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Abstract

Electrode materials with a three-dimensional (3D) layered framework and excellent electrochemical stability can provide a new avenue for enhancing the overall performance of promising sodium ion batteries. Here, we show that layered monoclinic (m) - ZnV₂O₆ nanobelts with high chemical activity for Na-ion energy storage have been effectively fabricated via a rapid microwave irradiation method over the reaction time of 8 h, in which the fabricating efficiency is 24.5 times greater in comparison with the traditional hydrothermal method. The morphology and phase evolutions were verified by means of X-ray diffraction, scanning electron microscopy, and transmission electron microscopy. This study also proposes the "topotactic transformation-Ostwald ripening" mechanism in layered m-ZnV₂O₆ nanobelts, from one-dimensional (1D) m-Zn₂V₂O₇ with tunnel structure to a 3D m-ZnV₂O₆ layered structure. In particular, the m-ZnV₂O₆ nanobelt anode exhibited a high discharge capacity of 480.5 mAh g⁻¹ at a current density of 10 mA g⁻¹, and maintained the considerable discharge capacity of 246.9 mAh g⁻¹ at the 100th cycle. The very preliminary results are promising and confirming that layered metallic vanadium can give a new insight into designing novel anode materials for high-efficiency energy storage in sodium ion batteries.

Keywords

highly, na, nanobelts, ion, znv₂o₆, rechargeable, m, layered, novel, active, energy, electrochemically, storage

Disciplines

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Electrochemically active, novel layered $m\text{-ZnV}_2\text{O}_6$ nanobelts for highly rechargeable Na-ion energy storage

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Abstract

Electrode materials with a three-dimensional (3D) layered framework and excellent electrochemical stability can provide a new avenue for enhancing the overall performance of promising sodium ion batteries. Here, we show that layered $m\text{-ZnV}_2\text{O}_6$ nanobelts with high chemical activity for Na-ion energy storage have been effectively fabricated via a rapid microwave irradiation method over the reaction time of 8 h, in which the fabricating efficiency is 24.5 times greater in comparison with the traditional hydrothermal method. The morphology and phase evolutions were verified by means of X-ray diffraction, scanning electron microscopy, and transmission electron microscopy. This study also illustrates the “topotactic transformation – Ostwald ripening” mechanism in layered $m\text{-ZnV}_2\text{O}_6$ nanobelts, from one-dimensional $m\text{-Zn}_2\text{V}_2\text{O}_7$ with tunnel structure to a 3D $m\text{-ZnV}_2\text{O}_6$ layered structure. In particular, the $m\text{-ZnV}_2\text{O}_6$ nanobelt anode exhibited a high discharge capacity of 484.9 mAh g^{-1} at a current density of 10 mA g^{-1} , and maintained the considerable discharge capacity of 235.3 mAh g^{-1} at the 50th cycle. The very preliminary results are evidence that layered metallic vanadium can give a new insight into controllably designing novel anode materials for high-efficiency energy storage in sodium ion batteries.

1. Introduction

Sodium ion batteries (SIBs), as a next generation alternative to lithium ion batteries (LIBs), have attracted tremendous efforts to develop them for foreseeable renewable energy storage in electrical devices, owing to the lower cost of sodium compared to lithium, much higher resource abundance in the earth's crust, and the great similarities in the electrochemical mechanism and assembly technologies.¹⁻⁸ For practical usage, sodium ion storage materials should present high theoretical capacity, low active energy for electrochemical reactions with excellent cyclability, and fast thermodynamics and kinetics for the insertion/extraction of Na^+

ions.⁹⁻²² Nevertheless, the lack of anode electrode materials with high capacity and cyclability greatly hinders the rapid development of these promising Na-ion batteries. While, the scientific issues of poor cyclability for the anode are assigned to the large volume changes during charging/discharging, the low electronic conductivity of the intrinsic material, and the sluggish kinetics.^{20, 23-25} To pursue the strict requirements on the desired anode, various interesting materials have been investigated based on intercalation compounds,²⁶⁻³⁰ metallic alloys,³¹⁻³⁵ and organic chemicals.³⁶⁻³⁸

