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High-yield and Eco-Friendly Fabrication of Ultra-Long (NH₄)₂V₆O₁₆·1.5H₂O Nanowires and Their Electrochemistry Performances

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Ultra-long $(NH_4)_2V_6O_{16}\cdot 1.5H_2O$ nanowires are synthesized in high-yield by a chitosan (CTS) assisted hydrothermal approach at 180 °C for 24 h. The as-prepared materials are characterized by various characterization methods. The experimental results reveal that the products are pure $(NH_4)_2V_6O_{16}\cdot 1.5H_2O$ single crystals with a width of 200-300 nm and a length of more than 150 µm. Such ultra-long $(NH_4)_2V_6O_{16}\cdot 1.5H_2O$ nanowires present great lithium-ion transmission ability, high electrochemical storage capacity. The nanowires deliver initial discharge specific capacity of 183.6 mAh g⁻¹ at 50 mA g⁻¹. After 50 cycles, they still retained discharge specific capacity of 161.6 mAh g⁻¹, exhibiting good cyclic stability.

Keywords: Ultra-long $(NH_4)_2V_6O_{16} \cdot 1.5H_2O$ nanowires; hydrothermal approach; electrochemical performance; Li-ion batteries

1. INTRODUCTION

Lithium-ion battery, a new type of rechargeable storage battery, is widely used in mobile phones, digital products, notebook computers and other portable electronic devices for mitigating greenhouse effect and the energy crisis [1]. Considerable efforts have been made to improve the availability, sustainability, safety and low cost of rechargeable storage battery [2]. Among them, vanadium oxides and their derivatives are considered very promising cathode materials in secondary lithium batteries for high electric conductivity, high theoretical electrochemical specific capacity, and thus have attracted much interest [3–8].

In order to improve the energy density and long cycle life of the Lithium-ion battery, various methods, such as hydrothermal method [9], solvothermal method [10], electrospinning method [11],

co-precipitation [12], glycothermal [13] and sol-gel [14] have been developed to synthesize vanadium oxides and ammonium vanadium oxides nanostructure materials for high specific surface area and high Li⁺ diffusion rate. For example, Wang fabricated the NH₄V₃O₈ nanorod by a sodium dodecyl benzene sulfonate (SDBS) assisted hydrothermal reaction and reported that the NH₄V₃O₈ nanorod exhibited high discharge capacity of 327.1 mAh g⁻¹ at 30 mA g⁻¹ [15]. They also prepared NH₄V₃O₈ $\cdot 0.2$ H₂O flakes with highest discharge capacity of 225.9 mAh g⁻¹ at 15mA g⁻¹ [16]. By homogeneous precipitation method, Park prepared $(NH_4)_2V_6O_{16}$ nanorods which indicated discharge capacity of 210 mAh g⁻¹ at the current density of 10 mA g⁻¹ [17]. The NH₄V₄O₁₀ nanobelts and nanowires have been prepared by Zhang and Fang, respectively. They all proved NH₄V₄O₁₀ could be thought as one promising cathode material in the lithium battery [18, 19]. Ma obtained (NH₄)_{0.6}V₂O₅ brick-like nanostructure which shown an initial specific discharge capacity of 244.3 mAh g⁻¹ at 20 mA g⁻¹ which is superior to the performance of (NH₄)_{0.5}V₂O₅ [20, 21]. Chithaiah and Wang have synthesized (NH₄)₂V₆O₁₆·1.5H₂O nest-like structure and nanowire, respectively [22, 23]. However, both of these methods didn't give electric chemical data of this kind of materials. Therefore, the research on highyield and eco-friendly methods to synthesize (NH₄)₂V₆O₁₆·1.5H₂O nanostructures for improving electrochemistry performances is still a big challenge.

In this work, ultra-long $(NH_4)_2V_6O_{16}\cdot 1.5H_2O$ nanowires were synthesized by an eco-friendly surfactant assisted hydrothermal approach. This method uses neither exotic seed and toxic reagents nor complex equipment. Systematic experiments were completed to investigate the effects of different reaction parameters on the morphology of the products. The electrochemical property of the asprepared $(NH_4)_2V_6O_{16}\cdot 1.5H_2O$, such as discharge capacity and cycling stability were explored. The research results demonstrated that the as-prepared $(NH_4)_2V_6O_{16}\cdot 1.5H_2O$ have great lithium-ion insertion and extraction ability and excellent cycling stability.

