Hydrothermal Synthesis of Crystalline Na$_2$V$_6$O$_{16}$·3H$_2$O Belts and Rings

P. Chithaiah, G. T. Chandrappa* and J. Livage “Formation of Crystalline Na$_2$V$_6$O$_{16}$·3H$_2$O Ribbons into Belts and Rings” Inorganic Chemistry, 51(2012) 2241
5.1. Introduction

A rich diversity of vanadium oxide bronzes and intercalation compounds based on the incorporation of either alkali or transition metals within the interstitial spaces of the vanadium oxide tunnel framework have been extensively studied [1-3]. Among them, alkali-metal, or alkaline earth metal vanadium oxide bronze hydrated compounds (M$_2$V$_6$O$_{16}$nH$_2$O, M = Na, K or MV$_6$O$_{16}$nH$_2$O, M = Mg, Ca) have been widely studied during the past decade. The unique physical-chemical properties of these compounds allow a wide range of practical applications such as electrochromic devices, cathodic electrodes for lithium batteries, humidity sensors, and so on [4-12]. Semiconducting oxide nanobelts are a unique group of quasi-one-dimensional nanomaterials, which have been systematically studied for a wide range of materials with distinct chemical compositions and crystallographic structures.

Control over the nucleation and growth may be crucial in the tailoring of the size, shape, surface structure and organization of particles constituting the gels and consequently to the final properties of the resultant vanadium oxide materials. This control has to be performed at the early stages of the polymerization reactions involved due to the high reactivity of the vanadium precursors. Several synthetic routes such as micro emulsion-mediated systems, arc discharge, laser-assisted catalysis growth, solution, vapor transport, solvothermal and hydrothermal methods have been successfully explored to fabricate various kinds of nanostructured vanadium oxides and their derived compounds.

A large family of trivanadates and hexavanadates phase has been synthesized under hydrothermal process [13-15]. But, to the best of our knowledge, there have been few literature examples on the synthesis of Na$_2$V$_6$O$_{16}$·3H$_2$O nanostructures [16-18]. The
importance of sodium hexavanadates has strongly increased because of the specific charge
and magnetic ordering associated with mixed valence states in the compounds [19].

Various kinds of vanadium oxide nanostructures such as nanowires, nanobelts, nanorods,
nanotubes, nanostructured foam, nanoribbons and rose-like structures have been reported
[20-21]. But presently, it has been demonstrated that several new geometrical configurations
such as nanosprings [22], nanorings [22-24], and nanohelices [25-26], grown from 1D
nanobelts/fibers or nanoribbons are of special interest due to their structural flexibility, size
and special morphology related properties. Nanorings in particular show many unusual
behaviors, receive an abnormal dispersion of magnetic field in semiconductor nanorings and
motivate much interest in the theoretical and experimental study of the electronic and optical
properties due to three-dimensional topological quantum effects for electrons confined in
nanorings [27-28].

In the present chapter, we report a simple and facile hydrothermal method to synthesize
Na₂V₆O₁₆·3H₂O nanobelts and nanorings on acidification of NaVO₃ with H₃PO₄ without the
use of any harmful solvents or surfactants. A possible reaction and growth mechanism
involved in the formation of nanobelts and nanorings are also discussed.

5.2. Experimental

5.2.1. Sample Preparation

Chemical reagents of analytical grade were purchased from Merck Ltd. and used as
received without further purification. Double distilled water was used throughout the
experiments. Na₂V₆O₁₆·3H₂O nanorings were prepared via hydrothermal technique in a
Teflon-lined stainless steel autoclave. A typical procedure followed in the synthesis of
Na₂V₆O₁₆·3H₂O nanorings is described as follows. 0.25 g sodium metavanadate (2.05 x10⁻³
mol, NaVO$_3$) powder was added into 15 mL distilled water taken in a 20 mL Teflon tube. The pH of the solution was adjusted to ~2.0 by adding three drop of orthophosphoric acid (H$_3$PO$_4$, 88%) using 2 ml pipette, resulting in the formation of a wine red solution and stirred for 15 minutes. Subsequently, the wine red solution was filled into Teflon-lined stainless steel autoclaves. The autoclaves were maintained at variable temperatures for different duration. Once, the hydrothermal treatment (HTT) is over, the autoclaves were cooled to ambient temperature naturally. The reddish brown non-adherent spongy like bulk material was collected and washed with distilled water followed by ethanol several times. The final product was dried in an oven at 60 °C for 2 h.