Among the intercalation compounds for the anode, metallic vanadates have been considered for a long time, because they display special crystal structure and electrochemical stability. Recently, Obrovac and co-workers found that transition metal vanadate (CoV_3O_8 , MnV_2O_6 , and VFeO_4) powders, fabricated via solid state reaction, showed significant volumetric capacities ($820\text{--}1163\text{ Ah L}^{-1}$), which far exceed that of graphite in LIBs ($\sim 730\text{ Ah L}^{-1}$).³⁹ However, these bulk products are always accompanied by a relatively low reversible specific capacity ($200\text{--}316\text{ mAh g}^{-1}$) owing to their shape and size uniformity. Despite the improvement of these potential vanadate anodes, high energy density and long lifespan still need to be further explored. Until now, it is not yet clear which kind of vanadate nanostructure is suitable for high-rate anode sodiation storage. To the best of our knowledge, few studies have been focused on monoclinic zinc vanadate ($m\text{-ZnV}_2\text{O}_6$) nanostructures, which show outstanding merits as electrode material: To begin with, $m\text{-ZnV}_2\text{O}_6$ has good structural stability with a large unit cell ($a = 9.242\text{ \AA}$, $b = 3.526\text{ \AA}$, and $c = 6.574\text{ \AA}$) to balance the volume changes during Na^+ insertion/extraction. In addition, $m\text{-ZnV}_2\text{O}_6$ crystal features a double-layered structure (Fig. 1a-d), in which there is stacking of chains of typical $[\text{VO}_4]$ tetrahedra through corner sharing along the b -axis. The octahedral coordination $[\text{ZnO}_6]$ chains are linked with $[\text{VO}_4]$ tetrahedra double chains via oxygen-sharing. While, the double layers have a suitable interlayer distance of 0.2533 nm , which is much larger than the Na^+ ion diameter (0.204 nm), and thus can provide prompt ionic kinetic transport and long-term cyclability. Moreover, attractive electrochemical activity is exhibited, based on $\text{V}^{5+}/\text{V}^{4+}$, $\text{V}^{4+}/\text{V}^{3+}$, and $\text{V}^{3+}/\text{V}^{2+}$ redox couples.

Herein, we describe a facile microwave irradiation route for preparing layered $m\text{-ZnV}_2\text{O}_6$ nanobelts with high electrochemical activity for highly rechargeable Na-ion energy storage. In the synthesis strategy, $m\text{-ZnV}_2\text{O}_6$ nanobelts were successfully achieved through the microwave irradiation method, using $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and NH_4VO_3 as precursors in a reaction time of only 8 h , in which the efficient fabrication of the highly-pure product in terms of time-saving is 24.5 times better in comparison with the traditional hydrothermal method ($210\text{ }^\circ\text{C}$, 196 h) in our previous report.⁴⁰ By continuously varying the dwell time parameter from 5 min to 4 h , detailed insight into a stepwise “topotactic transformation – Ostwald ripening” mechanism for the formation of layered $m\text{-ZnV}_2\text{O}_6$ nanobelts from tunnel-structured $m\text{-Zn}_2\text{V}_2\text{O}_7$ nanoflowers can be proposed. The topotactic transformation at the initial stage under microwave irradiation is related to

the crystal structural conversion of zinc vanadates and can provide an effective method for the controllable fabrication of uniform one-dimensional (1D) nanostructures with advanced applications. In terms of their sodium storage performance, *m*-ZnV₂O₆ nanobelts with intrinsic layered structure (interlayer distance of 0.2533 nm) exhibited a specific capacity of 235.3–484.9 mAh g⁻¹ at 100 mA g⁻¹, which is much better than that of *m*-Zn₂V₂O₇ nanoflowers (63.7–431.7 mAh g⁻¹) with tunnel structure. The enhanced properties are associated with the large S-shaped layered structures of the *m*-ZnV₂O₆ nanobelts, which allow particularly fast ion diffusion transport pathways, and the 1D shape with more electrochemical active sites provides reduced polarization of electron transport for Na⁺ high-rate capability. Therefore, layered *m*-ZnV₂O₆ nanobelt anode is very suitable for the sodium ion battery, with high energy, good reversibility, and long-term cycling.

