

# Hydrothermal Synthesis of V<sub>3</sub>O<sub>7</sub>·H<sub>2</sub>O Nanobelts and Study of Their Electrochemical Properties

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# ABSTRACT

Vanadium oxide hydrate  $V_3O_7 \cdot H_2O$  ( $H_2V_3O_8$ ) nanobelts have been synthesized by hydrothermal approach using  $V_2O_5$  as vanadium source and phenolphthalein as structure-directing agent. Techniques X-ray powder diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), infrared spectroscopy and nitrogen adsorption/desorption isotherms have been used to characterize the structure, morphology and composition of the nanobelts. The  $V_3O_7 \cdot H_2O$  nanobelts are up to several hundreds of nanometers, the widths and thicknesses are 90 and 40 nm, respectively. The electroactivity of the nanobelts has been investigated. The as-synthesized material is promising for chemical and energy-related applications such as catalysts, electrochemical device and it may be applied in rechargeable lithium-ion batteries.

Keywords: Nanobelts,  $V_3O_7$ · $H_2O$ , Phenolphthalein, Hydrothermal Synthesis, Electroactivity

# 1. Introduction

Among the various candidates for their much important applications in catalysts [1,2], cathodes materials [3-5] for rechargeable Li-ion batteries, chemical sensors [6,7], vanadium oxides have attracted much attention due to their layered structure and distinctive physicochemical properties [8-10]. In particular, one-dimensional (1D) nanostructural vanadium oxides have been successfully used as electrode materials with greatly enhanced electrochemical properties [11,12]. 1D nanostructural vanadium oxides containing either  $V^{4+}$  or  $V^{5+}$  have a large capacity which corresponds to reduction of the V<sup>4+</sup> or  $V^{5+}$  by the intercalation process in which Li enters the VO<sub>x</sub> layers. To best of our knowledge, however, the synthesis and electrochemical properties of 1D nanostructural vanadium oxide composed of  $V^{4+}$  and  $V^{5+}$  have rarely been reported [13]. Among them nanostructured vanadium oxides have been extensively studied since the discovery of  $VO_x$  nanotubes by R. Nesper and his group [14-15]. They exhibit a great variety of nanostructures, ranging from 1D to 3D [16] and V<sub>2</sub>O<sub>5</sub> has even been chosen as a model system for the description of nanostructured materials.

As one of the wet chemistry methods, hydrothermal

treatment has been extensively used for the synthesis of inorganic compounds [12]. Indeed, Sediri et al. [13] synthesized the nanoneedles, nanorods of B-VO<sub>2</sub>, and vanadium oxide nanotubes with high crystallinity via a one-step hydrothermal treatment using crystalline V<sub>2</sub>O<sub>5</sub> as a precursor and various aromatic amines as structure-dire-cting templates.  $V_3O_7 \cdot H_2O \cdot (H_2V_3O_8)$  has been studied for many years [19-21]. V<sub>3</sub>O<sub>7</sub>·H<sub>2</sub>O nanofibres have been prepared firstly by Theobald [19]. Their structure was described as layers that contain VO<sub>6</sub> octahedra and VO<sub>5</sub> trigonal bipyramids with vanadium oxidation states of +4 and +5, respectively [20]. Recently, the synthesis of V<sub>3</sub>O<sub>7</sub>·H<sub>2</sub>O nanobelts was reported by Li and coworkers [22]. In their synthesis, the nanobelts were hydrothermally grown from V<sub>2</sub>O<sub>5</sub> powder in the presence of appropriate amount of hydrochloric acid. Shi et al. [23] obtained single-crystalline vanadium oxide nanobelts through a surfactant-directed growth process under hydrothermal conditions using V<sub>2</sub>O<sub>5</sub> as a precursor.

While many methods have been developed to elaborate nanostructured vanadium oxides, to the best of our knowledge, it is the first time to report the optimization of reaction conditions of the synthesis of  $V_3O_7$ ·H<sub>2</sub>O nanobelts using phenolphthalein as structure-directing template by hydrothermal self-assembling process. The electrochemical properties of  $V_3O_7$ ·H<sub>2</sub>O nanobelts were also studied.