2. EXPERIMENTAL

2.1. Synthesis of ultra-long $(NH_4)_2V_6O_{16}$ ·1.5H₂O nanowires

The ultra-long $(NH_4)_2V_6O_{16}\cdot 1.5H_2O$ nanowires were prepared via a hydrothermal reaction in a Teflon-lined autoclave. In a typical procedure, 0.565 g NH₄VO₃ was dispersed in 60 ml distilled H₂O in a 100 ml beaker and stirred vigorously at 50 °C until it was dissolved. After the solution was cooled down to room temperature, 24.6 mg chitosan (CTS), which was used as the soft template surfactant, was added with constant stirring for 50 min until orange yellow solution was obtained. Then 5 ml H₂O₂ (30 wt %) was added to the above solution and stirred for 15 min. Next, a small amount of nitric acid was added drop wisely to adjust the pH value of the solution to 1.3. After then, the above solution was transferred into an 80 ml reaction kettle and continued to react for 24 h at 180 °C. The brick-red products (over 99% yield, according to the amount of (NH₄)₂V₆O₁₆·1.5H₂O input) were collected by centrifugation and then dried at 60 °C for 12 h.

2.2. Characterization

The phase structure was investigated by X-ray powder diffraction (XRD) (Beijing Purkinje General Instrument Co., Ltd.) with Cu Ka (λ =0.15406 Å) radiation with the scanning rate of 5° min⁻¹, ranging from5° to 55°. Fourier transform infrared spectroscopy (FTIR) was texted on a Nicolet 6700 spectrophotometer (Thermo Nicolet) ranging from 4000 to 400 cm⁻¹. The morphology of the products was characterized by SEM (Shimadzu JSM 6610) and TEM (Hitachi H-800).

2.3. Electrochemical measurements

The test electrode slurry was obtained by blending the prepared material, polyvinylidene fluoride (PVDF) and carbon black in the N-methylpyrrolidone solvent with the weight ratio of 70:10:20. The slurry was spread onto aluminum foil disks and dried in a vacuum oven at 120 °C for 12 h. The electrolyte used in assembling the battery was 1M LiPF₆ in ethylene carbonate (EC), propylene carbonate (PC) diethyl carbonate (DMC) (EC/PC/DMC, 1/1/1 vol.). The coin-like electrodes were placed on a LAND battery testing system for characterizing the electrochemical performances. The arbin electrochemical workstation was used for testing cyclic voltammetry curve (CV).

3. RESULTS AND DISCUSSION

Fig. 1a shows the XRD pattern of the standard samples prepared at 180 °C for 24 h. All of the diffraction peaks are perfectly indexed as the monoclinic (NH₄)₂V₆O₁₆·1.5H₂O crystals (PDF no. 51-0376) with lattice parameters a = 12.343Å, b = 3.592Å, c = 16.410Å. The sharp peaks indicate the high crystallinity of the sample. No other characteristic peaks of impurities, such as V₂O₅, NH₄V₄O₁₀ and $(NH_4)_2V_6O_{16}$, can be detected in this pattern, indicating that pure $(NH_4)_2V_6O_{16} \cdot 1.5H_2O$ are obtained. Fig. 1b shows the FTIR spectrum of the as-prepared sample. As can be observed, there are eight absorption bands at 3828, 3168, 1623, 1400, 1003, 957, 734 and 538 cm⁻¹, respectively. The absorbability at 3528 cm⁻¹ (O-H) and 1623 cm⁻¹ (H-O-H) confirm the existence of the water molecules [24]. The broad band at 3168 cm^{-1} and 1400 cm^{-1} are attributed to the asymmetric stretching and the symmetric bending vibrations of N-H of NH₄⁺ [25]. According to the report of Frederickson and Hausen, the stretching modes of VO could be observed in two distinct regions, 950 to 1000 cm⁻¹ and 720 to 760 cm⁻¹ [26]. That is to say, the notable bands of $(NH_4)_2V_6O_{16}$. 1.5H₂O appeared at 1003 cm⁻¹ and 957 cm⁻¹. They are ascribed to the stretching vibration of $V^{5+}=O$ and $V^{4+}=O$ groups, corresponding to the existence of the short-range order of the VO_6 unit [27]. The band at 734 cm⁻¹ and 538 cm⁻¹ are assigned to the asymmetric and symmetric stretching vibration of V-O-V bonds [28]. The FTIR spectra give further evidence that the as-prepared products are pure $(NH_4)_2V_6O_{16}\cdot 1.5H_2O$ phase, which is in agreement with the XRD result.