Fig. 1 (a-d) Schematic structural model of *m*-ZnV₂O₆ based on Rietveld refinement results, viewed along the (a) [100], (b) [010], and (c) [001] directions.

2. Results and discussion

The microstructure of the uniform *m*-ZnV₂O₆ nanobelts was identified by X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), and high resolution TEM (HRTEM). To confirm the phase of the nanomaterial, Fig. 1a identifies a representative Rietveld refinement XRD pattern of single phase *m*-ZnV₂O₆ nanobelts (sample 1) with a layered structure, obtained through microwave irradiation for 8 h. The profile *R*-factor, *R_p*^{*}, was 9.63% (Table S1 in the Electronic Supplementary Information (ESI)). It can be observed that all the diffraction peaks can be indexed to a monoclinic phase of *m*-ZnV₂O₆ with lattice constants *a* = 9.242 Å, *b* = 3.526 Å, *c* = 6.574 Å, and β = 111.55°, which correspond well with the standard values [space group: *C*2 (No. 5), ICDD-JCPDS card No. 74-1262]. No peaks from impurity phases were detected, confirming that the product synthesized via the highly-efficient microwave irradiation route is of high purity. Fig. 2a-d presents SEM images of the as-synthesized *m*-ZnV₂O₆ nanobelts at different magnifications. From the low-magnification SEM images (Fig. 2b-d), it can be seen that the overall morphology of the products consists of large quantities of belt-like structures with lengths in the range of 45-70 μm and thickness of 80 nm. These nanobelts are interconnected to create a crossed network architecture, as shown in Fig. 1d. The higher magnification SEM image (Fig. 2e) further demonstrates the uniformity of the *m*-ZnV₂O₆ nanobelts with an average diameter of approximately

140 nm. Moreover, these nanobelts have very smooth surfaces in the further enlarged SEM image, and the layered structure can be also clearly observed from the top of the nanobelts. Furthermore, detailed structural analysis of the m -ZnV₂O₆ nanobelts was conducted by transmission electron microscopy (TEM) and high-resolution TEM. Two straight nanobelts with a uniform diameter of around 120-140 nm can be obviously detected, as shown in Fig. 2f and its inset. The HRTEM image of the top of a nanobelt, as marked by the red square, illustrates clear lattice fringes with good orientation, spontaneously conforming to the single crystallinity of 1D growth. From Fig. 2g, the lattice fringes with a spacing of 0.3083 nm correspond to the (-202) lattice planes of layered m -ZnV₂O₆, demonstrating that the growth direction of the nanobelts is along [010]. Significantly, the ordered layered structure provides excellent pathways for Na ion transport into the material without damaging the nanobelt topology.

Fig. 2 (a) The Rietveld refined XRD pattern for m -ZnV₂O₆ nanobelts synthesized through microwave irradiation for 8 h, with the experimental data background indicated by black dots, the calculated curve by the red lines, the observed curve by “×” symbols, and the difference curve by the blue line at the bottom. (b-d) Low-magnification SEM images for m -ZnV₂O₆ nanobelts, illustrating their one-dimensional topology. (e) High-magnification SEM image for an individual nanobelt, demonstrating the smooth surface and the diameter. (f) TEM micrographs for m -ZnV₂O₆ nanobelts, showing the high crystallinity of the product. The inset in (f) illustrates a high-resolution TEM image of the top area of the single nanobelt, as marked by the red square. (g) High-resolution TEM image of the inset in (f) that is marked by blue circle. The clear lattice

with spacing of 0.3083 nm corresponds to the (-202) planes of the m -ZnV₂O₆ nanobelt, implying 1D growth along the [010] direction.