# 2. Experimental Section

## 2.1. Hydrothermal Synthesis

All of the chemical reagents were purchased from Across and used without further purification.  $V_2O_5$  was used as vanadium source and phenolphthalein was used as structure-directing template for the first time.

The detailed synthesizing process was as follows. In a typical synthesis, the preparation was made from a mixture of  $V_2O_5$  (0.079 g), phenolphthalein (0.46 g) and distilled water (10 mL). After 2 hours of stirring, the mixture was transferred into a Teflon lined steel autoclave with a capacity of 23 ml, and maintained at 180°C for 4 days under autogenous pression. The pH of the reaction mixture remains close to pH  $\approx$  7. After hydrothermal treatment, the pH of the solution was equal to 4.3. The resulting green powder was washed with water and ethanol to remove the organics residues and then dried at 80°C for 4 hours. The green color of the powder suggested the presence of the V<sup>4+</sup> ions [24].

#### 2.2. Characterization Techniques

X-ray powder diffraction data (XRD) were obtained on a X'Pert Pro Panalytical diffractometer with CoK $\alpha$  radiation ( $\lambda = 1.78901$  Å) and graphite monochromator. The XRD measurements were carried out by a step scanning method (2 $\theta$  range from 2° to 50°), the scanning rate is 0.03° s<sup>-1</sup> and the step time is 3 s.

Scanning electron microscopy (SEM) images were obtained with a Cambridge Instruments Stereoscan 120.

Transmission electron microscopy (TEM) was carried out with a Philips G20 Ultra-Twin Microscope at an accelerating voltage of 200 kV. One droplet of the powder dispersed in CH<sub>3</sub>CH<sub>2</sub>OH was deposited onto a carbon-coated copper grid and left to dry in air. Fourier transform infrared spectra (FTIR) were recorded with a Nicolet 380 Spectrometer.

The electrochemical measurements were performed using a potentiostat (Organic-Logic SA) workshop with Hg/HgCl<sub>2</sub>/KCl as reference electrode and a stainless grid as the counter electrode. The working electrode is a film of V<sub>3</sub>O<sub>7</sub>·H<sub>2</sub>O deposited on a plate of indium tin oxide (ITO). The operating voltage was controlled between -1.0 and 2.5 V at a scan rate of 50 mVs<sup>-1</sup>. The electrolyte was the lithium perchlorate 1M (LiClO<sub>4</sub>) dissolving in propylene carbonate (PC). All measurements were performed at room temperature.

# 3. Results and Discussion

### 3.1. X-ray Diffraction

The structural properties of the prepared samples were studied by using the X-ray diffraction (XRD). The X-ray diffraction (XRD) pattern of the as-obtained powder after hydrothermal treatment is shown in **Figure 1**. All of diffraction peaks can be perfectly indexed to orthorhombic vanadium oxide crystalline phase  $V_3O_7$ ·H<sub>2</sub>O·(H<sub>2</sub>V<sub>3</sub>O<sub>8</sub>) with lattice constants of a = 16.847 Å, b = 9.362 Å and c = 3.634 Å (JCPDS # 85-2401). No peaks of any other phases or impurities were observed from the XRD patterns, indicating that  $V_3O_7$ ·H<sub>2</sub>O crystalline phase with high purity could be obtained using the present synthetic process.

# 3.2. Scanning and Transmission Electron Microscopes

The surface morphology and size of the as-prepared samples were studied by using the scanning and transmission electron microscopes (SEM and MET). The observation by scanning electronic microscopy of the sample (**Figure 2**) shows that the as-obtained  $V_3O_7$ ·H<sub>2</sub>O is made of a homogenous phase with particles uniformly sized which display belt-like morphology, with a smooth



Figure 1. XRD pattern of the as- synthesized V<sub>3</sub>O<sub>7</sub>·H<sub>2</sub>O nanobelts.



