Chapter 3

Facile Synthesis and Evolution of (NH₄)₀.₅V₂O₅.mH₂O Belts, Triangles and Rings

3.1. Introduction

Vanadium oxide based compounds have received significant attention, due to their structural flexibility combined with chemical and physical properties [1]. They find a wide range of potential applications in high-energy density lithium ion batteries [2], catalysis [3], electrochromic devices [4], actuators [5] and sensors [6]. The wide range of available oxidation states of vanadium provides a myriad of compounds and coordination modes. Of the different stoichiometric vanadium oxides, the tunnel-like framework of V$_2$O$_5$ is especially notable since it allows the facile intercalation of a variety of organic and inorganic guest species. Vanadium oxides exhibit a layered structure and are well known for their intercalation properties. Among them, cation intercalated xerogels M$_x$V$_2$O$_5$.mH$_2$O (M = Li$^+$, NH$_4^+$, Na$^+$) have been extensively studied for their electrochemical properties. They are made of V$_2$O$_5$ bilayers whose interlayer space is occupied by water molecules (V$_2$O$_5$.mH$_2$O) and cations (M$_x$V$_2$O$_5$.mH$_2$O). M$_x$V$_2$O$_5$.mH$_2$O xerogels show significant differences from V$_2$O$_5$.mH$_2$O xerogels. Owing to cations intercalated between VO$_5$ pyramid sheets, M$_x$V$_2$O$_5$.mH$_2$O xerogels exhibit better electrochemical properties than V$_2$O$_5$.mH$_2$O xerogels. In ((NH$_4$)$_{0.5}$V$_2$O$_5$.mH$_2$O), NH$_4^+$ is intercalated between the vanadium oxide layers can be reversibly exchanged by various cations such as Li$^+$, Na$^+$, K$^+$, or Ca$^{2+}$ to form new M$_x$V$_2$O$_5$.mH$_2$O nanostructures [7]. Moreover, intercalated NH$_4^+$ ions can be easily removed upon calcination without altering the original morphology.

A large variety of vanadium oxide based compounds have been described, in which cations, transition metal complexes, organic molecules and even polymers have been intercalated. For instance, Nesper et al. synthesized vanadium oxide nanotubes via the intercalation of primary alkylamines [8]. Luca et al. prepared mesoporous sieves of
vanadium oxide via the intercalation of tetramethylammonium cations [9, 10]. Previously, Chandrappa et al. reported nanostructured vanadium pentoxide foams obtained through a new soft-chemical route by adding hexadecylamine to crystalline vanadium pentoxide followed by the addition of hydrogen peroxide at room temperature [11].

Various morphologies of vanadium oxide and derived compounds such as nanotubes, wires, fibers, belts, rods, mesoporous structures in micro/nano structures have so far been successfully synthesized by using a variety of synthetic routes [12-17]. Recently, nanorings/springs/helical structures for a number of inorganic materials such as CuO [18], SnO₂ [19], InGaN [20], α-Ga₂O₃ [21], InP nanosprings [22], PbSe [23], BN [24], AlN [25], ZnO [26-29], Gold [30], Zn₂SnO₄ [31], amorphous SiO₂ [32], SiC nanosprings [33] and carbon nanotube coils [34], have been reported.

In the present chapter, we present a facile approach for the synthesis of \((\text{NH}_4)_0.5\text{V}_2\text{O}_5\cdot m\text{H}_2\text{O}\) belts, rings, triangles, and oval forms by hydrothermal method. We suggested that the as-prepared \((\text{NH}_4)_0.5\text{V}_2\text{O}_5\cdot m\text{H}_2\text{O}\) rings, triangles and ovals have been formed by connecting two ends of the vanadium oxide sheet made of edge and corner sharing VO₅ square pyramids. A possible reaction mechanism and the growth process involved in the formation of belts/ rings /triangles and oval-like microstructures are also discussed.

3.2. Experimental Section

3.2.1. Sample Preparation

Chemical reagents of analytical grade were purchased from Merck Ltd., and utilized without further purification. Double distilled water was used throughout the experiments. Ammonium metavanadate (0.25 g) was dissolved in hydrogen peroxide solution (0.5 mL, 30 %) to form a clear, yellow solution. A citric acid solution (30 mL, 0.01M) was then added resulting in the formation of a red solution that was stirred for 15 min. The
obtained clear red solution was transferred into a Teflon-lined stainless steel autoclave with a capacity of 50 mL, then sealed and the autoclave was maintained at 160 °C for 48 h. After hydrothermal treatment, the autoclaves were naturally cooled down to ambient temperature. The spongy brown product was harvested by centrifugation, washed several times with distilled water and absolute alcohol to remove any possible residual impurities and finally dried at 60 °C in an oven for 2 h.