Reaction time is a critical factor that can greatly influence the crystallinity of 1D nanomaterials and the overall growth processes.⁴¹ To monitor the evolution of m -ZnV₂O₆ nanobelts via the highly-efficient microwave process, the shape and composition changes of products at a continuous dwell time were intensively investigated by SEM images and XRD patterns, as shown in Figs. 3-4. Fig. 3 shows the morphology variation of Samples S2–S6 synthesized over reaction times of 5 min, 15 min, 1 h, 2 h, and 4 h, respectively. In the initial 5 min for Sample S2, nanoflowers with coexisting phases of ZnV₃O₈ and m -Zn₂V₂O₇ show a novel structure with four-fold symmetry, according to the observation of Fig. 3(a1-a2). From the high-magnification image in Fig. 3(a3), these nanoflowers consist of uniform nanosheets with diameters averaging 3.5–4.5 μ m and thickness of 40–50 nm. Moreover, the nanosheets exhibit a regular morphology with sharp edges and smooth surfaces. After 15 min for Sample S3, the coexistence of large quantities of nanosheets and monodisperse nanoflowers was successfully achieved (Fig. 3(b1-b3)), implying that the remarkable reduction of nanoflowers is favorable for increasing the amount of nanosheets after prolonged reaction time. When the dwell time was further extended to 1 h for Sample 4, irregular nanosheets (mixed phases of m -Zn₂V₂O₇ and m -ZnV₂O₆) became dominant on a large scale, with diameters ranging from 2 to 4 μ m, as measured via the low and high magnification SEM images depicted in Fig. 3(c1-c3). After the reaction time was prolonged to 2 h, the main phase of m -Zn₂V₂O₇ and trace m -ZnV₂O₆ (Sample S5) was the result. In addition, the corresponding XRD pattern in Fig. 4(c) can be indexed to m -Zn₂V₂O₇ with monoclinic symmetry ($a = 7.429$ Å, $b = 8.340$ Å, $c = 10.098$ Å, and $\beta = 111.37^\circ$, JCPDF No. 28-1492). Surprisingly, many nanobelt bundles (100 nm in size and 2–5 μ m in length) radiate from the outer surfaces of nanosheets and nanoflowers, leading to the decreased diameter of individual nanosheets (2.5–3.5 μ m). After 4 h of microwave irradiation time, the pure m -ZnV₂O₆ nanobelts with thickness of only 30–50 nm for Sample S6 were split from the nanobelt bundles. Obviously, the microwave irradiation field is likely to be the driving force for forming the uniform nanobelts from nanoflowers with increasing dwell time. Furthermore, the fabrication efficiency in terms of time-saving is 24.5 times greater in comparison with the hydrothermal method (210 °C for 196 h) in our reported studies.⁴⁰ In an overview, the composition of the as-obtained products varies from a mixture of phases (ZnV₃O₈, m -Zn₂V₂O₇, and m -ZnV₂O₆) to pure m -ZnV₂O₆, and the morphologies grow from dispersed nanoflowers, to the combination of nanoflowers and nanobelt bundles, and finally to pure nanobelts. As confirmed by the above explanations in the SEM and XRD analyses, the “topotactic transformation – Ostwald ripening” mechanism in this work is proposed to thoroughly understand the process. Until now, the transformation from m -Zn₂V₂O₇ to m -ZnV₂O₆ is the first example of the interesting conversion of m -ZnV₂O₆ through the time-saving microwave irradiation method, from a 3D tunnel structure to a 1D layered structure.

Fig. 3 Representative SEM images indicating the morphology changes of $m\text{-ZnV}_2\text{O}_6$ nanobelts fabricated through the microwave irradiation route over different reaction times: (a1-a3) Sample 2: 5 min, uniform nanoflowers assembled from nanosheets with diameters of 3.5–4.5 μm and thickness of 40–50 nm; (b1-b3) Sample 3, 15 min, coexistence of nanosheets (diameter: 2–3 μm , thickness: 45 nm) and nanoflowers (diameter: 2.2–4.2 μm); (c1-c3) Sample 4: 1 h, nanosheets (diameter: 2–4 μm); (d1-d3) Sample 5: 2 h, coexistence of abundant microbelt bundles and a few nanoflowers; and (e1-e3) Sample 6: 4 h, uniform nanobelts with gradually reduced amounts of nanoflowers.

