Chapter 6

Synthesis and Characterization of 
\((\text{NH}_4)_2\text{V}_6\text{O}_{16}\cdot1.5\text{H}_2\text{O}\) Nest-like Structures
6.1. Introduction

One-dimensional (1D) nanostructures, such as nanowires, nanobelts, and nano-bundles are expected to play a crucial role due to their fundamental research importance and the wide range of their potential applications in nanodevices [1]. One-dimensional vanadium oxide-based nanostructured materials have attracted the interest of many researchers in the last few decades due to their outstanding structural flexibility [2-4], and has diverse technological applications in catalysis [5, 6], rechargeable lithium ion batteries [7], chemical sensors or actuators [8, 9], electrochemical pseudo-capacitors [10] and electrochromic coatings [11]. Several synthesis methods, such as thermal evaporation, surfactant-assisted solution, hydrothermal and solvothermal have been employed to prepare 1-D nanostructured vanadium oxides and their compounds [12–16]. However, there have been a few literatures on the synthesis of 1-D nanostructured single crystalline vanadates. For example, Durupthy et al. synthesized the crystalline NaV$_3$O$_8$·1.5H$_2$O at room temperature on acidification of a metavanadate solution [17]. Yu and Zhou groups have synthesized Na$_2$V$_6$O$_{16}$·3H$_2$O nanobelts and nanowires in the presence of F$^-$ and SO$_4^{2-}$ anions, respectively [18, 19]. Mai et al. reported on the synthesis, electrical transport measurements, and conduction mechanism on nanobelts of NH$_4$V$_3$O$_8$ vanadate [20]. Wang et al. reported that the one-dimensional ammonium vanadates are semiconductors at room temperature [1]. We also synthesized Na$_2$V$_6$O$_{16}$·3H$_2$O belts/rings and suggested that the Na$_2$V$_6$O$_{16}$·3H$_2$O rings were made of self-coiling of nanobelts [21]. However, it is still a big challenge for materials scientists to fabricate 1D nanostructured materials through a simple and facile route.

In the present chapter, we report the synthesis of nest-like (NH$_4$)$_2$V$_6$O$_{16}$·1.5H$_2$O architectures made of nanobelts by hydrothermal method and the possible reaction mechanism for the formation of (NH$_4$)$_2$V$_6$O$_{16}$·1.5H$_2$O architecture is discussed. The
orthorhombic phase of shcherbianite $V_2O_5$ was obtained on calcination of $(NH_4)_2V_6O_{16} \cdot 1.5H_2O$ at 350 °C for 2 h.

6.2. Experimental

6.2.1 Sample preparation

All reagents were of analytical grade and used as received without further purification. Double distilled water was used throughout the experiments. 0.5 g of $NH_4VO_3$ (4.27 x 10^{-3} mol) powder was added into 25 mL of distilled water and 0.2 mL of orthophosphoric acid ($H_3PO_4$, 88%) was added, resulting in the formation of a wine red solution. The solution was stirred for about 15 min and transferred to a 60 mL Teflon lined stainless steel autoclave, which was maintained at 130 °C for 3 days and then cooled to room temperature. The red product was collected and washed with distilled water and absolute alcohol and dried at 60 °C for 2 h.

6.3. Results and discussion

Figure 6.1A. PXRD pattern of $(NH_4)_2V_6O_{16} \cdot 1.5H_2O$. 

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The PXRD pattern of the as-prepared sample is shown in Figure 6.1A. All the diffraction peaks in the pattern can be readily indexed to a pure monoclinic crystalline phase of \((\text{NH}_4)_2\text{V}_6\text{O}_{16} \cdot 1.5\text{H}_2\text{O}\) (JCPDS Card No. 51-0376). No reflections of impurity are found in the pattern, which proves that pure \((\text{NH}_4)_2\text{V}_6\text{O}_{16} \cdot 1.5\text{H}_2\text{O}\) has been successfully synthesized.

The FTIR spectrum of the as-prepared sample is shown in Figure 6.1B. The bands at 1004 cm\(^{-1}\) and 964 cm\(^{-1}\) are corresponding to V=O stretching of distorted octahedral and distorted square-pyramids, the bands at 733 and 534 cm\(^{-1}\) are ascribed to asymmetric and symmetric stretching vibrations of V-O-V bonds. The two bands at 3501 and 1617 cm\(^{-1}\) are attributed to O-H stretching and H-O-H bending vibrations of water molecules respectively. The bands at 3154 and 1402 cm\(^{-1}\) are respectively assigned to the asymmetric stretching and the symmetric bending vibrations of \(\text{NH}_4^+\). Thus, the FTIR spectrum confirms that the nanobelts are composed of \((\text{NH}_4)_2\text{V}_6\text{O}_{16} \cdot 1.5\text{H}_2\text{O}\) [20].
The TG-DTA curves of the as-prepared sample are shown in Figure 6.1C. The first weight loss of 5.6 % in the range 100 °C to 255 °C mainly resulted from the evaporation of NH\textsubscript{3} and adsorbed water. The second weight loss of 8.0 %, from 260 °C to 375 °C was caused by the de-intercalation of strongly-bounded water. The exothermic peak at 412 °C can be assigned to the oxidation of V (IV) to V (V) [22].

