A Novel Process for the Synthesis of NaV$_2$O$_5$ Mesocrystals from Alkaline-Stripped Vanadium Solution via the Hydrothermal Hydrogen Reduction Method

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Abstract: NaV$_2$O$_5$ mesocrystals were successfully synthesized from an alkaline-stripped pentavalent vanadium solution through a novel hydrothermal hydrogen reduction process. The optimal conditions for the hydrogen partial pressure, reaction temperature, initial solution pH value, and reaction time for the pure-phase NaV$_2$O$_5$ synthesis were ascertained to be 4 MPa, 200 $^\circ$C, 4.0, and 2 h, respectively. The synthesis time (only 2 h) was greatly shortened, by nine times, compared with the most time-saving (18 h) hydrothermal process at present. X-ray diffraction (XRD) analysis revealed that the as-prepared powders demonstrated a typical layered orthorhombic structure of NaV$_2$O$_5$. The purity of the as-prepared NaV$_2$O$_5$ reached up to 99.98%. An electrochemical test showed that the as-prepared NaV$_2$O$_5$ has a potential application in sodium ion batteries. According to scanning electron microscopy (SEM) and transmission electron microscopy (TEM) analyses, the as-prepared NaV$_2$O$_5$ powders were identified to have rod-like mesocrystals consisting of small rods which preferentially grow along the (010) direction. Furthermore, the phase transformation mechanism and crystal growth mechanism in NaV$_2$O$_5$ preparation were discussed systematically, based on which the synthesis mechanism of NaV$_2$O$_5$ was proposed as pentavalent vanadates pre-sedimentation, hydrogen reduction with dehydration, sodium ions insertion, and finally self-assembly oriented attachment. The synthesis process is characterized as time-saving and low-cost, and thus it may have great application prospects.

Keywords: NaV$_2$O$_5$; hydrothermal; hydrogen reduction; vanadium

1. Introduction

Vanadium (V) and its compounds have been widely used in many fields such as electrode materials, catalysts, steel alloys, V redox flow battery, advanced materials, and the chemical industry [1–4]. NaV$_2$O$_5$ is one of the typical layered alkali vanadates of orthorhombic structure. In the NaV$_2$O$_5$ structure, Na-ions are located in the interlayer space [5–7]. NaV$_2$O$_5$ initially drew much attention for its spin-Peierls property [8–15]. In recent years, NaV$_2$O$_5$ has been considered to have a potential application as the cathode material in lithium ion batteries or sodium ion batteries owing to its layered orthorhombic structure [16–19]. Therefore, the preparation of NaV$_2$O$_5$ has been attracting increasing attention.
NaV$_2$O$_5$ can be prepared by a solid-state reaction process, but this process requires a reaction temperature of 650 °C and a long reaction time (more than two days) [20–23]. In order to lower the reaction temperature, some hydrothermal methods have been developed [5,6,16–18,24]. In the hydrothermal methods, V$_2$O$_5$, NH$_4$VO$_3$, and NaVO$_3$ are usually used as vanadium resources, NaOH and Na$_2$CO$_3$ are usually used as sodium resources, and NH$_2$OH·HCl, ethylene diamine tetraacetic acid (EDTA), H$_2$C$_2$O$_4$, and Na$_2$C$_2$O$_4$ are usually used as reducing agents. Through hydrothermal methods, the reaction temperature for the preparation of NaV$_2$O$_5$ can be lowered to about 200 °C, while the reaction time still must be at least 18 h. Moreover, reducing agents such as NH$_2$OH·HCl and EDTA are very expensive. The long reaction time and the high price of the agents are disadvantages for the large-scale preparation and application of NaV$_2$O$_5$. Therefore, there is high demand for the development of a time-saving and low-cost process to prepare NaV$_2$O$_5$.

Vanadium-bearing shale is a unique and a strategic vanadium resource that is used in China. Vanadium-bearing shale is also an important raw material for the preparation of V$_2$O$_5$, NH$_4$VO$_3$, NaVO$_3$, and other vanadium compounds through various vanadium extraction processes [25]. Alkaline-stripped pentavalent vanadium solution (ASPVS) is a vanadium-enriched solution obtained in the vanadium extraction process. The typical flowsheet for ASPVS formation is shown in Figure 1 [26]. The extraction agent for pentavalent vanadium (V(V)) ions enrichment is trialkylamine and the stripping agent is sodium hydroxide solution. After the formation process, the ASPVS containing vanadium (V) and sodium (Na) with high concentrations as well as trace impurity ions is prepared [26]. Hence, ASPVS may be expected to be both a sodium resource and a vanadium resource for the preparation of NaV$_2$O$_5$.

![Alkaline stripped pentavalent vanadium solution](image)

**Figure 1.** Typical flowsheet for alkaline stripped pentavalent vanadium solution formation.

In previous research, a vanadium precipitation process of hydrothermal hydrogen reduction (HHR) for synthesizing V$_2$O$_3$ from ASPVS was first developed [27,28]. In the research, it was found that V(V) ions in the solution could be reduced to trivalent vanadium (V(III)) compounds or tetravalent vanadium (V(IV)) compounds by hydrogen (H$_2$). In the HHR reaction, the thermodynamic feasibility of the reaction increases as the solution pH value decreases, while the activity of hydrogen (H$_2$) and the solubility of hydrogen increase as the reaction temperature and the hydrogen partial pressure increase, respectively. Therefore, the degree of the reduction of the product obtained by this method is related to the solution pH value, reaction temperature, hydrogen (H$_2$) gas partial pressure, and reaction time. Additionally, it was found that NaV$_2$O$_5$ was first precipitated from ASPVS in the HHR process, which was further transformed to VO$_2$(H$_2$O)$_{0.5}$ and finally reduced to V$_2$O$_3$. Therefore, it is reasonable to prepare pure-phase NaV$_2$O$_5$ through the HHR method by controlling reaction conditions. If so, the synthesis process can be low-cost, because ASPVS and H$_2$ are much cheaper than the raw materials.
and reducing agents used in the previous processes. Moreover, it will be more exciting if the synthesis time can be greatly shortened.