Fig. 4 Typical XRD patterns of *m*-ZnV₂O₆ nanobelts at stepwise dwell times: (a) Sample 2: 5 min, combination of ZnV₃O₈ and *m*-Zn₂V₂O₇; (b) Sample 3: 15 min, main phases of *m*-Zn₂V₂O₇ and ZnV₃O₈; (c) Sample 4: 1 h, the main phase of *m*-ZnV₂O₆ and trace *m*-Zn₂V₂O₇; (d) Sample 5: 2 h, main phase of *m*-ZnV₂O₆ and small amount of *m*-Zn₂V₂O₇; and (e) Sample 6: 4 h, high-purity *m*-ZnV₂O₆.

Because of the similarities of the symmetries and crystal lattices, crystal structure models and TEM/HRTEM images demonstrate in detail the topotactic transformation from main phase *m*-Zn₂V₂O₇ nanoflowers with a tunnel structure to pure *m*-ZnV₂O₆ nanobelts with a well-organized layer structure, as depicted in Fig. 5. Perspective views of *m*-ZnV₂O₆ and *m*-Zn₂V₂O₇ along the *b* axis are shown in Fig. 5a-b, respectively. In the crystal diagram of Fig. 5a, *m*-Zn₂V₂O₇ exhibits a one-dimensional tunnel structure with alternating Zn–O and V–O layers, and the continuous channels along the [010] direction are perpendicular to the V–O layer to accommodate ionic insertion and extraction. Partial clear fringes with an interplanar spacing of 0.2637 nm in TEM/HRTEM images (Fig. 5c) are in good agreement with the separation distance between the (–222) lattice planes, which indicates the preferential one-dimensional tunnel framework. In the microwave irradiation process, VO₃[–] ions with an appropriate microwave dielectric property rapid diffuse into the *m*-Zn₂V₂O₇ crystal along the open tunnel pathways in the [010] direction. After extending the reaction time to 4 h, pure phase *m*-ZnV₂O₆ nanobelts (Fig. 5b) are built up from a layered framework of corner-sharing [VO₄] tetrahedra and [ZnO₄] tetrahedra that form layers running along the [010] direction.

Moreover, it is interesting to find that $[\text{ZnO}_4]$ tetrahedra chains are interconnected with each other through oxygen corner-sharing of $[\text{VO}_4]$ tetrahedral chains to generate a unique layered structure, in which they are arranged in an alternating pattern, as shown by the crystallographic view along the a -axis. In addition, the TEM/HRTEM images (Fig. 5d) indicate the interplanar d -spacing of 0.3083 nm, which is well indexed to the (-202) lattice planes of single-crystalline phase $m\text{-ZnV}_2\text{O}_6$, identified as the layer direction in the crystallographic $[010]$ view (Fig. 5b). After the topotactic reaction, the two phases of $m\text{-ZnV}_2\text{O}_6$ and $m\text{-Zn}_2\text{V}_2\text{O}_7$ have great monoclinic structural similarities and similarities in the relative positions of the Zn and V atoms, in spite of the different space groups, C2 (no. 5) and C2/c (no. 15), respectively. The interlayer spacing is estimated at approximately 0.2533 nm, which is very much larger in comparison with the Na^+ ion diameter of 0.204 nm. Surprisingly, the unique structure of $m\text{-ZnV}_2\text{O}_6$ nanobelts as an intriguing candidate opens up a simple way to tailor the electrochemical performance of reversible Na^+ insertion/extraction with high power density and long cycle life.

Fig. 5 Schematic diagrams of transformation conversion from (a) main phase of $m\text{-Zn}_2\text{V}_2\text{O}_7$ with tunnel structure (Sample S4) to (b) pure $m\text{-ZnV}_2\text{O}_6$ with layered structure (Sample S6). Representative TEM/HRTEM images of (c) an individual $m\text{-Zn}_2\text{V}_2\text{O}_7$ nanoflower, and (d) the pure $m\text{-ZnV}_2\text{O}_6$ nanobelts. The insets in (c)-(d) display the corresponding lattice structures.