5.3. Results and discussion

![Figure 5.1. PXRD pattern of Na$_2$V$_6$O$_{16}$·3H$_2$O product.](image)
Figure 5.1 shows the PXRD pattern of the as synthesized product. All of the diffraction peaks in the pattern can be indexed to a pure monoclinic crystalline phase of Na$_2$V$_6$O$_{16}$3H$_2$O (according to JCPDS No. 16-601 for Na$_2$V$_6$O$_{16}$3H$_2$O). No reflections of impurity were found in the pattern, which proves that pure Na$_2$V$_6$O$_{16}$3H$_2$O has been successfully synthesized. The basal distance for strong (001) peak is 7.87 Å, which matches well with a previously reported value [18].

Figure 5.2 shows the FTIR spectrum of the as synthesized product. The bands between 400 and 1001 cm$^{-1}$ can be indexed to various vibrational modes of V–O groups. The bands located at 535 and 826 cm$^{-1}$ are attributed to the symmetric and asymmetric vibrational modes of V–O–V stretching vibrations, respectively. The two main bands at 1001 and 964 cm$^{-1}$ are respectively assigned to the stretching vibrations of V$^{5+}$=O and V$^{4+}$=O groups, corresponding to the existence of the short-range order of VO$_6$ unit. The band at 728 cm$^{-1}$ is ascribed to a V-OH$_2$ stretching mode due to coordinated water [29]. The band located at 1626 cm$^{-1}$ is related to the bending vibrations of O–H groups of water molecules [30].
Figure 5.3 shows thermogravimetric analysis of as synthesized Na$_2$V$_6$O$_{16}$·3H$_2$O product. The TG profile shows a weight loss of 7.9 % from 100 to 360 °C, corresponding to the removal of adsorbed water molecules. This value matches well with the water content (8.16%) of the Na$_2$V$_6$O$_{16}$·3H$_2$O sample. The results from XRD, FTIR, and TGA studies confirmed that the product is Na$_2$V$_6$O$_{16}$·3H$_2$O.

The morphology of the as-synthesized Na$_2$V$_6$O$_{16}$·3H$_2$O nanostructures at different temperatures was investigated by scanning electron microscopy. Figures 5.4 (A-I) show the representative SEM images of the as synthesized Na$_2$V$_6$O$_{16}$·3H$_2$O nanostructures with different magnifications. When the temperature is maintained at 130 °C for 24 h, as shown in Figure 5.4A, the reddish brown product exhibits flexible beltlike morphology. After 48 h, as observed in low-magnification SEM image (Figure 5.4B), one can observe that the
resulting product reveals a large amount of flexible beltlike nanostructures with typical lengths up to several hundreds of micrometers in addition to a significant amount of nanorings. A high magnification SEM image (Figure 5.4C) shows that the nanorings are made of nanobelts. Figure 5.4 (D, E) exhibit low and high magnification SEM images of Na$_2$V$_6$O$_{16}$·3H$_2$O nanorings obtained at 150 °C for 48 h. Figure 5.4 (F, G) reveal low and high magnification SEM images of Na$_2$V$_6$O$_{16}$·3H$_2$O nanorings obtained at 180 °C for 48 h. Figure 5.4 (H, I) shows low and high magnification SEM images of Na$_2$V$_6$O$_{16}$·3H$_2$O nanorings obtained at 150 °C for 72 h. It is found that all the Na$_2$V$_6$O$_{16}$·3H$_2$O nanorings have perfect circular with uniform shapes and flat surfaces. Typical nanorings have diameters of 4.5 to 6.5 µm with a thickness of 100-300 nm respectively. The process is of high reproducibility from run to run and the percentage yield of nanorings is relatively not very high.