In this paper, the HHR method for preparing pure-phase NaV$_2$O$_5$ from ASPVS is proposed. Through controlling the reaction temperature, solution pH value, H$_2$ consumption, and reaction time, the pure-phase NaV$_2$O$_5$ was successfully synthesized. The effects of different synthesis conditions on the vanadium precipitation percentage and the phase composition of the as-prepared product were investigated in detail. Importantly, the reaction time was shortened to 2 h. Furthermore, the synthesis mechanism of NaV$_2$O$_5$ was revealed in detail.

2. Materials and Methods

2.1. Materials and Reagents

Alkaline stripped pentavalent vanadium solution was prepared from vanadium-bearing shale by a typical vanadium extraction process [26]. H$_2$ gas (99.9% purity) and N$_2$ gas (99.9% purity) were used as the reducing agent and flushing gas, respectively, in the experiment. Distilled water was used in the whole process.

2.2. Synthesis Methods

For NaV$_2$O$_5$ synthesis, ASPVS (150 mL) was first adjusted to a certain pH value by sulfuric acid to prepare the feed solution. The feed solution was then poured into a 250 mL autoclave. The autoclave was flushed by N$_2$ gas three times. After this was done, it took 1 h to heat the solution to the reaction temperature, following which H$_2$ gas was transferred into the autoclave. After the hydrothermal reaction had taken place for a certain period of time, the heating procedure was turned down to cool the autoclave. The collected powder was first washed by distilled water and then dried at 90 °C for 10 h to obtain the final product.

2.3. Characterization

The phase composition of the as-prepared product was analyzed by X-ray diffraction (XRD, D/MAX 2500PC, Rigaku, Tokyo, Japan) using Cu Kα radiation. The micro morphology of the product was investigated by scanning electron microscopy (SEM, JSM-IT300, JEOL Ltd., Tokyo, Japan) and transmission electron microscopy (TEM, JEM-2100F, JEOL Ltd., Tokyo, Japan). The elemental analysis was conducted on an energy-dispersive spectrometer (EDS, X-Act, Oxford Instruments, Oxford, UK). The concentration of the solution and the chemical composition of the product were detected through inductively coupled plasma–atomic emission spectroscopy (ICP–AES, Optima-4300DV, Perkin Elmer, Waltham, MA, USA).

2.4. Electrochemical Testing

The electrochemical performance of the obtained NaV$_2$O$_5$ was characterized by coin cell assembly (2016-type). The obtained NaV$_2$O$_5$, acetylene black, and polyvinylidene difluoride (10 wt.%) were mixed well in weight ratios of 8:1:1, dissolved in N-methyl pyrrolidone solution to obtain a slurry. The obtained slurry was coated uniformly onto aluminum foil, and then dried at 90 °C for 12 h. The dried aluminum foil was punched into round discs with a diameter of 8 mm. The surface density of active materials was about 2 mg·cm$^{-2}$. The coin cell (2025) was assembled in an argon-filled glove box with sodium metal as the counter electrode and Grade GF/D (Whatman, Maitstone, UK) as the separator. NaPF$_6$ (1.0 mol/L) dissolved in ethylene carbonate/ethyl methyl carbonate (weight ratio of 3:7) was used as the electrolyte solution. Galvanostatic charge/discharge measurement was performed by a multichannel battery testing system (LAND CT2001A, 5V10Ma-K, Wuhan Blue Electronic Co. Ltd., Wuhan, China) at a current density of 100 mA·g$^{-1}$ with a voltage region between 0.01 and 3.0 V.
2.5. Data Treatment

Equation (1) was used to calculate the V precipitation percentage:

\[
\gamma = [1 - (\alpha V / \beta V_f)] \times 100\% 
\]

where \(\gamma\) stands for the V precipitation percentage (%), \(\alpha\) stands for the V concentration (mg/L) of the filtrate, \(\beta\) stands for the V concentration of the feed solution, \(V_a\) stands for the volume (L) of the filtrate, and \(V_f\) stands for the volume (L) of the feed solution.

3. Results and Discussion

The concentrations of the main elements in the alkaline-stripped pentavalent vanadium solution are listed in Table 1. As shown in Table 1, the concentrations of V and Na in the solution reached up to 20.5 g/L and 23.1 g/L, respectively, while the concentrations of other elements were very low. Thus, the solution can be used to prepare NaV_2O_5.

**Table 1.** Concentrations of the main elements in the alkaline-stripped pentavalent vanadium solution (ASPVS).

| Items | V  | Na  | P   | Al  | Fe  | Si   | Mg  |
|-------|----|-----|-----|-----|-----|------|-----|
| Concentration (g/L) | 20.5 | 23.1 | 0.013 | 0.009 | 0.007 | 0.012 | 0.008 |

3.1. Effect of Initial Solution pH Value

To investigate the effects of the initial solution pH value during NaV_2O_5 preparation, several experiments at different initial solution pH values were conducted. The reaction temperature, H_2 gas partial pressure, and reaction time were fixed at 200 °C, 4 MPa, and 2 h, respectively.

Figure 2 shows that V precipitation percentage decreased from 99% to 11% when the initial solution pH value increased from 4.0 to 12.0. This result indicates that the increase of the initial solution pH value can hinder the reaction proceeding efficiency, because the increase of the initial solution pH can cause the decrease of the thermodynamic driving force of the reaction during the HHR process for vanadium precipitation [27]. Therefore, the initial pH of the solution should be kept at a relatively low value in order to obtain a high recovery.

Figure 2. The effect of initial solution pH value on vanadium precipitation percentage.
As shown in Figure 3a,d,e, the diffraction peaks of the products prepared from solutions with initial pH values of 4.0, 7.0, and 8.0 were all attributed to NaV$_2$O$_5$, indicating that the as-prepared powders were pure-phase NaV$_2$O$_5$. The phase compositions of the products prepared from solutions with initial pH values of 5.0, 6.0, and 9.0 were identified as NaV$_2$O$_5$ mixed with VO$_2$(H$_2$O)$_{0.5}$ (Figure 3b,c,f). When the initial pH value was increased above 10.0, the phase of NaV$_2$O$_5$ could not be detected in the product and the as-prepared products were ascertained as VO$_2$(H$_2$O)$_{0.5}$ (Figure 3g,h,i).

