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# Synthesis of single crystalline $(NH_4)_2V_6O_{16}\cdot 1.5H_2O$ nest-like structures

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## HIGHLIGHTS

- Nest-like $(NH_4)_2V_6O_{16}\cdot 1.5H_2O$ structures have been facilely synthesized.
- A hydrothermal method has been employed.
- A reaction mechanism for the formation of $(NH_4)_2V_6O_{16}\cdot 1.5H_2O$ structures is discussed.

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## ABSTRACT

Novel nest-like $(NH_4)_2V_6O_{16}\cdot 1.5H_2O$ structures made of nanobelts have been synthesized by a facile hydrothermal approach. The powder X-ray diffraction pattern of the sample reveals the monoclinic crystalline phase of $(NH_4)_2V_6O_{16}\cdot 1.5H_2O$. The scanning electron microscopy images of the sample obtained at 130 °C for 3 days exhibit nest-like morphology. The transmission electron microscopy result reveals that the nanobelts have a smooth surface. The selected area electron diffraction pattern of the nanobelts indicates single crystalline nature. The two major weight losses occur in thermogravimetric analysis which correspond to the removal of water and ammonia molecules. Further, calcination of the $(NH_4)_2V_6O_{16}\cdot 1.5H_2O$ product results in the formation of orthorhombic phase of shcherbianite $V_2O_5$.



## 1. Introduction

Over the past few years, considerable attention has been devoted to the synthesis of one-dimensional (1D) nanostructured materials such as nanotubes, nanorods, nanowires and nanobelts, because of their novel physical and chemical properties [1–3]. Among various metal oxide nanostructures, one-dimensional vanadium oxide-based nanostructured materials have interested many researchers over the last few decades due to their outstanding structural flexibility [4], diverse technological applications in catalysis [5,6], rechargeable lithium ion batteries [7], chemical sensors or actuators [8,9], electrochemical pseudo-capacitors [10] and electro-chromic 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 reports on the synthesis of 1-D nanostructured single crystalline vanadates. For example, Durupthy et al. synthesized the crystalline $NaV_3O_8\cdot 1.5H_2O$ at room temperature on acidification of a metavanadate solution [17]. Yu et al. and Zhou et al. have synthesized $Na_2V_6O_{16}\cdot 3H_2O$ nanobelts and nanowires in the presence of $F^-$ and $SO_4^{2-}$ anions, respectively [18,19]. Mai et al. reported the synthesis, electrical transport measurements, and conduction mechanism on nanobelts of $NH_4V_3O_8$ vanadate [20]. Wang et al. reported that the one-dimensional ammonium vanadates are semiconductors at room temperature [2]. More recently, we reported the synthesis of $Na_2V_6O_{16}\cdot 3H_2O$ belts/rings and suggested that the $Na_2V_6O_{16}\cdot 3H_2O$ rings were made of self-coiling 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 study, we report the synthesis of nest-like $(NH_4)_2V_6O_{16}\cdot 1.5H_2O$ architectures made of nanobelts by the hydrothermal method and the possible reaction mechanism for the formation of $(NH_4)_2V_6O_{16}\cdot 1.5H_2O$ architecture is discussed. The orthorhombic phase of shcherbianite $V_2O_5$ is obtained on calcination of $(NH_4)_2V_6O_{16}\cdot 1.5H_2O$ at 350 °C for 2 h.

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## 2. Experimental

### 2.1. Synthesis

All reagents were of analytical grade and used as received without further purification. Distilled water was used throughout. 0.5 g of $NH_4VO_3$ ($4.27 \times 10^{-3}$ mol) powder was added into 25 mL of distilled water and 0.2 mL of orthophosphoric acid ($H_3PO_4$, 88%, pH ~ 1.5) was also 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 then dried at 60 °C for 2 h.

### 2.2. Characterization

Powder X-ray diffraction (PXRD) data were recorded on a Philips X'pert PRO X-ray diffractometer with graphite-monochromatized Cu Kα radiation ($\lambda = 1.541$ Å) operated at 40 kV and 30 mA. The Fourier transform infrared (FTIR) spectrum of the sample was collected using a Thermo Nicolet FTIR spectrometer. The water content in the sample was investigated by thermogravimetric analysis (TGA) using a SDT Q600 thermomicrobalance in $N_2$ atmosphere from room temperature to 600 °C at a heating rate of 10 °C $min^{-1}$. The morphologies of the products were examined by a Quanta-200 scanning electron microscope (SEM) equipped with an energy dispersive X-ray spectroscopy (EDX). The nano-/microstructure of the product was observed by transmission electron microscopy (TEM) and selected area electron diffraction (SAED) which were performed with a Hitachi model H-600 instrument operating at 100 kV.

