT-VO_x precursors and reversible copper intercalation in NT-VS_2. *Angewandte Chemie International Edition*, 2005, **44(2):** 262–265.

[17] ROUT C S, KHARE R, KASHID R V, *et al*. Metallic few-layer flowerlike VS_2 nanosheets as field emitters. *Euro J. Inorg. Chem.*, 2014**(31):** 5331–5336.

[18] XU X D, JEONG S Y, ROUT C S, *et al*. Lithium reaction mechanism and high rate capability of VS_4–graphene nanocomposite as an anode material for lithium batteries. *J. Mater. Chem.*, 2014, **2(28):** 10847–10853.

[19] ZHONG M, LI Y, XIA Q, *et al*. Ferromagnetism in VS_2 nanostructures: nanoflowers versus ultrathin nanosheets. *Materials Letters*, 2014, **124:** 282–285.

[20] ROUT C S, KIM B H, XU X D, *et al*. Synthesis and characterization of patronite form of vanadium sulfide on graphitic layer. *J. Am. Chem. Soc.*, 2013, **135(23):** 8720–8725.

[21] VAN L B, IJDO D J. Preparation, crystal structure, and magnetic structure of $LiCrS_2$ and $LiVS_2$. *Journal of Solid State Chemistry*, 1971, **3(4):** 590–595.

[22] HWANG H, KIM H, CHO J. MoS_2 nanoplates consisting of disordered graphene-like layers for high rate lithium battery anode materials. *Nano Letters*, 2011, **11(11):** 4826–4830.

VS_2 纳米片: 一种十分有潜力的锂电池阳极材料

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摘 要: 通过一种单步水热法成功制备了花状 VS_2 纳米片。利用 X 射线衍射仪(XRD)、拉曼光谱、场发射扫描电镜(SEM)和透射电子显微镜(TEM)等手段对样品进行表征, 并研究了其生长机制。实验结果表明: 反应温度及时间的不同直接影响着 VS_2 纳米片的形貌。此外, 通过使用 VS_2 纳米片作为锂离子电池阳极材料, 分别研究了充放电电压和循环性能等性质。在 200 mA/g 电流密度下, 电池初始充放电能力分别为 195.4 和 90.6 mAh/g。随着循环充放电的进行, 该电极材料的库伦效率高达 98%。可以认为 VS_2 纳米材料具备高效、高能量密度锂离子电池的阳极材料。

关 键 词: VS_2; 纳米片; 锂电池; 阳极材料

中图分类号: TQ174 **文献标识码:** A