Electrochimica Acta 274 (2018) 334–342

Contents lists available at ScienceDirect

Electrochimica Acta

journal homepage: www.elsevier.com/locate/electacta

Controlled construction of 3D self-assembled VS_4 nanoarchitectures as high-performance anodes for sodium-ion batteries

Wenbin Li [a], Jianfeng Huang [a, **], Liyun Cao [a], Liangliang Feng [a, *], Chunyan Yao [b]

[a] School of Materials Science & Engineering, Shaanxi University of Science and Technology, Xi'an Shaanxi 710021, PR China
[b] Culture and Communication School, Shaanxi University of Science and Technology, Xi'an Shaanxi 710021, PR China

ARTICLE INFO

Article history:
Received 26 February 2018
Received in revised form
6 April 2018
Accepted 15 April 2018
Available online 16 April 2018

Keywords:
VS_4
3D nanoarchitectures
Sodium ion batteries
Anode
pH value

ABSTRACT

Developing desirable anode materials with 3D self-assembled structure is of paramount importance for enhancing the performance of sodium-ion batteries. Here, we report the controlled synthesis of three novel 3D VS_4 nanoarchitectures: nanorods (Nanorod-VS_4), nanocones and nanobelts self-assembled VS_4 microspheres. When serving as anode materials for sodium-ion batteries, Nanorod-VS_4 exhibits the better electrochemical performances than the latter two, delivering a high reversible capacity of 225 $mAhg^{-1}$ at 0.5 Ag^{-1} after 200 cycles and that of 203 and 168 $mAhg^{-1}$ even at 1.0 and 2.0 Ag^{-1}, respectively. The remarkable sodium storage properties of the Nanorod-VS_4 material is mainly ascribed to the synergistic effect of the self-assembled structure of radial nanorods and the preferred orientation growth along (110) planes. Moreover, the reversible insertion reaction and diffusion-dominant Na^+ storage process between 0.50 and 3.00 V occurring in the Nanorod-VS_4 are clearly revealed.

1. Introduction

Because of the increasing demand for sustainable and renewable power sources, much effort has been devoted to energy storage innovation over the past decades. Although, lithium-ion batteries (LIBs) have been successfully applied in many aspects of our daily life, the geographically constrained Li resources in the earth may not be sufficient to satisfy the increased demand for LIBs [1,2]. Given the natural abundance, more democratic global distribution and low cost of sodium resource, a wide range of compounds functioning as the anodes have been used for sodium-ion batteries (SIBs) [3–10]. Among these anode materials, TMSs (transition metal sulfides) have been considered as very potential candidates owing to their excellent redox reversibility and relatively high capacity [11]. As a family of typical TMSs, vanadium sulfides (VS_2, VS_4 and V_5S_8 et al.), regarded as high-performance electrode materials, are receiving tremendous attention in the field of energy storage due to their unique physical and chemical properties [12–16].

In particular, patronite VS_4 with S_2^{2-} dimers, attracts more interest owing to its characteristics of one-dimensional chain-like crystal structure with the interchain distance of 5.83 Å, weak interaction between neighboring chains and high content of sulfur [13,17–19]. These features can not only offer more potential sites for Na^+ insertion/extraction, but also improve the charge transfer [20,21]. To the best of our knowledge, however, pure VS_4 material that employed in SIBs has never been reported. While acting as the anode for LIBs, VS_4 shows obvious capacity degradation and poor rate capability, which are mainly resulted from by the serious volume expansion/contraction and the sluggish electrochemical reaction dynamics during Li^+ insertion/extraction [21,22]. It is worth mentioning the fact that Na^+ possessing a larger radius (1.02 Å) than that of Li^+ (0.76 Å) could lead to a more serious expansion/contraction and worse electrochemical reaction dynamics. Although, in the previous studies, coupling VS_4 with carbon materials can relieve the volume variation in some extent, the reversible capacity, cycling stability and rate capability are still unsatisfactory for SIBs [13,20,21,23].