## 3. Results and discussion

The PXRD pattern of the as-prepared sample is shown in Fig. 1a. All the diffraction peaks in the pattern can be readily indexed to a pure monoclinic crystalline phase of $(NH_4)_2V_6O_{16} \cdot 1.5H_2O$ (JCPDS Card no. 51-0376). No reflections of impurity are found in the pattern, which proves that pure $(NH_4)_2V_6O_{16} \cdot 1.5H_2O$ has been successfully synthesized.

The FTIR spectrum of the as-prepared sample is shown in Fig. 1b. The bands at 1004 $cm^{-1}$ and 964 $cm^{-1}$ correspond to V=O stretching of distorted octahedral and distorted square-pyramids respectively; 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

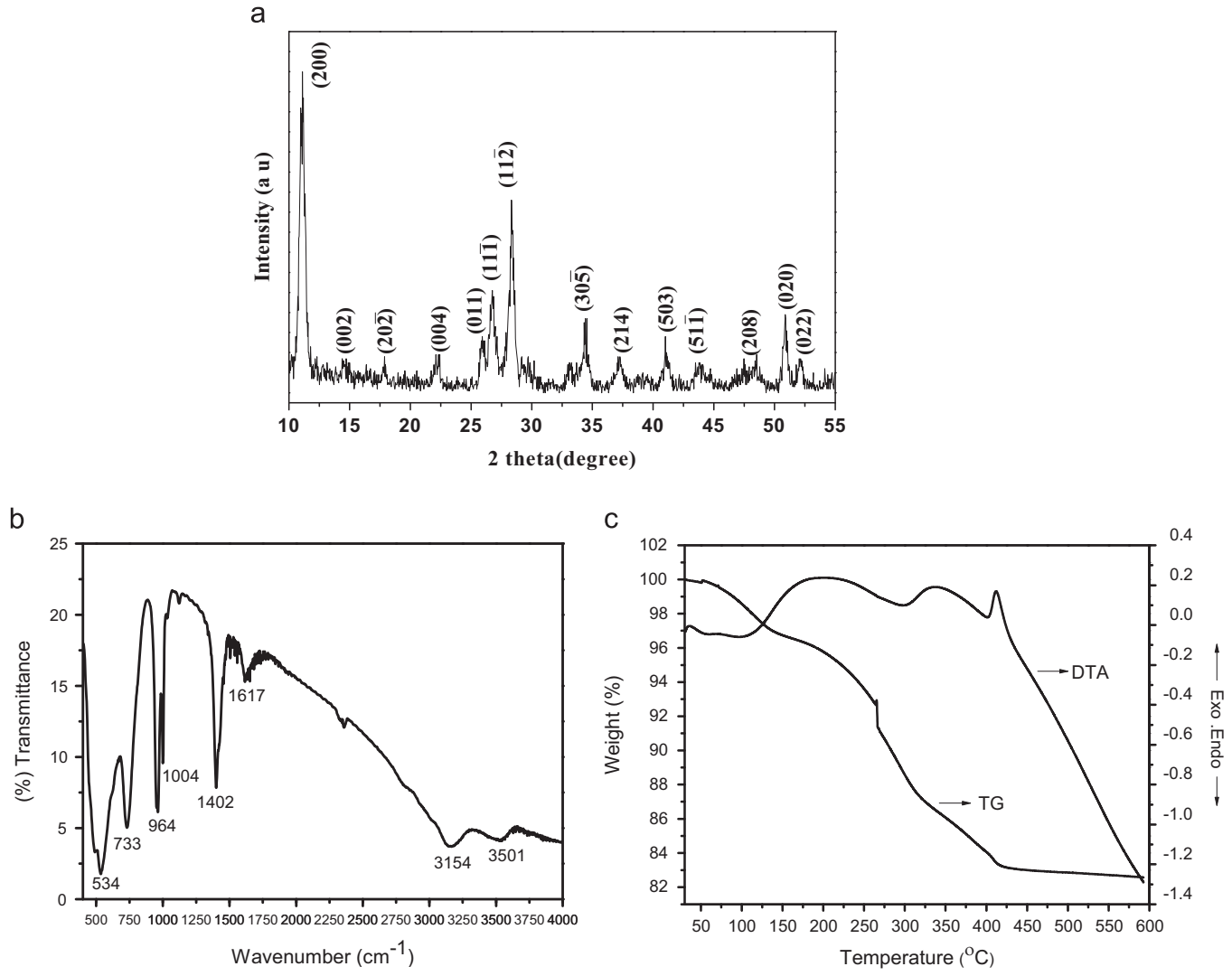


**Fig. 1.** (a) PXRD pattern (b) FTIR spectrum and (c) TG-DTA curves of $(NH_4)_2V_6O_{16} \cdot 1.5H_2O$.