The electrochemical performance of zinc vanadium for sodium storage, with 1 M NaClO₄ in a mixture of ethylene carbonate (EC) and diethyl carbonate (DEC) with a volume ratio of 1:1 used as the electrolyte over a cell voltage window between 3.0–0.02 V, was systematically characterized as shown in Fig. 6. The potential profiles of the three electrodes in Fig. 6(a-c) demonstrate sloping curves, exhibiting the initial discharge capacity of 484.9, 422.1, and 431.7 mAh g⁻¹, respectively. Furthermore, the discharge capacities for the second cycle are reduced to 327.2, 289.2, and 264.4 mAh g⁻¹. The slight capacity fading between the initial two cycles is associated with the generation of a very thin solid electrolyte interface film after electrode reaction and the irreversible trapping of Na⁺ ions diffused into the interlayer galleries of the host material.^{3,42} After the second cycle, the voltage profiles are mainly below 1.5 V, operating with an average voltage plateau of 1.0 V. Importantly, *m*-ZnV₂O₆ nanobelts (Sample S1) with layered structure deliver a remarkable higher discharge capacity than the mixed phase of *m*-Zn₂V₂O₇ and *m*-ZnV₂O₆ (Samples S4), and the coexistence morphology of *m*-ZnV₂O₆ nanobelts and nanoflowers (Sample S6). With decreasing percentage of *m*-Zn₂V₂O₇ with tunnel structure, an increasing phase representation of *m*-ZnV₂O₆ nanobelts results, leading to significant improvement in the electrochemical activity and feasible layer channels for Na⁺ insertion/extraction. Moreover, Fig. 6d demonstrates the long-term cyclability for these products at the same current density. What is more, the irreversible capacity loss in these electrodes shows the following sequence: Sample S1 < Sample S6 < Sample S4, implying that pure *m*-ZnV₂O₆ nanobelts achieve excellent structural stability (capacity of 235.3 mAh g⁻¹ at the 50th cycle) with high energy density. These improved performances are associated with two factors: (1) The *m*-ZnV₂O₆ nanobelts with a large S-shaped layered structure help to stabilize the high mobility of fast Na⁺ ion insertion/extraction pathways along the [010] direction and exhibit little rearrangement of the crystal structure during the cell cycles. (2) The 1D *m*-ZnV₂O₆ nanobelt topology with more electrochemically active sites considerably permits reduced polarization of electron transport and reduced energetic barriers for rechargeable Na⁺ ion storage. Therefore, our research provides a promising candidate as anode material and lays the foundation for a new way of designing electrode structures for the sodium ion battery.

Fig. 6 Sodium storage properties of m - ZnV_2O_6 nanobelts as a highly reversible anode material: (a-c) the 1st, 2nd, 3rd, and 5th galvanostatic charge-discharge curves of Samples S1 (high-purity m - ZnV_2O_6 nanobelts), Sample S4 the main phase of m - ZnV_2O_6 and trace m - $\text{Zn}_2\text{V}_2\text{O}_7$, nanosheets), and Sample S6 (high-purity m - ZnV_2O_6 , uniform nanobelts with gradually reduced amounts of nanoflowers), respectively, at a current density of 10 mA g^{-1} in the voltage window of 0.02–3.0 V versus Na^+/Na at 25°C . (d) Long-term cycling performance of m - ZnV_2O_6 nanobelts anode at a current density of 10 mA g^{-1} for 50 cycles.