### 3.3. Results and Discussion

The PXRD pattern of the sample prepared through hydrothermal method is shown in Figure 3.1. All the diffraction peaks on the curve match the standard data of monoclinic (NH₄)₀.₅V₂O₅·mH₂O [JCPDS No. 31-0075; (NH₄) V₄O₁₀·mH₂O may be regarded as (NH₄)₀.₅V₂O₅·mH₂O)]. The XRD pattern of the product exhibits the (00l) peak series in which the (002) harmonic is missing, suggesting that the double layer structure of the (NH₄)₀.₅V₂O₅·mH₂O network is preserved. The X-ray pattern of the product also exhibits the (hkl) set of reflections suggesting that the ordered stacking of the NH₄⁺ intercalated V₂O₅ belts is not markedly present in the product [14]. The basal distance estimated from PXRD pattern for strong (001) peak (~ 9.4 Å) is close to that observed for NH₄⁺ intercalated xerogels [35]. The presence of salts or bases during the formation of the vanadium oxide gels favors the intercalation of the corresponding cations between the vanadium oxide layers. The smaller interplanar spacing of the obtained product (~ 9.4 Å) as compared to 11.5 Å in V₂O₅·nH₂O xerogel should be due to the intercalation of ammonium ions that decreases the amount of water molecules. The presence of ammonium ions may introduce attractive electrostatic forces between the vanadium oxide layers, which is in good agreement with what has been reported in the literature [35, 36].
The FT-IR spectrum of the as-prepared sample is shown in Figure 3.2. The band centered at 981 cm\(^{-1}\) is assigned to V=O stretching vibration, which is sensitive to intercalation and suggests that NH\(_4^+\) ions are inserted between the vanadium oxide layers, in full agreement with previous results [36]. The splitting of this 981 cm\(^{-1}\) band into two absorption peaks (965 and 996 cm\(^{-1}\)) as compared to standard V\(_2\)O\(_5\) (~1020 cm\(^{-1}\)) arises from the formation of two inequivalent V=O groups [12]. The bands at 965 and 996 cm\(^{-1}\) are respectively assigned to the V=O stretching of distorted octahedral and distorted square pyramids. The band at 530 cm\(^{-1}\) corresponds to edge-sharing V-O stretching vibration. The band at 736 cm\(^{-1}\) could be assigned to a V-OH\(_2\) stretching mode due to coordinated water [38]. The two bands at 3495 and 1628 cm\(^{-1}\) are attributed to the stretching and bending vibrations of water molecules respectively [39]. The bands at 3180 and 1400 cm\(^{-1}\) are respectively assigned to the asymmetric stretching and the symmetric bending.
vibrations of NH$_4^+$, which indicated that ammonium ions could be present inside the interlayer space of the V$_2$O$_5$ [40].

![Figure 3.2. FTIR spectrum of (NH$_4$)$_{0.5}$V$_2$O$_5$·mH$_2$O product.](image)

Thermogravimetric analysis (TGA) was carried out in order to determine the water content in the sample. The TGA curve shown in Figure 3.3 indicates the existence of two dehydration steps due to the removal of physical and chemically adsorbed water molecules. The first weight loss (14.5 %) up to 230 °C can be attributed to the release of water adsorbed on the sample. The second weight loss (9.4 %) between 260 and 350 °C was ascribed to the departure of co-ordinated water molecules embedded between the V$_2$O$_5$ layers. The departure of ammonium ions was not observed presumably because most of the weight loss was due to water molecules.
The morphology of the products was examined by scanning electron microscopy. Figure 3.4 (A-F) show SEM images of \((\text{NH}_4)_0.5\text{V}_2\text{O}_5\cdot m\text{H}_2\text{O}\) product synthesized at 160 °C for different reaction times. After 24 h (Figure 3.4A) the product exhibits large-scale belt-like morphology with rectangular ends as shown by arrowheads. The width and thickness of the nanobelts are in the range of 402-551 and 235-305 nm, respectively, with typical lengths up to tens of micrometers. After 36 h (Figure 3.4B) the reaction product exhibits “bent-belt” morphology. This bending arises from the formation of a twin boundary at the \((100)\) planes, which cause an abrupt 60°, change in direction of the belt. After 48 h, in the low magnification SEM image (Figure 3.4C), it is found that the resulting brown spongy-like product exhibits large-scale belt-like morphology together with other geometrical shapes of \((\text{NH}_4)_0.5\text{V}_2\text{O}_5\cdot m\text{H}_2\text{O}\) such as triangles, rings and rectangles.
Figure 3.4. SEM images of ($\text{NH}_4)_0.5\text{V}_2\text{O}_5\cdot\text{mH}_2\text{O}$ product synthesized at 160 °C for (A) 24 h, (B) 36 h, (C) 48 h, (D-F) High-magnification SEM images.
The high-magnification SEM image (Figure 3.4D) reveals a triangular-like morphology with unequal sides. High-magnification SEM images (Figure 3.4E and F) show that the ring-like microstructures are made of packed nanobelts having a perfect circular shape and flat surfaces.