Fig. 1c shows a representative SEM image of the sample prepared at 180 °C for 24 h. It indicates that the as-synthesized products are composed of one-dimensional $(NH_4)_2V_6O_{16}\cdot 1.5H_2O$ nanowires with the length beyond 150 µm. Fig. 1d is the high magnification SEM image of the sample.

It reveals that the $(NH_4)_2V_6O_{16}\cdot 1.5H_2O$ crystallites are smooth nanowires without the presence of fractures and defects. Fig. 1e shows a typical TEM image of the ultra-long $(NH_4)_2V_6O_{16}\cdot 1.5H_2O$ nanowires. It can be seen that the diameter of products is 200-300 nm, consisting with the SEM results. The TEM images of an individual nanowire (Fig. 2f) and corresponding SAED pattern (inset of Fig. 2f) indicate that the samples are single crystal with good crystallinity, which is consistent with the XRD result.

According to our experiments, the chemical reaction for the formation of $(NH_4)_2V_6O_{16} \cdot 1.5H_2O$ can be proposed as following:

$$5[V_{4}O_{12}]^{4-} + 8H^{+} \rightarrow 2[V_{10}O_{28}]^{6-} + 4H_{2}O$$

$$2[V_{10}O_{28}]^{6-} + H^{+} \rightarrow [HV_{10}O_{28}]^{5-}$$

$$(2)$$

$$[HV_{10}O_{28}]^{5-} + H^{+} \rightarrow 2[H_{2}V_{10}O_{28}]^{4-}$$

$$(3)$$

$$[H_{2}V_{10}O_{28}]^{4-} + 4H^{+} + 32H_{2}O \rightarrow 10[VO(OH)_{3}(H_{2}O)_{2}]$$

$$(4)$$

$$6[VO(OH)_{3}(H_{2}O)_{2}] + 2NH_{4}^{+} \rightarrow (NH_{4})_{2}V_{6}O_{16} \cdot 1.5H_{2}O + 18.5H_{2}O + 2H^{+}$$

$$(5)$$

In this process, ammonium metavanadate (NH₄VO₃) in the aqueous solution can forms NH₄⁺ and $[V_4O_{12}]^{4-}$ ions. When acid ion was added to the solution, the pH value of the solution decreased gradually and generated different complex of polyvanadates. Adding more nitric acid (HNO₃), the complex of polyvanadates remained unchanged and the materials begin to react with hydrogen ion. The mixture changed rapidly from faint yellow (Eq 2) to orange yellow (Eq 3), indicating the formation of $[HV_{10}O_{28}]^{5-}$.



Figure 1. (a) XRD pattern and (b) typical FTIR spectrum of the as-prepared sample; (c) and (d) the magnification SEM image; (e) TEM image of the $(NH_4)_2V_6O_{16}\cdot 1.5H_2O$; (f) TEM image of an individual $(NH_4)_2V_6O_{16}\cdot 1.5H_2O$ nanowire; inset: corresponding SAED pattern.

When the HNO₃ was added drop wisely to the solution, the color changed to salmon pink (Eq 4). Then the decavanadate $[H_2V_{10}O_{28}]^{4-}$ species gets protonated (Eq 5) to provide neutral $[VO(OH)_3(H_2O)_2]$ precursors at the early process of hydrothermal approach with the reaction at 180 °C for 24 h. At last, in the existence of the NH₄⁺ ion and H₂O₂, the (NH₄)₂V₆O₁₆·1.5H₂O phase results from polycondesation of the neutral $[VO(OH_3)(H_2O)_2]$ precursors (Eq 6). Such formation process is similar to the previous report [27].

More experiments were completed to investigate the effects of different reaction parameters on the morphology of the products. Fig. 2d shows the XRD pattern of the samples obtained at 180 °C for 10 h, 16 h and 32 h, respectively. As shown in Fig. 2d. (1) and (2), three diffraction peaks are observed at 20 11.291°, 22.723° and 59.011°, which correspond to (100), (200) and (500) planes of $(NH_4)_2V_6O_{16}$ (PDF no. 22-1046), respectively. In addition, there are still exist other characteristic peaks, such as 9.203° in the pattern, which was related to (101) plane of $(NH_4)_2V_6O_{16} \cdot 1.5H_2O$. When the reaction parameters are 180 °C for 24 h, the characteristic peaks of $(NH_4)_2V_6O_{16} \cdot 1.5H_2O$ and $(NH_4)_2V_6O_{16}$ are simultaneously existed. With prolonging the reaction time, the $(NH_4)_2V_6O_{16}$ decrease while the $(NH_4)_2V_6O_{16} \cdot 1.5H_2O$ increase and the aspect ratio of the samples is becoming higher gradually (compared with Fig. 2a and Fig. 2b).