![Figure 3](image_url)

**Figure 3.** The phase compositions of the products prepared from solutions with different initial pH values of (a) 4.0, (b) 5.0, (c) 6.0, (d) 7.0, (e) 8.0, (f) 9.0, (g) 10.0, (h) 11.0, and (i) 12.0 under a reaction temperature of 200 °C, a H$_2$ gas partial pressure of 4 MPa, and a reaction time of 2 h.

As shown in Figure 4, the increasing trend of the final pH value was not the same as the increase of the initial pH value. Unexpectedly, the final pH values from initial pH values of 7, 8, and 9 were lower than the final pH values from initial pH values of 5 or 6. However, it was common for the final pH value to be higher than the initial pH value, which indicated that the reaction could consume hydrogen ions. So, the final pH value of the solution during the reaction depends on the percentage of the vanadium precipitation. As the vanadium percentages at initial pH values of 7, 8, and 9 were much lower than the vanadium percentage at an initial pH of 6 (Figure 2), the final pH values at initial pH of 7, 8 and 9 were lower than the final pH values at initial pH values of 5 or 6.

Combining the results shown in Figure 3 with the results shown in Figure 4, when the final solution pH value was below 8.6 (the corresponding initial pH values were 4, 7, and 8), the product obtained was identified as the pure-phase NaV$_2$O$_5$. When the final solution pH value was between 8.6 and 10.6 (the corresponding initial pH values were 5, 6, and 9), the phase of the prepared product was identified as NaV$_2$O$_5$ mixed with VO$_2$(H$_2$O)$_{0.5}$. As the final pH value of the solution was above 10.7 (the corresponding initial pH values were 10, 11, and 12), the product obtained was ascertained to be VO$_2$(H$_2$O)$_{0.5}$. Some researchers found that the solubility of NaV$_2$O$_5$ dropped sharply when the solution pH value was above 9.0 [24]. Hereby, it is rational to conclude that some V(IV) in the reduced solution would preferentially precipitate from the solution in the form of VO$_2$(H$_2$O)$_{0.5}$ instead of NaV$_2$O$_5$ when the solution pH value is above 8.6. Moreover, when the solution pH value is above 10.7, NaV$_2$O$_5$ cannot precipitate from the solution and all the V(IV) in the reduced solution will form the VO$_2$(H$_2$O)$_{0.5}$ precipitates. Therefore, the solution pH value for the preparation of pure-phase NaV$_2$O$_5$
should be controlled below 8.6. As the solution pH value increase as the reaction progresses, the range of the reaction solution pH values needs to be controlled by the initial solution pH value.

![Figure 4](image-url)  
**Figure 4.** The effect of the initial solution pH value on final solution pH value.

To save the consumption of sulfuric acid during the process of adjusting pH value, the optimal initial solution pH value for the synthesis of the pure-phase NaV$_2$O$_5$ with a high recovery was proposed to be 4.0.

### 3.2. Effect of Reaction Temperature

To investigate the effects of reaction temperature during NaV$_2$O$_5$ preparation, several experiments with different reaction temperatures were conducted. The initial solution pH value, H$_2$ gas partial pressure, and reaction time were fixed at 4.0, 4 MPa, and 2 h, respectively.

Figure 5 shows that the V precipitation percentage increased from 86% to 99% by raising the reaction temperature from 150 to 200 °C. However, by further raising the reaction temperature, the V precipitation percentage was no longer increased. This result indicates that the increase of the reaction temperature is beneficial to the HHR reaction, because the increase of the temperature can enhance the reaction activity of hydrogen [29,30].

As shown in Figure 6, only a few diffraction peaks of the product obtained at 150 °C were attributed to the desired product of NaV$_2$O$_5$, most of which were indexed to a mixture of V(V) vanadates of Na$_2$V$_6$O$_{15}$·3H$_2$O and Na$_2$V$_6$O$_{16}$. This result revealed that the reaction activity of H$_2$ at 150 °C was too low to reduce all the V(V) to NaV$_2$O$_5$. After increasing the reaction temperature to 175 °C, the characteristic peaks ascribed to Na$_2$V$_6$O$_{15}$·3H$_2$O and Na$_2$V$_6$O$_{16}$ disappeared, and were replaced by the diffraction peaks ascribed to a mixture of NaV$_{0.64}$O$_5$ and NaV$_2$O$_5$ (Figure 6b). After increasing the reaction temperature to 200 °C, the product could be identified as the pure-phase NaV$_2$O$_5$ (Figure 6c). Moreover, the intensity of the diffraction peaks of NaV$_2$O$_5$ obtained at 200 °C was much stronger than that obtained at 180 °C. The diffraction peaks of the product obtained at 225 °C had no obvious change (Figure 6d,e). Combined with the results obtained from Figure 5, it was revealed that almost all the V(V) (99%) can be reduced to the pure-phase NaV$_2$O$_5$ by H$_2$ gas with a facile reaction temperature of 200 °C.
To save the consumption of energy in heating the autoclave, the optimal reaction temperature for the synthesis of pure-phase NaV$_2$O$_5$ with a high recovery was proposed to be 200 °C.

![Figure 5](image_url)

**Figure 5.** The effect of reaction temperature on vanadium precipitation percentage.

![Figure 6](image_url)

**Figure 6.** The phase compositions of the products obtained at (a) 150 °C, (b) 175 °C, (c) 200 °C, (d) 225 °C, and (e) 250 °C under an initial solution pH value of 4, a H$_2$ gas partial pressure of 4 MPa, and a reaction time of 2 h.
3.3. Effect of H\textsubscript{2} Gas Partial Pressure

To explore the effects of H\textsubscript{2} gas partial pressure during NaV\textsubscript{2}O\textsubscript{5} preparation, the initial solution pH value, reaction temperature, and reaction time were fixed at 4.0, 200 °C, and 2 h, respectively.

As shown in Figure 7, V precipitation percentage improved from 82% to 99% when the H\textsubscript{2} gas partial pressure was improved from 1 MPa to 4 MPa. V precipitation percentage had no obvious change when the H\textsubscript{2} gas partial pressure was increased above 4 MPa. This result indicates that the increase of the H\textsubscript{2} gas partial pressure can facilitate the hydrothermal hydrogen reduction reaction, because the increase of the H\textsubscript{2} gas partial pressure can enhance the thermodynamic driving force of the hydrothermal hydrogen reduction and increase the solubility of hydrogen in the solution [29,30].