3. Conclusion

To summarize, we have reported that a microwave irradiation route allows for the preparation of uniform layered m - ZnV_2O_6 nanobelts within the dwell time of 8 h and demonstrated their tremendous potential for usage in sodium ion batteries. In the synthesis process, the m - ZnV_2O_6 nanobelts with ordered layer architectures were achieved through a structure-directed “topotactic transformation – Ostwald ripening” mechanism governing the transition from m - $\text{Zn}_2\text{V}_2\text{O}_7$ nanoflowers with 1D tunnel structure to layered m - ZnV_2O_6 due to the high similarity of the two crystal structures. Moreover, layered m - ZnV_2O_6 nanobelts deliver an initial specific capacity of 484.9 mAh g^{-1} and a reversible specific capacity of 235.3 mAh g^{-1} at 10 mA g^{-1} , which is very much higher than that of tunnel-structured m - $\text{Zn}_2\text{V}_2\text{O}_7$ nanoflowers (63.7 – 431.7 mAh g^{-1}). The enhanced energy density and cycling performance of the m - ZnV_2O_6 nanobelt anode were attributed to the stable layered structure for high mobility of Na^+ ion transport along the [010] direction, and the

reduced polarization of electron transport and reduced energetic barriers for the 1D nanomaterials. It is believed that this study opens up a new pathway for extending this highly-efficient method to the design of novel nanostructures for reversible sodium ion batteries with high energy density and power density.

4. Methods

4.1 Synthesis of layered *m*-ZnV₂O₆ nanobelts

Zinc nitrate (Zn(NO₃)₂·6H₂O), and ammonium metavanadate (NH₄VO₃) were purchased from No.3 Factory of Tianjin Chemical Reagent Company (China). Both of the chemical reagents were of analytical grade and used without further purification.

Zinc vanadium oxide nanomaterials were successfully synthesized through the microwave irradiation method (Table S2 in the ESI). In a typical procedure, the fabrication process can be described as follows. Zn(NO₃)₂ aqueous solution was obtained by dissolving 0.2976 g of Zn(NO₃)₂·6H₂O crystals in 5 mL of distilled water at room temperature. Then, 0.002 mole of NH₄VO₃ powders were transferred into 18.5 mL of distilled water with continuous stirring to form a homogeneous and clear solution. Subsequently, the NH₄VO₃ solution was added dropwise into the Zn(NO₃)₂ solution under intense stirring for 10 min. The above mixture was transferred into the reacting vessel of a modified cyclic microwave reactor (model: Midea PJ21C-AU, power: 700 W, frequency: 2450 MHz). After the reaction was completed, the fluffy wool-like products were obtained and naturally cooled to ambient temperature. Finally, the products were collected through centrifugation, washed several times with distilled water and absolute ethanol, and then dried in a vacuum oven at 80 °C for 12 h for further analysis.

4.2 Materials characterization

The X-ray diffraction (XRD) patterns of the as-prepared ZnV₂O₆ samples were recorded on a Rigaku D/Max2500PC (Japan) diffractometer with Cu-K α radiation ($\lambda = 1.54056 \text{ \AA}$).⁴³⁻⁴⁵ Field-emission scanning electron microscope (FE-SEM) images were collected by a Hitachi S-4800 operating at an accelerating voltage of 10 kV to measure the shape of samples. Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) were performed on a Philips Tecnai G2 F20 transmission electron microscope using an accelerating voltage of 200 kV.

4.3 Electrochemical analyses

Sodium ion battery properties were measured in CR2032 type coin cells, consisted of a working electrode, a polypropylene separator and a Na foil counter electrode. These coin cells were sealed in an argon-filled glove-box (Mbraun, Unilab, Germany). The electrolyte solution was 1 M NaClO₄ in a 50:50

vol.% mixture of ethylene carbonate (EC) and diethylene carbonate (DEC). The working electrodes were prepared from the as-obtained zinc vanadium nanomaterials, acetylene black (AB), and polyvinylidene fluoride (PVDF) with a weight ratio of 80:10:10. All discharge–charge performances were tested galvanostatically on a LAND CT 2001A Battery Test System in the voltage range of 0.02–3.0 V. Three times of parallel measurements were performed to ensure reliability.

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Supporting Information

Electronic Supplementary Information (ESI) available: (1) Table S-2: The refined data of high-purity *m*-ZnV₂O₆ nanobelts for Sample 1 achieved through the microwave irradiation route. (2) Table S1: Microwave irradiation fabrication conditions for novel zinc vanadium micro/nanomaterials.

Notes and references

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