Recently, 3D self-assembled structures with nanosized building blocks have provided new opportunities to simultaneously circumvent the severe volume expansion/contraction and the sluggish electrochemical reaction dynamics [24–27]. On the one hand, 3D self-assembled structures can provide a buffering for self-expansion and self-shrinkage to effectively accommodate the volume variation during Na^+ insertion/extraction. On the other hand,

---

* Corresponding author.
** Corresponding author.
E-mail addresses: huangjf@sust.edu.cn (J. Huang), fengll@sust.edu.cn (L. Feng).

https://doi.org/10.1016/j.electacta.2018.04.106

the building blocks in nanoscale can reduce the transport length of electrons, shorten diffusion path of ions, and then improve the electrochemical reaction dynamics. Particularly, it is generally believed that the nanostructure presenting the oriented growth along a certain crystallographic plane with large interplanar spacing can offer more open channels for flexible sodiation/desodiation without a serious structural distortion, which is more conducive to the enhancement of electrochemical reaction dynamics [28–30]. Therefore, realizing the controllable construction of unique self-assembled VS_4 nanoarchitectures, and then exploring and optimizing their sodium storage performances, are highly desirable.

Herein, we present three novel 3D VS_4 nanoarchitectures with different building blocks, including nanorods (denoted as Nanorod-VS_4), nanocones (denoted as Nanocone-VS_4) and nanobelts (denoted as Nanobelt-VS_4), which are hydrothermally synthesized using a facile template-free method by controlling the pH value of precursor. Such architectures are firstly evaluated in this study as SIB anodes, and the synergistic effect of the self-assembled building blocks and crystal structures on sodium storage performance are systemically investigated. In particular, Nanorod-VS_4 with the (110)-oriented crystal structure exhibits superior electrochemical performance. After 200 cycles, the reversible capacity is maintained at 225 $mAhg^{-1}$ at 0.5 Ag^{-1}. The high reversible capacities of 203 and 168 $mAhg^{-1}$ are reached even at high current densities of 1.0 and 2.0 Ag^{-1}. Finally, the reversible insertion reaction and diffusion-dominant Na^+ storage process of VS_4 anode between 0.50 and 3.00 V are revealed, for the first time.

2. Experimental work

2.1. Material synthesis

Firstly, 1.0 g of $NaVO_3$ (Aladdin, AR, 99.0%) and 3.6 g of C_2H_5NS (Sinopharm Chemical Reagent, AR, $\geq$99.0%) were dissolved in 60 ml of distilled (DI) water. After magnetic stirring for 10 min, a series of pH values from 9.3 to 1.0 were adjusted by dropwise adding HCl solution (3 mol/L) to the reaction solution accompanied by continuously magnetic stirring at room temperature (see SI for further details (Fig. S1)). Then the above solutions were transferred to a 100 mL Teflon-lined stainless steel autoclave and heated at 180 °C for 24 h at a rotating speed of 10 rpm. After being cooled down naturally, the precipitate was filtered and washed with DI water and ethanol in turn for three times. Finally, the resulting materials were dried at 60 °C for 12 h in vacuum. Note that the original pH value of the precursor solution is 9.3.

2.2. Battery fabrication and electrochemical measurements

As-synthesized VS_4 active materials, acetylene black and polyvinylidene fluoride (PVDF) binder in a weight ratio 8:1:1 were dispersed in N-methyl-2-pyrrolidone (NMP) solution to make the slurry, which were coated onto a copper foil by MSK -AFA-III automatic thick film coater and dried in a vacuum oven at 120 °C for 12 h to make the anodes. Standard CR2032-type button cells were assembled in an argon-filled glove box, with sodium metal foil as the counter electrode, microporous glass fiber as the separator ((CAT No. 1823-090, GF/D, 25 circles, GE Healthcare UK Limited)), and 1.0 M $NaSO_3CF_3$ in DIGLYME = 100 vol% as the electrolyte. The diameter of the electrode roundels was 16 mm and the mass loading of the active materials was 0.6–1.0 mg cm^{-2}. The galvanostatic charge/discharge measurements between 0.50 and 3.00 V were carried out using CT-3008 potentiostat at different current densities. Cyclic voltammetry (CV) at different scan rates from 0.1 to 1.0 mVs^{-1} in the potential range of 0.50–3.00 V (*vs.* Na^+/Na) and electrochemical impedance spectroscopy (EIS) with an amplitude of 5 mV in the frequency range from 100 kHz to 0.01 Hz were tested by CHI660E electrochemical workstation. All electrochemical tests were performed at room temperature.