![Graph showing the effect of H\textsubscript{2} gas partial pressure on vanadium precipitation percentage.](image)

Figure 7. The effect of H\textsubscript{2} gas partial pressure on vanadium precipitation percentage.

As shown in Figure 8a, when the H\textsubscript{2} gas partial pressure was only 1 MPa, the as-prepared product was a mixture of some pentavalent vanadates of Na\textsubscript{2}V\textsubscript{6}O\textsubscript{16}·3H\textsubscript{2}O, Na\textsubscript{6}V\textsubscript{10}O\textsubscript{28}·18H\textsubscript{2}O, and Na\textsubscript{2}V\textsubscript{6}O\textsubscript{16} and the reduced powers of Na\textsubscript{0.287}V\textsubscript{2}O\textsubscript{5} and NaV\textsubscript{2}O\textsubscript{5}. As the H\textsubscript{2} gas partial pressure was increased to 2 MPa, some diffraction peaks indexed to those pentavalent vanadates disappeared, and were replaced by the diffraction peaks ascribed to the desired product of NaV\textsubscript{2}O\textsubscript{5} (Figure 8b). When the H\textsubscript{2} gas partial pressure was increased to 3 MPa, the amount of the diffraction peaks attributed to NaV\textsubscript{2}O\textsubscript{5} increased further (Figure 8c). After increasing the H\textsubscript{2} gas partial pressure to 4 MPa, the prepared product was identified as pure-phase NaV\textsubscript{2}O\textsubscript{5} without any other phases (Figure 8d). The diffraction peaks had no obvious change as the H\textsubscript{2} gas partial pressure was increased to 5 MPa (Figure 8e).

To reduce the consumption of the H\textsubscript{2} gas, the optimal H\textsubscript{2} gas partial pressure for the synthesis of pure-phase NaV\textsubscript{2}O\textsubscript{5} with a high recovery was proposed to be 4 MPa.
As shown in Figure 7, the V precipitation percentage improved from 82% to 99% when the H2 gas partial pressure was increased from 1 MPa to 4 MPa. The V precipitation percentage had no obvious change when the H2 gas partial pressure was increased above 4 MPa. This result indicates that the increase of the H2 gas partial pressure can facilitate the hydrothermal hydrogen reduction reaction, because the increase of the H2 gas partial pressure can enhance the thermodynamic driving force of the hydrothermal hydrogen reduction and increase the solubility of hydrogen in the solution [29,30].

Figure 7. The effect of H2 gas partial pressure on vanadium precipitation percentage.

3.4. Effect of Reaction Time

To investigate the effects of the reaction time during NaV2O5 preparation, the initial solution pH value, reaction temperature, and H2 gas partial pressure were fixed at 4.0, 200 °C, and 4 MPa, respectively.

As shown in Figure 9, the V precipitation percentage rose greatly, from 87.88% to 99.58%, as the reaction time was prolonged from 0.5 to 2 h. However, further prolonging the reaction time did not cause the V precipitation percentage to increase.

Figure 9. The effect of reaction time on vanadium precipitation percentage.
As can be seen from Figure 10a, some pentavalent vanadates of \( \text{Na}_2\text{V}_6\text{O}_{16} \cdot 3\text{H}_2\text{O}, \text{Na}_6\text{V}_{10}\text{O}_{28} \cdot 18\text{H}_2\text{O}, \) and \( \text{Na}_2\text{V}_6\text{O}_{16} \) could be precipitated from the solution before the reduction reaction. As the reaction lasted for 0.5 h, the pentavalent vanadates of \( \text{Na}_2\text{V}_6\text{O}_{16} \cdot 3\text{H}_2\text{O} \) and \( \text{Na}_2\text{V}_6\text{O}_{16} \) mostly disappeared, and the reduction intermediate powers of \( \text{Na}_{0.287}\text{V}_2\text{O}_5 \) and the desired product of \( \text{NaV}_2\text{O}_5 \) could be observed (Figure 10b). When the reaction time was prolonged to 1 h, the intensity of the diffraction peaks ascribed to \( \text{Na}_2\text{V}_6\text{O}_{16} \cdot 3\text{H}_2\text{O}, \text{Na}_6\text{V}_{10}\text{O}_{28} \cdot 18\text{H}_2\text{O}, \) and \( \text{Na}_2\text{V}_6\text{O}_{16} \) became weak; on the contrary, the intensity of the diffraction peaks of \( \text{NaV}_2\text{O}_5 \) became strong (Figure 10c). Additionally, the diffraction peaks ascribed to \( \text{Na}_{0.287}\text{V}_2\text{O}_5 \) could not be observed, and a new peak ascribed to \( \text{Na}_{0.64}\text{V}_2\text{O}_5 \) was observable. When the reaction lasted for 1.5 h, most of the diffraction peaks attributed to \( \text{Na}_2\text{V}_6\text{O}_{16} \cdot 3\text{H}_2\text{O}, \text{Na}_6\text{V}_{10}\text{O}_{28} \cdot 18\text{H}_2\text{O}, \) and \( \text{Na}_2\text{V}_6\text{O}_{16} \) could not be detected, and the intensity of the diffraction peaks ascribed to \( \text{NaV}_2\text{O}_5 \) became stronger than before (Figure 10d). When the reaction proceeded for 2 h, the product was identified as pure-phase \( \text{NaV}_2\text{O}_5 \) without any other phases (Figure 10e). By extending the reaction time to 4 h, no obvious change was detected in the diffraction peaks of the product (Figure 10f). Therefore, it only takes 2 h to prepare the pure-phase \( \text{NaV}_2\text{O}_5 \).

Figure 10. The phase compositions of the products obtained at (a) 0 h, (b) 0.5 h, (c) 1.0 h, (d) 1.5 h, (e) 2 h, and (f) 4 h under an initial solution pH value of 4, a reaction temperature of 200 °C, and a \( \text{H}_2 \) gas partial pressure of 4 MPa.

To make the process less time-consuming, the optimal reaction time was proposed to be 2 h to synthesize the pure-phase \( \text{NaV}_2\text{O}_5 \) with a high recovery.