Energy dispersive X-ray spectroscopy (EDX) was also measured to determine the chemical composition of (NH₄)₀.₅V₂O₅·mH₂O. Result from EDX shows (Figure 3.4G) that the product contains only V, N, and O (H cannot be detected by EDX).

![Figure 3.4G. EDX spectrum of (NH₄)₀.₅V₂O₅·mH₂O product.](image)

In order to investigate the effect of temperature on the morphological evolution of (NH₄)₀.₅V₂O₅·mH₂O product, the similar experiment was carried out at 180 °C for 48 h. Representative SEM images of the resulting product synthesized at 180 °C for 48 h are shown in the Figure (3.5A-D). In the low-magnification SEM image (Figure 3.5A), it is found that the resulting product also exhibits large-scale belt-like morphology together with (NH₄)₀.₅V₂O₅·mH₂O rings. High-magnification SEM images (Figure 3.5B-D) show the ring-like microstructures.
The ring/triangle/oval and belt-like structures of the product were further checked using TEM and HRTEM. Figure 3.6(A-E) shows the TEM images of typical (NH$_4$)$_{0.5}$V$_2$O$_5$.mH$_2$O rings/ triangles/ ovals and belts. A typical TEM image of a ring (Figure 3.6A), confirms that the thickness and width of the rings are found to be respectively ~454 nm and ~1 µm and their surface is smooth. Figure 3.6B shows the triangle shape with three unequal sides having a thickness of ~143 nm and a width of ~1 µm.

Figure 3.5. SEM images of (NH$_4$)$_{0.5}$V$_2$O$_5$.mH$_2$O product synthesized at 180 °C for 48 h: (A) Low magnification (B-D) High magnifications
Figure 3.6. TEM images of morphological evolution of $(\text{NH}_4)_0.5\text{V}_2\text{O}_5\cdot\text{mH}_2\text{O}$ product: (A) ring (B) triangle, (C) rectangle, (D) oval and (E) belt and (F) HRTEM image.
The HRTEM image (Figure 3.6F) recorded from single nanobelt shows that the interplanar spacing is about 0.93 nm, close to the separation between the adjacent two (001) lattice planes of monoclinic \((\text{NH}_4)_{0.5}\text{V}_2\text{O}_5.\text{mH}_2\text{O}\), as evidenced from strong (001) peak of PXRD pattern. This suggests that the \((\text{NH}_4)_{0.5}\text{V}_2\text{O}_5.\text{mH}_2\text{O}\) nanobelts exhibit a preferred growth direction along the (100) crystal axis. The selected area electron diffraction (SAED) pattern taken from a single nanobelt (Figure 3.6G) and recorded from the (100) zone axis indicates that the nanobelts are single crystalline in nature.

![SAED pattern of (NH₄)₀.₅V₂O₅.mH₂O product](image)

Figure 3.6G. SAED pattern of \((\text{NH}_4)_{0.5}\text{V}_2\text{O}_5.\text{mH}_2\text{O}\) product

The effect of calcination on the crystallization and morphology of the \((\text{NH}_4)_{0.5}\text{V}_2\text{O}_5.\text{mH}_2\text{O}\) belts/rings/triangles and ovals was investigated. After calcination at 350 °C for 2h, \((\text{NH}_4)_{0.5}\text{V}_2\text{O}_5.\text{mH}_2\text{O}\), leads to pure crystalline \(\text{V}_2\text{O}_5\). Figure 3.7(A-D) show representative SEM images of post-calcined \(\text{V}_2\text{O}_5\) sample, indicating that the individual morphologies of the pre-calcined \((\text{NH}_4)_{0.5}\text{V}_2\text{O}_5.\text{mH}_2\text{O}\) do not change after calcination.
All the PXRD peaks (Figure 3.7E) could be attributed to the orthorhombic shcherbianite V$_2$O$_5$ phase (JCPDS card no. 86-2248), indicating that all intercalated molecules were driven out leading to V$_2$O$_5$. The energy dispersive X-ray spectrum analysis (Figure 3.7F) of V$_2$O$_5$ confirms that the product contains only V and O elements.
We also investigated the morphological evolution as a function of the amount of citric acid. A vanadium dioxide VO$_2$ was obtained for a citric acid concentration of 0.02 M. The composition and purity of as-synthesized VO$_2$ was confirmed by X-ray diffraction. As shown in Figure 3.8A, the diffraction peaks of the resulting product correspond to the monoclinic crystalline phase of VO$_2$ (P2/m JCPDS card no 01-071-0290).