![TG-DTA curves](image)

**Figure 6.1C.** TG-DTA curves of (NH\textsubscript{4})\textsubscript{2}V\textsubscript{6}O\textsubscript{16}.1.5H\textsubscript{2}O.

The morphology and structure of the (NH\textsubscript{4})\textsubscript{2}V\textsubscript{6}O\textsubscript{16}.1.5H\textsubscript{2}O product was investigated by SEM and TEM. The product obtained at 120 °C for 1 d (Figure 6.2A) does not indicate any regular, well-defined shaped structure and composed of a mixture of nanorods and nanobelts. When the experiment was performed at 130 °C for 3 d, the product exhibits nest-like morphology made of flexible nanobelts (Figure 6.2B, C). When the reaction was performed at 160 °C for 3 d (Figure 6.2D), the dispersive nanobelts were obtained. The
obtained nanobelts have smooth surface with an average width of 300-400 nm and the length of several tens of micrometers.

Figure 6.2. SEM images of the (NH₄)₂V₆O₁₆.1.5H₂O product prepared at (A) 120 °C, 24 h; (B) 130 °C, 3d; Low magnification (C) 130 °C, 3d; High magnification (D) 160 °C, 3d;

Figure 6.3A is the TEM image of selected individual (NH₄)₂V₆O₁₆.1.5H₂O nanobelts. A typical TEM image of nanobelts confirms that the surface of nanobelts is smooth. The SAED pattern (Figure 6.3B) showed clear diffraction spots, indicates single crystal
structure. The result from EDX shows (Figure 6.3F) that the product contains only V, N, and O.

Figure 6.3(A). TEM image (B) SAED pattern of an individual \((\text{NH}_4)_2\text{V}_6\text{O}_{16} \cdot 1.5\text{H}_2\text{O}\) nanobelt (C) EDX spectrum of \((\text{NH}_4)_2\text{V}_6\text{O}_{16} \cdot 1.5\text{H}_2\text{O}\)
The effect of calcination on the crystallization and morphology of the \((\text{NH}_4)_2\text{V}_6\text{O}_{16}.1.5\text{H}_2\text{O}\) was investigated. After calcination of \((\text{NH}_4)_2\text{V}_6\text{O}_{16}.1.5\text{H}_2\text{O}\) at 350 °C for 2h, pure crystalline \(\text{V}_2\text{O}_5\) was obtained. Figure 6.4(A, B) show representative low and high magnification SEM images of postcalcined \(\text{V}_2\text{O}_5\) sample, indicating that the nest-like morphology of the precalcined \((\text{NH}_4)_2\text{V}_6\text{O}_{16}.1.5\text{H}_2\text{O}\) do not change after calcination.

Figure 6.4C shows the PXRD pattern of \(\text{V}_2\text{O}_5\) by calcining \((\text{NH}_4)_2\text{V}_6\text{O}_{16}.1.5\text{H}_2\text{O}\) at 350 °C for 2h. All the PXRD peaks could be readily indexed to the orthorhombic shcherbianite \(\text{V}_2\text{O}_5\) phase (JCPDS card no. 86-2248).
The EDX spectrum analysis (Figure 6.4D) of V$_2$O$_5$ confirms that the product contains only V and O elements. The calcined sample was gold coated prior to the EDX analysis.

Figure 6.4C. PXRD pattern of V$_2$O$_5$ sample.

Figure 6.4D. EDX spectrum of V$_2$O$_5$ sample.
6.3.1. Reaction mechanism

The basic reactions for the formation of \((\text{NH}_4)_2\text{V}_6\text{O}_{16} \cdot 1.5\text{H}_2\text{O}\) phase can be tentatively proposed in a similar way as previously proposed for \(\text{Na}_2\text{V}_6\text{O}_{16} \cdot 3\text{H}_2\text{O}\) [21].