Based on the above, the optimal conditions of initial solution pH value, reaction temperature, \( \text{H}_2 \) gas partial pressure, and reaction time for the preparation of pure-phase \( \text{NaV}_2\text{O}_5 \) were ascertained as 4.0, 200 °C, 4 MPa, and 2 h, respectively. Excitingly, the formation time was greatly shortened, by nine times, compared with the most time-saving (18 h) hydrothermal process at present [16]. Moreover, the synthesis process can be considered as low-cost due to the low-cost raw material of ASPVS. Therefore, this novel fast process for \( \text{NaV}_2\text{O}_5 \) synthesis may have great application prospects.

3.5. Structural Characterization

To further verify the structure of the as-prepared product, the single XRD pattern of the powder obtained at the optimal conditions was measured, as shown in Figure 11.
Figure 11 shows that all the diffraction peaks of the as-prepared powders agree with the orthorhombic NaV$_2$O$_5$ with lattice constants $a = 1.132$ nm, $b = 0.361$ nm, and $c = 0.480$ nm according to the values reported in the literature (JCPDS No. 70-0870). No peaks of impurities or any other phases could be detected, indicating that the product is of high purity. Moreover, the diffraction peaks are very sharp and strong, indicating the high crystallization of the product. According to the ISCD collection data, a model of the orthorhombic NaV$_2$O$_5$ can be drawn out (inset in Figure 11). It can be seen that NaV$_2$O$_5$ demonstrates a typical layer structure. The vanadium atom in NaV$_2$O$_5$ is bonded with five oxygen atoms to form an individual structure unit of VO$_5$, which looks like a pyramid. Two VO$_5$ units with the same underlying orientation bond with each other along the $a$ axis by sharing one oxygen atom to form a bridge unit. Two bridge units with the opposite underlying orientation bond together by sharing three corner oxygen atoms to form a ladder-like unit with double chains. The ladder-like unit with double chains arranges in a zigzag pattern along the $a$ axis and arranges in parallel along the $b$ axis forming the $ab$ plane of the crystal. Sodium ions are located in the layers, which are stacked along the $c$ axis, acting as scaffolds in the layer structure. The layered structure provides a fast passage for the de-intercalation of sodium ions; thus, NaV$_2$O$_5$ may be used as an electrode material. These results agree well with those of previous research works [5,6,16,18,24].

![Figure 11. X-ray diffraction (XRD) pattern of the as-obtained NaV$_2$O$_5$.](image)

Based on the results shown in Table 2, the molar ratio of Na to V$_2$O$_5$ was close to 1, indicating the as-obtained product was NaV$_2$O$_5$. The sum of the content of sodium and vanadium reached up to 99.98%, indicating the purity of the as-obtained NaV$_2$O$_5$ reached up to 99.98%. The contents of other elements appeared in trace accounts, indicating impurity elements hardly co-precipitated with NaV$_2$O$_5$ during the reaction.

| Items | V$_2$O$_5$ | Na  | P  | Al  | Fe  | Si  | Mg  |
|-------|-----------|-----|----|-----|-----|-----|-----|
| Content (wt. %) | 88.74 | 11.24 | 0.003 | 0.001 | 0.002 | 0.001 | 0.001 |
3.6. Electrochemical Performance

The NaV₆O₉ powders obtained under the optimal conditions were assembled as sodium ion batteries to conduct corresponding electrochemical performance tests, as shown in Figure 12. It was clear that the initial discharge capacity was 196.4 mAh/g, and the sodium ion battery still had a specific discharge capacity of 120 mAh/g after 50 cycles. The Coulombic efficiency at different currents was no less than 97% from the second cycle to the 40th. These results indicate that the as-prepared NaV₆O₉ powders have a potential application in sodium ion batteries.

![Cycling performance at the current density of 100 mA/g in 0.01–3 V.](image)

**Figure 12.** Cycling performance at the current density of 100 mA/g in 0.01–3 V.

3.7. Synthesis Mechanism

The synthesis of NaV₂O₅ in the hydrothermal hydrogen reduction is a complex process which not only involves a series of reduction reactions with the phase transformation from V(V) ions to NaV₂O₅ but also involves a crystal growth process. Herein, the synthesis mechanism of NaV₂O₅ was divided into a phase transformation mechanism and a crystal growth mechanism in order to better understand the synthesis mechanism of NaV₂O₅.

3.7.1. Phase Transformation Mechanism

The phase transformation mechanism can be determined by further investigating the results shown in Figure 10. It can be seen that several kinds of vanadates, including Na₂V₆O₁₆·3H₂O, Na₆V₁₀O₂₈·18H₂O, Na₂V₆O₁₆, Na₀.2₈V₂O₅, Na₀.₆₄V₂O₅, and NaV₂O₅, were obtained during the whole synthesis process. The models of those vanadates are shown in Figure 13. Based on the phase transformation in the synthesis process, the phase transformation mechanism can be proposed as follows.

On the one hand, before the reduction reaction, V(V) ions can bond with the free sodium ions in a certain proportion to precipitate from the solution in the form of Na₂V₆O₁₆·3H₂O, Na₆V₁₀O₂₈·18H₂O, and Na₂V₆O₁₆ (Figures 10a and 13a), because the high temperature and high pressure can cause a low solubility for those vanadates. The relevant chemical reaction of this pentavalent vanadate pre-sedimentation process is expressed as Equations (2) to (4). In the initial period of the reduction, the V(V) ions can be reduced by H₂, so the polarity of V(V) ions will be reduced, resulting in a decrease in the binding force between V ions and water molecules (H₂O), as well as between V and oxygen atoms [18]. As a result, the water molecules in the interlayer of Na₂V₆O₁₆·3H₂O and Na₆V₁₀O₂₈·18H₂O...
are gradually removed, and the vanadate of Na$_{0.287}$V$_2$O$_5$ is formed in the reduction process (Figure 10b). The relevant chemical reaction of this process of hydrogen reduction with dehydration is expressed as Equations (5) to (7). As the reduction proceeds, the V ions valence state can be further lowered and sodium ions will be inserted into the structure of Na$_{0.287}$V$_2$O$_5$ in order to balance the charge [18], leading to the transformation of Na$_{0.287}$V$_2$O$_5$ to Na$_{0.64}$V$_2$O$_5$ and then to the desired product of NaV$_2$O$_5$ (Figure 10c–e, Figure 13b). The relevant chemical reaction of this sodium ion insertion process is expressed as Equations (8) and (9). On the other hand, in the initial period of the reduction reaction, some V ions that have been reduced to a lower valence state can also bond to the non-reduced V(V) ions and free sodium ions in a certain proportion to precipitate from the solution as Na$_{0.287}$V$_2$O$_5$ [18]. The relevant chemical reaction of this process is expressed as Equations (10) and (11). With a prolonged time, the valence state of V ions in the Na$_{0.287}$V$_2$O$_5$ is further lowered and the free sodium ions will be inserted into the structure of Na$_{0.287}$V$_2$O$_5$ to maintain the charge in balance [18], which also leads to the formation of NaV$_2$O$_5$. Both of the above two aspects simultaneously lead to the formation of pure-phase NaV$_2$O$_5$.