Figure 2. (a) SEM image of the products synthesized at 180 °C for different reaction times: (a) 10 h, (b) 16 h, (c) 32 h; (d) the relevant of XRD pattern: (1) 10 h, (2) 16 h, (3) 32 h; (e) XRD pattern of the samples with (a) obtained at 24 h for different reaction temperature and (f) different amounts of H₂O₂.

When the reaction parameters are 180 °C for 32 h, the sample is $(NH_4)_2V_6O_{16}\cdot 1.5H_2O$ with no peaks of other materials (Fig. 2d). The morphology of the sample collected at 32 h is general long nanowire, but the surface of the nanowire have many small sticks (Fig. 2c) compared with the product obtained at 180 °C for 24 h (Fig. 1d). That is to say, when the reaction time is too long, the ultra-long nanowire tends to cracks.



Figure 3. (a) Discharge-charge curves of the 1st, 2nd, 50th cycles of (NH₄)₂V₆O₁₆·1.5H₂O electrodes at 50 mA g⁻¹ current density in the voltage of 2.0-3.8 V vs. Li/Li⁺. (b) Its corresponding cyclic performance and the coulombic efficiency. (c) CV curves of (NH₄)₂V₆O₁₆·1.5H₂O at 0.1 mv s⁻¹. (d) Cycling performance of the (NH₄)₂V₆O₁₆·1.5H₂O at various current densities.

Fig. 2e shows a representative XRD pattern of the samples obtained at 24 h for 140 °C, 180 °C and 220 °C, respectively. As shown in Fig. 2e, When the reaction temperature is 140 °C, there are coexist the characteristic peaks of $(NH_4)_2V_6O_{16}$ and $(NH_4)_2V_6O_{16} \cdot 1.5H_2O$. When the reaction temperature reach to 180 °C, the characteristic peaks of $(NH_4)_2V_6O_{16}$ disappeared, and pure $(NH_4)_2V_6O_{16} \cdot 1.5H_2O$ was obtained without impurities. When the reaction temperature rise to 220 °C,

the characteristic peaks of $(NH_4)_2V_6O_{16}\cdot 1.5H_2O$ can be seen in the XRD pattern, Meanwhile, there also exist the peaks of impurities. Apparently when the reaction parameters are 180 °C at 24 h, pure ultralong $(NH_4)_2V_6O_{16}\cdot 1.5H_2O$ nanowires can be obtained.

In this system, it should be noted that H_2O_2 is a critical factor for the formation of $(NH_4)_2V_6O_{16} \cdot 1.5H_2O$ nanostructures. Fig. 2f shows a representative XRD pattern of the simples with different amounts of H_2O_2 . In the absence of H_2O_2 , the products are indexed to $NH_4V_4O_{10}$ with a little $(NH_4)_2V_6O_{16}$. With increasing the amount of H_2O_2 , the peaks of $NH_4V_4O_{10}$ gradually decreased. At the same time, there are obvious increase in the intensity of $(NH_4)_2V_6O_{16}$ and $(NH_4)_2V_6O_{16} \cdot 1.5H_2O$ peaks. Upon the introduction of 3 ml H_2O_2 , the crystalline structures are mainly $(NH_4)_2V_6O_{16} \cdot 1.5H_2O$ with a bit of $NH_4V_4O_{10}$. When the amount of H_2O_2 reach to 5 ml, high purity of $(NH_4)_2V_6O_{16} \cdot 1.5H_2O$ with good crystallinity is prepared (see Fig. 1a). Above results reveal that H_2O_2 can effectively shorten the reaction time, Comparing with the precious report [23].