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\begin{align*}
3\text{NH}_4\text{VO}_3 + \text{H}_3\text{PO}_4 &\rightarrow 3\text{VO}_3^- + (\text{NH}_4)_3\text{PO}_4 + 3\text{H}^+ & \quad \cdots \cdots (1) \\
11\text{VO}_3^- + 8\text{H}^+ + \text{H}_2\text{O} &\rightarrow [\text{H}_2\text{V}_{10}\text{O}_{28}]^{4-} + [\text{VO}_2(\text{H}_2\text{O})_4]^+ & \quad \cdots \cdots (2) \\
[\text{H}_2\text{V}_{10}\text{O}_{28}]^{4-} + 4\text{H}^+ + 32\text{H}_2\text{O} &\rightarrow 10[\text{VO(OH)}_3(\text{H}_2\text{O})_2] & \quad \cdots \cdots (3) \\
[\text{VO}_2(\text{H}_2\text{O})_4]^+ &\rightarrow [\text{VO(OH)}_3(\text{H}_2\text{O})_2] + \text{H}^+ & \quad \cdots \cdots (4) \\
6[\text{VO(OH)}_3(\text{H}_2\text{O})_2] + 2\text{NH}_4^+ &\rightarrow (\text{NH}_4)_2\text{V}_6\text{O}_{16} \cdot 1.5\text{H}_2\text{O} + 18.5\text{H}_2\text{O} + 2\text{H}^+ & \quad \cdots \cdots (5)
\end{align*}
\]

Ammonium metavanadate in aqueous solution forms \(\text{NH}_4^+\) and \(\text{VO}_3^-\). Adding \(\text{H}_3\text{PO}_4\) gives a wine-red solution of vanadic acid \((\text{HVO}_3)\) as shown in equation 1. The \(\text{HVO}_3\) solution then progressively gets converted into a mixture of decavanadate \([\text{H}_2\text{V}_{10}\text{O}_{28}]^{4-}\) and \([\text{VO}_2(\text{H}_2\text{O})_4]^+\) ions (equation 2). The resulting solution was subjected to hydrothermal treatment. During the reaction process, decavanadate \([\text{H}_2\text{V}_{10}\text{O}_{28}]^{4-}\) species get protonated (equation 3) and the cationic \([\text{VO}_2(\text{H}_2\text{O})_4]^+\) species undergoes deprotonation (equation 4) in order to provide neutral \([\text{VO(OH)}_3(\text{H}_2\text{O})_2]\) precursors. Then, \((\text{NH}_4)_2\text{V}_6\text{O}_{16} \cdot 1.5\text{H}_2\text{O}\) (equation 5) phase results from polycondensation of the neutral \([\text{VO(OH)}_3(\text{H}_2\text{O})_2]\) precursors, leading to the formation of \(\text{V}_3\text{O}_8^-\) layers, and the \(\text{NH}_4^+\) ions can accommodate within these \(\text{V}_3\text{O}_8^-\) framework tunnels in order to compensate for the negative charge of the layers.
6.3.2. Growth mechanism

The formation of (NH$_4$)$_2$V$_6$O$_{16} \cdot 1.5$H$_2$O nanobelts can be explained in a manner similar to that previously proposed for the formation of Na$_2$V$_6$O$_{16} \cdot 3$H$_2$O. Since, these two compounds have similar crystal structure and the same growth direction. The difference of these crystal structure parameters between (NH$_4$)$_2$V$_6$O$_{16} \cdot 1.5$H$_2$O and Na$_2$V$_6$O$_{16} \cdot 3$H$_2$O lies in the different length of the c-axis and the different $\beta$ angles [23]. The (NH$_4$)$_2$V$_6$O$_{16} \cdot 1.5$H$_2$O structure consists of V$_3$O$_8$$^-$ layers. NH$_4^+$ ions and water molecules are intercalated between these layers. During hydrothermal process, the presence of anions plays an important role in nanobelts formation as observed previously for the formation of vanadates [21]. Therefore, in the present work, we assume that the PO$_4^{3-}$ anions are crucial for the growth of (NH$_4$)$_2$V$_6$O$_{16} \cdot 1.5$H$_2$O nanobelts because PO$_4^{3-}$ has a stronger coordination ability and may adsorb selectively to the special crystal facets, leading to the formation of flexible (NH$_4$)$_2$V$_6$O$_{16} \cdot 1.5$H$_2$O belts [21]. Further, the residual NH$_4^+$ ions from the solution could be escaped as NH$_3$ gas through the formation of bubbles and the flexible (NH$_4$)$_2$V$_6$O$_{16} \cdot 1.5$H$_2$O belts reside on the gas bubble. Finally, the bubble could be destroyed and leads to the formation of nest-like morphology. However, further study is needed to precisely understand the formation mechanism of the nest like morphology.
References