\[
\begin{align*}
V_{10}O_{28}^{6-} + 6Na^+ + 18H_2O &= Na_6V_{10}O_{28}·18H_2O \\
V_{6}O_{16}^{2-} + 2Na^+ + 3H_2O &= Na_2V_{6}O_{16}·3H_2O \\
V_{6}O_{16}^{2-} + 2Na^+ &= Na_2V_{6}O_{16} \\
400Na_6V_{10}O_{28}·18H_2O + 287H_2 + 1826H^+ &= 2000Na_{0.287}V_2O_5 + 1826Na^+ + 8400H_2O \\
2000Na_2V_{6}O_{16}·3H_2O + 861H_2 + 2278H^+ &= 6000Na_{0.287}V_2O_5 + 2278Na^+ + 8000H_2O
\end{align*}
\]

Figure 13. Schematic of the synthesis mechanism for rod-like NaV$_2$O$_5$ mesocrystals. (a) The phase transition in the process of the formation of Na$_2$V$_6$O$_{16}$·3H$_2$O, Na$_6$V$_{10}$O$_{28}$·18H$_2$O, and Na$_2$V$_6$O$_{16}$ before the introduction of H$_2$ gas to the autoclave; (b) the phase transition mechanism in the formation of NaV$_2$O$_5$ during the hydrothermal hydrogen reduction; (c) the crystal growth of rod-like NaV$_2$O$_5$ mesocrystals follows a self-assembly oriented attachment mechanism.
To investigate the crystal growth mechanism, the products prepared at different reaction times were analyzed by SEM.

Figure 14a shows that the resultant products were composed of a disorderly accumulation of small rods when the reaction lasted for 0.5 h. These small rods were identified as a mixture of un-reduced and reduced sodium vanadates, according to the XRD results (Figure 10b). As the reaction time was increased to 1 h, the small rods became much longer compared with those obtained at 0.5 h. In addition, evidence could be found that a few rods assembled with each other and demonstrated a “slender belts” morphology (Figure 14b). After increasing the reaction time to 1.5 h, more evidence could be found that the long rods further assembled together to form some rod-like mesocrystals (Figure 14c). When the reaction lasted for 2 h, the as-prepared product was demonstrated to consist of typical rod-like mesocrystals (Figure 14d). The corresponding EDS element mapping analysis revealed that the rod-like mesocrystals only consist of the elements Na, V, and O (Figure 14f). Moreover, the relevance of Na, V, and O was quite good. Combining with the XRD results drawn from Figure 10e, the rod-like mesocrystals could be confirmed as NaV$_2$O$_5$. From the partial magnified image of the rod-like NaV$_2$O$_5$ mesocrystals, it can be seen that the individual NaV$_2$O$_5$ rods in the bunch were aligned in the same direction and assembled together (Figure 14e). The fact that the crystals stack preferentially in a certain direction indicates that the growth of NaV$_2$O$_5$ crystals in the HHR process may follow a self-assembly oriented attachment mechanism [16–18].

3.7.2. Crystal Growth Mechanism

To investigate the crystal growth mechanism, the products prepared at different reaction times were analyzed by SEM.

Figure 14a shows that the resultant products were composed of a disorderly accumulation of small rods when the reaction lasted for 0.5 h. These small rods were identified as a mixture of un-reduced and reduced sodium vanadates, according to the XRD results (Figure 10b). As the reaction time was increased to 1 h, the small rods became much longer compared with those obtained at 0.5 h. In addition, evidence could be found that a few rods assembled with each other and demonstrated a “slender belts” morphology (Figure 14b). After increasing the reaction time to 1.5 h, more evidence could be found that the long rods further assembled together to form some rod-like mesocrystals (Figure 14c). When the reaction lasted for 2 h, the as-prepared product was demonstrated to consist of typical rod-like mesocrystals (Figure 14d). The corresponding EDS element mapping analysis revealed that the rod-like mesocrystals only consist of the elements Na, V, and O (Figure 14f). Moreover, the relevance of Na, V, and O was quite good. Combining with the XRD results drawn from Figure 10e, the rod-like mesocrystals could be confirmed as NaV$_2$O$_5$. From the partial magnified image of the rod-like NaV$_2$O$_5$ mesocrystals, it can be seen that the individual NaV$_2$O$_5$ rods in the bunch were aligned in the same direction and assembled together (Figure 14e). The fact that the crystals stack preferentially in a certain direction indicates that the growth of NaV$_2$O$_5$ crystals in the HHR process may follow a self-assembly oriented attachment mechanism [16–18].

![Figure 14](image.png)  
**Figure 14.** Scanning electron microscopy (SEM) image of the products obtained at different reaction times of (a) 0.5 h, (b) 1 h, (c) 1.5 h, and (d) 2 h under an initial solution pH value of 4, a reaction temperature of 200 °C, and a H$_2$ gas partial pressure of 4 MPa. (e) The partial magnified image; (f) energy-dispersive spectrometry (EDS) element mapping analysis of the product obtained at 2 h.
The NaV$_2$O$_5$ samples were further investigated by TEM to obtain more details of the microstructure. Figure 15a,b reveal that the NaV$_2$O$_5$ mesocrystals obtained had a rod-like morphology, which appeared similar to that in the images obtained from the SEM analysis. From the magnified image of the end of the individual NaV$_2$O$_5$ mesocrystal (Figure 15c), it can be clearly observed that the mesocrystal was composed of many nanorods with the same preferred orientation. Moreover, some cleavages between the nanorods at the ends of the crystal supply more evidence for the self-assembled oriented attachment mechanism for rod-like NaV$_2$O$_5$ formation (Figure 15c). The lattice fringes of 0.473 nm associated with the (001) plane [16,18] can be measured from the high-resolution transmission electron microscope (HRTEM) image of NaV$_2$O$_5$ (Figure 15d). The lattice fringes in the direction of the length measured as 0.375 nm correspond to the (010) plane [16], revealing that the crystal’s preferential growth direction is (010) (Figure 10d). These agree with the XRD results. From the analysis of the selected area electron diffraction (SAED) pattern, diffraction spots of (010), (001), and (011) can be clearly identified, which is in good agreement with the orthorhombic NaV$_2$O$_5$. From the above information, it can be concluded that NaV$_2$O$_5$ nanorods with the same preferential crystal growth direction assemble together in the (001) direction to form rod-like NaV$_2$O$_5$ mesocrystals with a preferential crystal growth direction of (010).