2.3. Materials characterization

The crystal structures were identified by X-ray diffraction (XRD, D/max2200 PC with Cu Ka radiation ($\lambda = 0.15406$ nm), 10–70°, 10°/min). XPS spectra were obtained by X-ray photoelectron spectrometer (XPS, AXIS SUPRA) with monochromatic Al Kα radiation as the X-ray source, where C1s = 284.6 eV is used as a reference. Raman spectra were taken on a Renishaw-invia confocal microprobe Raman system (Laser: 532 nm edge). Infrared spectra were performed on a Bruker Alpha type infrared spectrometer (FITR, VECTOR-22) with KBr compression method. The morphologies and energy dispersive X-ray spectroscopies (EDS) were characterized by field emission scanning electron microscope (FESEM, S-4800). Transmission electron microscopy (TEM), high-resolution transmission electron microscopy (HRTEM), selected area electron diffraction (SAED) and fast-fourier transform (FFT) images were acquired from a transmission electron microscopy (TEM, JEM-3010). Before TEM measurement, the samples were ultrasonically dispersed for 30 min. Brunauer Emmet-Teller (BET) surface areas were characterized by the nitrogen adsorption with ASAP2460 specific surface area instrument. Prior to the gas sorption measurements, the samples were outgassed at 200 °C for 5 h under a vacuum.

3. Results and discussion

3.1. Structure characterization

Nanorod-VS_4, Nanocone-VS_4 and Nanobelt-VS_4 were obtained by adjusting the pH value of precursor to 9.3, 2.7 and 1.0, respectively. As can be found from Fig. 1 and Fig. S2, all the samples exhibit the 3D self-assembled spherical structures and the pH value of precursor has a profound influence on their self-assembled structures. When pH = 9.3, VS_4 microspheres are assembled of radially straight/curved nanorods, with the diameter of ~2 μm (Fig. 1(a, d) and Fig. S2(a)), and this structure is further confirmed by the SEM images of the interior of cracked Nanorod-VS_4 microspheres (Fig. S3(a, b)). When the pH is decreased to 2.7, the resulting VS_4 sample appears as the homogeneous cauliflower-like morphology with the diameter of ~1.0 μm (Fig. 1(b) and Fig. S2(b)) and these microspheres are self-assembled with radially irregular nanocones (~200 nm in length, Inset of Fig. 1(e) and Fig. S3(c, d)), whose outer ends are seemingly irregular nanoparticles (Fig. 1(e)). On further decreasing the pH to 1.0, the morphology evolves to the irregular clew-like microspheres with the diameter of 1–2 μm (Fig. 1(c)), which are self-assembled with irregular curved nanobelts (Fig. 1(f) and Fig. S2(c)). Further BET analysis demonstrates that the specific surface areas of Nanorod-VS_4, Nanocone-VS_4 and Nanobelt-VS_4 are 13.51, 13.53 and 10.25 m^2/g, respectively, which are similar and have little influence on the electrochemical performances.

The crystal structures of three typical VS_4 self-assembled microspheres are then characterized by XRD and the analysis results are listed in Table S1. It is found from Fig. 2(a) that all the diffraction peaks in each sample are well indexed to monoclinic VS_4 [PDF# 72-1294], which is composed of V^{4+} ions coordinated to sulfur dimers forming linear chains extending along *c* axis (Fig. 2(b)). Observably, Nanorod-VS_4 demonstrates the dominated crystal growth along (110) plane while Nanobelt-VS_4 along (110) and (020) planes, and Nanocone-VS_4 display the synergetic crystal growth along (110), (020), (2(—)02), (2(—)04) and (2(—)24) planes, respectively. As