![SEM image of Na$_2$V$_6$O$_{16}$·3H$_2$O product synthesized at 130 °C for 24 h.](image-url)
Figure 5.4(B, C). Low and high magnification SEM images of Na$_2$V$_6$O$_{16}$·3H$_2$O product synthesized at 130 °C for 48h.

Figure 5.4(D, E). Low and high magnification SEM images of Na$_2$V$_6$O$_{16}$·3H$_2$O product synthesized at 150 °C for 48h.
Figure 5.4 (F, G). Low and high magnification SEM images of Na$_2$V$_6$O$_{16}$·3H$_2$O product synthesized at 180 °C for 48h.

Figure 5.4 (H, I). Low and high magnification SEM images of Na$_2$V$_6$O$_{16}$·3H$_2$O product synthesized at 150 °C for 72h.
The energy-dispersive X-ray spectrum (Figure 5.4J) was measured to determine the chemical composition of Na₂V₆O₁₆·3H₂O sample. The spectrum exhibits the characteristic Na, V and O absorption peaks (H cannot be detected by EDX).

The detailed morphology and structure of Na₂V₆O₁₆·3H₂O nanobelts/rings was further characterized by TEM and HRTEM. The TEM image (Figure 5.5A) shows that the width and thickness of nanobelts are in the range of 200-300 nm and 100-200 nm, respectively. Figure 5.5B shows the TEM image of Na₂V₆O₁₆·3H₂O nanobelts/rings. From HRTEM shown in Figure 5.5C, it is found that the distance between neighboring planes is ~7.81 Å. This distance is consistent with the (001) plane of the monoclinic Na₂V₆O₁₆·3H₂O structure, as observed in the XRD pattern, which shows that these nanobelts/rings grow along the (001) direction. The SAED pattern (Figure 5.5D) taken from an individual nanobelts/rings can be attributed to monoclinic Na₂V₆O₁₆·3H₂O nanostructures indicating that the nanobelts and nanorings are structurally uniform and a good single-crystal structure.
5.3.1. Reaction mechanism

The chemical reactions involved for the formation of $\text{Na}_2\text{V}_6\text{O}_{16}\cdot3\text{H}_2\text{O}$ nanobelts/rings can be formulated as follows:
In this process, sodium metavanadate in aqueous solution forms Na\(^+\) and VO\(^3^-\). On acidification of VO\(^3^-\) with H\(_3\)PO\(_4\) leads to the formation of wine red solution of vanadic acid (H\(\text{VO}_3\), pH \(\approx 2\)) as shown in eq 1. The H\(\text{VO}_3\) solution is then progressively gets converted into a mixture of deca-vanadate \([\text{H}_2\text{V}_{10}\text{O}_{28}]^{4-}\) and \([\text{VO}_2(\text{H}_2\text{O})_4]^+\) ions (shown in eq 2), which has been observed previously by \(^{51}\text{V}\) NMR spectroscopy [16]. The resulting solution was subjected to the hydrothermal treatment. At the early stage of hydrothermal treatment, we could expect that the decavanadate \([\text{H}_2\text{V}_{10}\text{O}_{28}]^{4+}\) species get protonated (eq 3) and the cationic \([\text{VO}_2(\text{H}_2\text{O})_4]^+\) species undergoes deprotonated (eq 4) in order to provide neutral \([\text{VO(OH)}_3(\text{H}_2\text{O})_2]\) precursors. It is well-known that the composition of the V\(^{5+}\) solution changes with pH. According to the so-called partial charge model [32], a vanadate solution of pH>1 should contain a mixture of a neutral species \([\text{VO(OH)}_3(\text{H}_2\text{O})_2]\) and a negatively charged precursor \([\text{VO(OH)}_4(\text{H}_2\text{O})_2]^-\). Therefore, the hydrated sodium hexavanadate Na\(_2\)V\(_6\)O\(_{16}\) 3H\(_2\)O phase results from the polycondensation of these Na\(^+\) ions can accommodate within these V\(_6\)O\(_{16}\)\(^{2-}\) framework tunnels in order to compensate the negative charge of the layers, in a similar way as previously proposed for the formation of Na[V\(_3\)O\(_8\)] [16, 32].
5.3.2. Growth mechanism