Figure 15. Transmission electron microscopy (TEM) characterization of NaV$_2$O$_5$ mesocrystals synthesized under the optimal conditions. (a,b) TEM images of NaV$_2$O$_5$ mesocrystals; (c) partial magnified image of the NaV$_2$O$_5$ mesocrystals; (d) high-resolution transmission electron microscope (HRTEM) image of NaV$_2$O$_5$ (inset is the corresponding selected area electron diffraction (SAED) pattern).
Based on the above, a crystal growth mechanism can be proposed (Figure 13c). First of all, many small rod nuclei are obtained through nucleation. As the surface energy can be drastically reduced when the interface is eliminated, the generated small NaV$_2$O$_5$ rods will then spontaneously combine with each other along the same crystal orientation (010) to maintain the system at the lowest systematic energy. Ultimately, rod-like NaV$_2$O$_5$ mesocrystals with a (010) preferential crystal growth orientation, consisting of many nanorods stacking with each other along the (001) direction, are obtained.

4. Conclusions

In summary, we reported a novel fast process for synthesizing NaV$_2$O$_5$ mesocrystals from an alkaline-stripped pentavalent vanadium solution by introducing the technology of hydrothermal hydrogen reduction. The optimal conditions for NaV$_2$O$_5$ synthesis were ascertained to be an initial solution pH value of 4.0, a reaction temperature of 200 °C, a H$_2$ gas partial pressure of 4 MPa, and a reaction time of 2 h. The synthesis time (only 2 h) was greatly shortened, by nine times, compared with the most time-saving (18 h) hydrothermal process at present. XRD analysis revealed that the as-prepared powders demonstrate a typical layered orthorhombic structure of NaV$_2$O$_5$. The purity of the as-prepared NaV$_2$O$_5$ reached up to 99.98%. Electrochemical tests showed that the as-prepared powder had a potential application in sodium ion batteries. Electron microscopy analysis revealed that the rod-like NaV$_2$O$_5$ mesocrystals demonstrated a preferential growth direction of (010), and were formed by a large number of nanorods assembled in the (001) direction. Furthermore, the synthesis mechanism of NaV$_2$O$_5$ was proposed as follows: pentavalent vanadate pre-sedimentation, hydrogen reduction with dehydration, sodium ion insertion, and finally self-assembly oriented attachment. The synthesis process can be considered to be time-saving and low-cost, thus offering promising application prospects for NaV$_2$O$_5$ synthesis.

Author Contributions: G.Z. and Y.Z. provided the original ideas and designed the experiments; G.Z. and L.Z. performed the experiments; G.Z. analyzed the data; S.B. contributed reagents/materials/analysis tools; and G.Z. wrote the paper.

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References

1. Hu, P.; Zhang, Y.; Liu, T.; Huang, J.; Yuan, Y.; Xue, N. Source separation of vanadium over iron from roasted vanadium-bearing shale during acid leaching via ferric fluoride surface coating. J. Clean. Prod. 2018, 181, 399-407. [CrossRef]
2. Hu, P.; Zhang, Y.; Huang, J.; Liu, T.; Yuan, Y.; Xue, N. Eco-friendly leaching and separation of vanadium over iron impurity from vanadium-bearing shale using oxalic acid as a leachant. ACS Sustain. Chem. Eng. 2018, 6, 1900-1908. [CrossRef]
3. Xue, N.; Zhang, Y.; Huang, J.; Liu, T.; Wang, L. Separation of impurities aluminum and iron during pressure acid leaching of vanadium from stone coal. J. Clean. Prod. 2017, 166, 1265–1273. [CrossRef]
4. Xue, N.; Zhang, Y.; Liu, T.; Huang, J.; Zheng, Q. Effects of hydration and hardening of calcium sulfate on muscovite dissolution during pressure acid leaching of black shale. J. Clean. Prod. 2017, 149, 989–998. [CrossRef]
5. Mjejin, I.; Etteyeb, N.; Sediri, F. NaV$_2$O$_5$ nanoplates: Hydrothermal synthesis, characterization and study of their optical and electrochemical properties. Ceram. Int. 2014, 40, 5379–5386.
6. Hu, F.; Ming, X.; Chen, G.; Wang, C.; Li, A.; Li, J.; Wei, Y. Synthesis and characterizations of highly crystallized α’-NaV$_2$O$_5$ needles prepared by a hydrothermal process. J. Alloys Compd. 2009, 47, 888–892. [CrossRef]
7. Aichhorn, M.; Sherman, E.Y.; Evertz, H.G. Single-particle spectral function of quarter-filled ladder systems. Phys. Rev. B 2005, 72, 155110. [CrossRef]
8. Kamioka, H.; Saito, S.; Isobe, M.; Ueda, Y.; Suemoto, T. Coherent magnetic oscillation in the spin ladder system $\alpha'$-NaV$_2$O$_5$. *Phys. Rev. Lett.* **2002**, *88*, 127201. [CrossRef]

9. Yoshihama, T.; Nishi, M.; Nakajima, K.; Kakurai, K.; Takesue, N.; Fujii, Y.; Isobe, M.; Kagami, C.; Ueda, Y. Magnetic excitations in spin-Peierls compound NaV$_2$O$_5$. *Phys. B Condens. Matter* **1997**, *234–236*, 539–540.