Figure 3.7E. PXRD pattern of the calcined V$_2$O$_5$ product.

Figure 3.7F. EDX spectrum of the calcined V$_2$O$_5$ product.
Figure 3.8(B, C) represents typical SEM images of VO₂ square nanoplatelets synthesized at 160 °C for 48 h. Square VO₂ nano-platelets of ~100 nm thick and ~2 μm wide are obtained.

Figure 3.8A. PXRD pattern of the VO₂ product.

Figure 3.8(B, C). SEM images (B) low magnification (C) high magnification of the as-synthesized VO₂ product
3.3.1. Reaction mechanism

In this approach, NH$_4$VO$_3$ was used as the precursor with a hydrogen peroxide solution and citric acid. The basic reactions involved in the synthesis of (NH$_4$)$_{0.5}$V$_2$O$_5$.mH$_2$O and V$_2$O$_5$ can be expressed as follows:

\[
\begin{align*}
\text{NH}_4\text{VO}_3 + 4\text{H}_2\text{O}_2 &\rightarrow \text{NH}_4[\text{VO(O}_2 \text{)}_2] + 4\text{H}_2\text{O} + \text{O}_2 \quad (1) \\
\text{NH}_4[\text{VO(O}_2 \text{)}_2] + \text{H}^+ &\rightarrow \text{H}[\text{VO(O}_2 \text{)}_2] + \text{NH}_4^+ \quad (2) \\
10\text{H}[\text{VO(O}_2 \text{)}_2] &\rightarrow [\text{H}_2\text{V}_{10}\text{O}_{28}]^{4+} + 4\text{H}_2\text{O} + 9\text{O}_2 \quad (3) \\
[\text{H}_2\text{V}_{10}\text{O}_{28}]^{4+} + 4\text{NH}_4^+ &\rightarrow (\text{NH}_4)_{0.5}\text{V}_2\text{O}_5.m\text{H}_2\text{O} + 7/2 \text{NH}_4^+ \quad (4) \\
(\text{NH}_4)_{0.5}\text{V}_2\text{O}_5.m\text{H}_2\text{O} &\xrightarrow{350^\circ\text{C}/2\text{h}} \text{V}_2\text{O}_5 + m\text{H}_2\text{O} + 1/2 \text{NH}_3 \quad (5)
\end{align*}
\]

In the formation process, it is believed that hydrogen peroxide has a tendency to co-
ordinate V$^{5+}$ to form peroxy complexes [41]. Therefore, the dissolution of ammonium
metavanadate in hydrogen peroxide leads to the formation of a yellow solution of
diperoxo anions [VO(O$_2$)$_2$]$^-$ as observed in equation (1). Adding citric acid gives a red
solution (pH~2) of diperoxovanadic acid H[VO(O$_2$)$_2$] as shown in equation (2).

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\text{Structure of the [V}_{10}\text{O}_{28}]^{6-} \text{cluster}
\]

This diperoxovanadic acid appears to be unstable. It decomposes slowly with the
evolution of oxygen gas leading to the formation of an aqueous solution of decavanadic
acid [H$_2$V$_{10}$O$_{28}$]$^{4+}$ as observed in equation (3). Then, the aqueous solution of decavanadic
acid was subjected to hydrothermal treatment. At the initial stage of the hydrothermal process, decavanadic acid underwent condensation leading to the formation of a layered structure of $V_2O_5\cdot mH_2O$ belts via a homogeneous nucleation and solution growth process. The presence of cations during the formation of the $V_2O_5\cdot mH_2O$ leads to their intercalation within the vanadium oxide layers made of edge and corner sharing $VO_5$ square pyramids. The interlayer space in this layered $V_2O_5$ is occupied by water molecules and ammonium ions resulting in the formation of $(NH_4)_{0.5}V_2O_5\cdot mH_2O$ belts. Wadsley et al. reported that the addition of cations does not significantly alter the structure and size of the $V_2O_5$ framework [42]. Therefore, $(NH_4)_{0.5}V_2O_5\cdot mH_2O$ should remain isostructural with the pristine $V_2O_5\cdot xH_2O$ xerogel. The structure of $(NH_4)_{0.5}V_2O_5\cdot mH_2O$ can be described as an assembly of stacked $V_2O_5$ bilayers. Vanadium coordination is based on $[VO_5]$ square pyramids with a short V=O double bond along the ‘z’ axis perpendicular to the basal planes. Ammonium ions and water molecules are intercalated between the vanadium oxide layers.