The electrochemical performance of the $(NH_4)_2V_6O_{16}\cdot 1.5H_2O$ nanowires was studied by assembling the materials into LIR2032 coin type cells. As is shown in Fig. 3a, the initial discharge specific capacity can reach 183.6 mAh g⁻¹. The $(NH_4)_2V_6O_{16}\cdot 1.5H_2O$ exhibits good discharge ability for the second discharge curve almost overlap the first one. What's more, the discharge capacity of 161.6 mAh g⁻¹ is retained after 50 cycles. It is believed that under the low current density, Lithium ion may encounter a low resistance on the process of Li⁺ transmission [15]. Fig. 3b shows the cycling performance of $(NH_4)_2V_6O_{16}\cdot 1.5H_2O$ and the corresponding coulombic efficiency at current density of 50 mA g⁻¹. In general, the discharge capacity of the product shows a slow capacity fading, but it still retains 143.4 mAh g⁻¹ at 150th cycle (about 80% capacity). The coulombic efficiency of the product maintains 99% throughout the overall cycling test. That is, the electrode is able to charge and discharge in the organic electrolyte, for Li-ion can highly reversibly insert into and extract from $(NH_4)_2V_6O_{16}\cdot 1.5H_2O$ crystal.

Fig. 3c shows the initial three consecutive cyclic voltammograms at a scan rate of 0.1 my s⁻¹ in the voltage of 2.0-3.6 V vs. Li/Li⁺. The scans are starting at the open circuit potential to 2.0 V, so there are high current at the first scan. One pair of redox peaks with the reduction peak at 2.63 V and the corresponding oxidation peak at 2.87 V is observed for the product. The CV curve of $(NH_4)_2V_6O_{16} \cdot 1.5H_2O$ present only one obvious reduction peak, while the $(NH_4)_2V_6O_{16}$ exist four reduction peaks, indicating one step insertion of Li-ion into the matrix which almost consistent with the discharge plateau in Fig. 3a. That is to say, $(NH_4)_2V_6O_{16} \cdot 1.5H_2O$ can be used as cathode materials with fewer discharge platform. It is noted that the CV curve have completely maintained the initial state after two cycles, suggesting $(NH_4)_2V_6O_{16} \cdot 1.5H_2O$ have good reversibility and great cycling stability in the Li-ion transmission process. In addition, the rate capability of the $(NH_4)_2V_6O_{16} \cdot 1.5H_2O_{16} \cdot 1.5$ was also evaluated between 100 mA g⁻¹ and 800 mA g⁻¹ (shown in Fig. 3d). The discharge capacities of 153.1, 135.5, 104.8, 53.5 and 27.9 mAh g^{-1} are observed at 100, 200, 300, 500 and 800 mA g^{-1} , respectively. In general, the specific discharge of the product decreased with increasing the current rates. When the rates revert to lower values, the electrode recovers nearly the initial capacity. When cycling at 100 mA g⁻¹ again, a high capacity of 148.7 mAh g⁻¹ is recovered without obvious capacity fading after cycling at various current densities. What's more, the discharge capacity of the product still shows 140.1 mAh g⁻¹ (about 91.5% capacity) after the subsequent 40 cycles.



Figure 4. Discharge cycling performance of the $(NH_4)_2V_6O_{16}\cdot 1.5H_2O$ at various current densities; inset: corresponding discharge curves.

Fig. 4 shows the discharge curves and its corresponding cycling performance at various current densities. The initial discharge capacities of 147.8, 135.3 and 105.9 mAh g⁻¹ were observed at 100, 200, 300 mA g⁻¹, respectively which is consistent with the Fig. 3d. The shapes of the curve at different current rates didn't change compared with the Fig. 3a. Even the current density reach 300 mAh g⁻¹, the $(NH_4)_2V_6O_{16} \cdot 1.5H_2O$ was still stable in insertion/extraction processes without obvious capacity fading and the discharge capacity of the product still showed a capacity of 70.5 mAh g⁻¹ (with a retention of 66.6%) after 150 cycles. Apparently, the as-prepared $(NH_4)_2V_6O_{16} \cdot 1.5H_2O$ nanowire possess great Liion storage stability and cycling stability.

4. CONCLUSIONS

In summary, ultra-long $(NH_4)_2V_6O_{16}\cdot 1.5H_2O$ nanowires with good cycling stability have been synthesized by a facile and eco-friendly hydrothermal method. The ultra-long nanowires are about 200-300 nm in width and the length up to 150 µm. The as-obtained $(NH_4)_2V_6O_{16}\cdot 1.5H_2O$ electrode shows the initial discharge capacity of 183.6 mAh g⁻¹ at 50 mA g⁻¹ and the capacity retention of the product still maintains 80% after 150 cycles. Due to the great lithium-ion transmission ability, high specific capacities and excellent cycling stability, such ultra-long $(NH_4)_2V_6O_{16}\cdot 1.5H_2O$ nanowires could be found potential applications as a promising cathode material for lithium-ion battery.

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