10. Isobe, M.; Kagami, C.; Ueda, Y. Crystal growth of new spin-Peierls compound NaV$_2$O$_5$. *J. Cryst.* **1997**, *181*, 314–317. [CrossRef]

11. Isobe, M.; Ueda, Y. Magnetic susceptibility of quasi-one-dimensional compound NaV$_2$O$_5$. *J. Phys. Soc. Jpn.* **1996**, *65*, 1178–1181. [CrossRef]

12. Horsch, P.; Mack, F. A new view of the electronic structure of the spin-Peierls compound $\alpha'$-NaV$_2$O$_5$. *Eur. Phys. J. B* **1998**, *5*, 367–370. [CrossRef]

13. Ohwada, K.; Fujii, Y.; Murakami, Y.; Noda, Y.; Osumi, H.; Ikeda, N.; Shobu, T.; Isobe, M.; et al. Structural relations between two ground states of NaV$_2$O$_5$ under high pressure: A synchrotron x-ray diffraction study. *Phys. Rev. B* **2007**, *76*, 094113. [CrossRef]

14. Spitaler, J.; Sherman, E.Y.; Draxl, C.A. Zone-center phonons in NaV$_2$O$_5$: A comprehensive ab initio study including Raman spectra and electron-phonon interaction. *Phys. Rev. B* **2007**, *75*, 014302. [CrossRef]

15. Ming, X.; Fan, H.; Huang, Z.; Hu, F.; Wang, C.; Chen, G. Magnetic gap in Slater insulator $\alpha'$-NaV$_2$O$_5$. *J. Phys. Condens. Matter* **2008**, *15*, 155203. [CrossRef]

16. Liu, P.; Zhu, K.; Bian, K.; Xu, Y.; Zhang, F.; Zhang, W.; Huang, W.; Zhang, J. One-step and short-time synthesis of 3D NaV$_2$O$_5$ mesocrystals as anode materials of Na-ion batteries. *J. Power Sources* **2018**, *395*, 158–162. [CrossRef]

17. Liu, P.; Zhu, K.; Gao, Y.; Luo, H.; Lu, L. Recent progress in the applications of vanadium-based oxides on energy storage: From low-dimensional nanomaterials synthesis to 3D micro/nano-structures and free-standing electrodes fabrication. *Adv. Energy Mater.* **2017**, *7*, 1700547. [CrossRef]

18. Liu, P.; Zhou, D.; Zhu, K.; Wu, Q.; Wang, Y.; Tai, G.; Zhang, W.; Gu, Q. Bundle-like $\alpha'$-NaV$_2$O$_5$ mesocrystals: From synthesis, growth mechanism to analysis of Na-ion intercalation/deintercalation abilities. *Nanoscale* **2016**, *8*, 1975–1985. [CrossRef]

19. Muller-Bouvet, D.; Baddour-Hadjian, R.; Tanabe, M.; Huynh, L.T.N.; Le, M.L.P.; Pereira-Ramos, J.P. Electrochemically formed $\alpha'$-NaV$_2$O$_5$: A new sodium intercalation compound. *Electrochim. Acta* **2015**, *176*, 586–593. [CrossRef]

20. Smolinski, H.; Gros, C.; Weber, W.; Peuchert, U.; Roth, G.; Weiden, M.; Geibel, C. NaV$_2$O$_5$ as a quarter-filled ladder compound. *Phys. Rev. Lett.* **1998**, *80*, 5164. [CrossRef]

21. Smirnov, A.I.; Popova, M.N.; Sushkov, A.B.; Golubchik, S.A.; Khomskii, D.I.; Mostovoy, M.V.; Vasil’ev, A.N.; Isobe, M.; Ueda, Y. High-frequency dielectric and magnetic anomaly at the phase transition in NaV$_2$O$_5$. *Phys. Rev. B* **1999**, *59*, 14546. [CrossRef]

22. Smirnov, A.I.; Sosin, S.S.; Calemczuk, R.; Villar, V.; Paulsen, C.; Isobe, M.; Ueda, Y. Thermal and magnetic properties of defects in the spin-gap compound NaV$_2$O$_5$. *Phys. Rev. B* **2000**, *63*, 014412. [CrossRef]

23. Onoda, M.; Mizuguchi, Y. Correlation and disorder effects for the electronic transport in the low-dimensional system Na$_x$Ca$_{1-x}$V$_2$O$_5$ and Na$_x$V$_2$O$_5$. *J. Phys. Condens. Matter* **2008**, *20*, 445207. [CrossRef]

24. Gui, Z.; Fan, R.; Chen, X.; Hu, Y.; Wu, Y. Hydrothermal synthesis and magnetic property of NaV$_2$O$_5$ nanorods. *Trans. Nonferrous Met. Soc. China* **2001**, *11*, 324–327.

25. Zhang, Y.; Bao, S.; Liu, T.; Chen, T.; Huang, J. The technology of extracting vanadium from stone coal in China: History, current status and future prospects. *Hydrometallurgy* **2011**, *109*, 116–124. [CrossRef]

26. Yang, X.; Zhang, Y.; Bao, S.; Shen, C. Separation and recovery of vanadium from a sulfuric-acid leaching solution of stone coal by solvent extraction using trialkylamine. *Sep. Purif. Technol.* **2016**, *164*, 49–55. [CrossRef]

27. Zhang, G.; Zhang, Y.; Bao, S.; Huang, J.; Zhang, L. A novel eco-friendly vanadium precipitation method by hydrothermal hydrogen reduction technology. *Minerals* **2017**, *7*, 182. [CrossRef]

28. Zhang, G.; Zhang, Y.; Bao, S. The effects of sodium ions, phosphorus, and silicon on the eco-friendly process of vanadium precipitation by hydrothermal hydrogen reduction. *Minerals* **2018**, *8*, 294. [CrossRef]

29. Agrawal, A.; Kumar, V.; Pandey, B.D.; Sahu, K.K. A comprehensive review on the hydro metallurgical process for the production of nickel and copper powders by hydrogen reduction. *Mater. Res. Bull.* **2006**, *41*, 879–892. [CrossRef]
30. Saarinen, T.; Lindfors, L.E.; Fugleberg, S. A review of the precipitation of nickel from salt solutions by hydrogen reduction. *Hydrometallurgy* **1998**, *47*, 309–324. [CrossRef]

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