The growth mechanism for the formation of nanorings of vanadium oxide based materials can be understood on the basis of their layered structures. For example, Shen and Chen [23], proposed the loop-by-loop coaxial, uniradius, self-coiling of a single nanobelt in order to explain the formation of Ag$_2$V$_{4}$O$_{11}$ nanorings and microloops from solutions in a similar way as proposed previously, for the formation of ZnO nanorings in the vapor phase [31]. A ‘Cation induced coiling growth mechanism’ was suggested by Liu and Xue [24], to describe the formation of V$_2$O$_5$·xH$_2$O nanorings and microloops. We suggested a similar process for the formation of (NH$_4$)$_{0.5}$V$_2$O$_5$·mH$_2$O rings, triangles, and ovals from solutions and proposed that these were formed when two ends of a belt connect through edge and corner sharing of VO$_5$ square pyramids. However, the exact mechanism for the formation of Na$_2$V$_6$O$_{16}$·3H$_2$O nanostructures is still unclear. It is well known that Na$_2$V$_6$O$_{16}$·3H$_2$O phase cannot be result from a solid state transformation, and then the structural transformation should involve a redissolution–precipitation process under hydrothermal process. Previously, Yu and Zhou groups [17, 18] 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. They suggested that the anions are crucial for the formation of Na$_2$V$_6$O$_{16}$·3H$_2$O nanobelts and nanowires. Therefore, in the present work, we could expect
that H₃PO₄ plays an important role because of its polar nature, highly soluble in water and
dissociate into H⁺ and PO₄³⁻ ions in the solution. The H⁺ ions maintain the pH of the solution
(pH ≈ 2). With the support of the F⁻ and SO₄²⁻ anions, we believed that the PO₄³⁻ anions are
crucial for the growth of Na₂V₆O₁₆·3H₂O nanobelts. Since, the PO₄³⁻ has stronger
coordination ability than F⁻ and SO₄²⁻ anions, and may adsorb selectively to the special
crystal facets leading to the formation of flexible Na₂V₆O₁₆·3H₂O nanobelts.

The formation of Na₂V₆O₁₆·3H₂O nanorings can also be explained in a similar way as
previously proposed for the formation of V₂O₅·xH₂O. The Na₂V₆O₁₆·3H₂O structure consists
of V₃O₈²⁻ layers and hydrated Na⁺ ions are intercalated between these layers in order to
compensate the negative charge of the layers. The V₃O₈ layers are made of VO₆ octahedra
and V₂O₈ units of edge-sharing square pyramids. A “Cation induced coiling” model should
be involved in the formation of Na₂V₆O₁₆·3H₂O nanorings, owing to the presence of residual
or non-intercalated Na⁺ ions from the solution under hydrothermal process. According to the
so called “Cation induced coiling” model, we may assume that the non-intercalated Na⁺ ions
can be adsorbed by the V=O⁶ dipoles on both sides of the Na₂V₆O₁₆·3H₂O nanobelt. When
the amount of Na⁺ ions adsorb asymmetrically on both the top or the bottom surface of thin,
straight Na₂V₆O₁₆·3H₂O nanobelt, the asymmetric strain energy induces. When this
asymmetric induced strain energy becomes larger than the elasticity energy, the straight
Na₂V₆O₁₆·3H₂O nanobelt tends to self-coil into a circular ring. The over-lapping end of the
belt is clearly observed in the SEM image of Figure 5.4G (shown by arrowhead), which
suggests the possible self-coiling of a single nanobelt into rings. However, the detailed
formation mechanism of Na₂V₆O₁₆·3H₂O rings might require further investigation.
References


86