3.3.2. Growth mechanism

The growth of ring, triangle, rectangle and oval structures can be understood on the basis of this layered structure (Figure 3.9). Many models have been pushed forward to explain the formation of inorganic ring-like nanostructures. According to Liu and Zeng, CdS rings, were synthesized via the self-assembly of nanoparticles with an intrinsic hexagonal symmetry [43]. Murray proposed an oriented attachment mechanism of nanoparticles to explain the formation of PbSe nanorings [23]. A cation induced coiling growth mechanism was suggested by Liu et al. to describe the formation of vanadium pentoxide nanorings and microloops [44]. Wang et al. proposed the loop-by-loop coaxial, uniradius, self-coiling of a single nanobelt in order to explain the formation of ZnO nanorings in the vapor phase [27].
Figure 3.9. Schematic illustration of a possible process for the formation of \((\text{NH}_4)_0.5\text{V}_2\text{O}_5\cdot\text{mH}_2\text{O}\) rings, triangles, ovals and belts.
A similar process was suggested by Shen et al, for the synthesis of Ag$_2$V$_4$O$_{11}$ nanorings and microloops from solutions [45]. These growth mechanisms cannot be extended to explain the formation of our (NH$_4$)$_{0.5}$V$_2$O$_5$.mH$_2$O ring-like structures, synthesized from solutions. Their morphologies are different from those of ZnO, CdS, V$_2$O$_5$, and Ag$_2$V$_4$O$_{11}$ nanorings. However, the ‘cation induced coiling growth mechanism’ proposed by Liu et al, could, to a certain extent, be applied to the formation of (NH$_4$)$_{0.5}$V$_2$O$_5$.mH$_2$O rings. This compound has a layered structure made of edge and corner sharing VO$_5$ square pyramids.

These vanadium oxide sheets exhibit a polar structure arising from the V=O$^-$ double bonds perpendicular to the layer plane within the VO$_5$ square pyramids. Moreover, NH$_4^+$ ions and water molecules intercalated between the vanadium oxide bilayers favor the flexibility of (NH$_4$)$_{0.5}$V$_2$O$_5$.mH$_2$O nanobelts [7].

Positively charged NH$_4^+$ ions can be attracted by the V=O$^-$ dipoles on both side of the bilayers. According to the so-called ‘cation-induced coiling’ model [46], we may assume that during the growth process of (NH$_4$)$_{0.5}$V$_2$O$_5$.mH$_2$O nanobelts, asymmetric strain
emerges (Figure 3.10A, B) as soon as the amount of adsorbed NH$_4^+$ becomes different on both top or bottom surfaces. When this asymmetric induced strain energy becomes larger than the elasticity energy, nanobelts will tend to bend or curve without fracture as shown in the Figure 3.10C.

![Figure 3.10C. TEM image of the curved or bending of the belt into a circular shape](image)

Furthermore, we could expect that NH$_4^+$ ions intercalated at both ends of the belts can be easily removed as ammonia gas allowing the edges of vanadium oxide sheets to roll up. Edge sharing polar VO$_5$ square pyramids at both ends of the belt then connect (shown in Figure 3.10 D, E) in order to minimize the total energy arising from the electrostatic polarization energy and elastic deformation energy, leading to the formation of a perfect circular ring with a triangular tip (shown by arrowhead in Figure 3.7D). The curving/self coiling of VO$_5$ pyramid sheets does not occur when the amount of NH$_4^+$ ions adsorbed on both, top and bottom, sides of (NH$_4$)$_{0.5}$V$_2$O$_5$.mH$_2$O belts is same. The reaction product also exhibits a triangular-like morphology. This special kind of morphology arises from the presence of twin boundaries within the (100) plane of a single belt. An abrupt 60°
change in the direction of the belt then occurs leading to the formation of triangles at both ends of the belt. This model might be too simple and detailed formation mechanism of \((\text{NH}_4)_0.5\text{V}_2\text{O}_5.\text{mH}_2\text{O}\) triangles, rectangles and ovals might require further investigation.

Figure 3.10 (D, E). SEM images of the edge shared polar VO\(_5\) square pyramids at both ends of the belt into a circular shape (shown by dotted circles)
References