Figure 2. SEM micrographs (a and b) of the as-synthesized material.

surface and a rectangular cross-section, 2 - 10 min length. The transmission electron microscopy photos of the as-obtained V<sub>3</sub>O<sub>7</sub>·H<sub>2</sub>O shows that the nanobelts are typically 90 nm wide and 40 nm thick (**Figure 3**). The high magnification HRTEM image clearly exhibits high



Figure 3. TEM photos (a and b) of V<sub>3</sub>O<sub>7</sub>·H<sub>2</sub>O nanobelts.

crystallinity (**Figure 4**). The lattice fringes correspond to a d spacing of 0.47 nm which is consistent with the distance between two (020) crystal planes of the orthorhombic  $V_3O_7$ ·H<sub>2</sub>O crystal, according to JCPDS # 85 -2401 [25]. This result is good agreement with X-ray diffraction.

## **3.3. Infrared Spectroscopy**

The structure information was further provided by FTIR spectroscopy. Figure 5 displays the infrared spectrum of as-synthesized V<sub>3</sub>O<sub>7</sub>·H<sub>2</sub>O nanobelts. The bands at 1021 cm<sup>-1</sup>, 980 cm<sup>-1</sup>, and 557 cm<sup>-1</sup> are attributed to the characteristic of V-O vibration bonds. Indeed, the bands at 1021 cm<sup>-1</sup> and 980 cm<sup>-1</sup> correspond to the symmetric stretching of the vs  $(V^{5+} = O)$  and vs $(V^{4+} = O)$  bonds, respectively, which indicates the similarity of the as-prepared phase with the structure of the layered orthorhombic  $V_2O_5$  [26]. The band at 534 cm<sup>-1</sup> corresponds to the stretching vibrations of the vs (V-O-V) bridging bonds [27]. The bands located at 3407 cm<sup>-1</sup> and 1634  $cm^{-1}$  come from the vs (H-O-H) and vs (H<sub>2</sub>O) vibration, which might indicate that a certain amount of water molecules is embedded between the layers [23]. The results demonstrates that the



Figure 4. HRTEM image of V<sub>3</sub>O<sub>7</sub>·H<sub>2</sub>O nanobelts.



Figure 6. Cyclic voltammogams of the as-synthesized V<sub>3</sub>O<sub>7</sub>·H<sub>2</sub>O nanobelts.

material consist of mixed valance state vanadium atoms and water.

# **3.4. Electrochemical Properties**

As an intercalation compound,  $V_3O_7$ ·H<sub>2</sub>O is promising cathode material in lithium-ion batteries [23]. It was reported that the electrochemical properties of the electrode materials are influenced by many factors such as instinctive structure, morphology, and preparation processes. Therefore, in this paper, we also investigated the electrochemical properties of lithium ion intercalation/deintercalation of  $V_3O_7$ ·H<sub>2</sub>O nanobelts. The cyclic voltammogram (CV) curves of  $V_3O_7$ ·H<sub>2</sub>O are shown in **Figure**  **6**. This clearly exhibits that there is a broad cathodic reduction peak at -0.5 V which result from the lithium ion intercalation process and anodic oxidation peak at 1.2 V, which is attributed to lithium ion deintercalation process, which means that the crystalline structure is reversible. This is a typical phenomenon of VO<sub>x</sub> active materials and is often reported in the literature [28]. The lithium ion intercalation and deintercalation process can be described by the following process:

 $V_3O_7 \cdot H_2O + x Li^+ + x e^- \leftrightarrow Li_xV_3O_7 \cdot H_2O$ 

#### 3.5. Brunauer-Emmett-Teller (BET)

The specific surface area ( $S_{BET}$ ), pore volume ( $V_{por}$ ) and



Figure 7. N<sub>2</sub> adsorption/desorption isotherms of V<sub>3</sub>O<sub>7</sub>·H<sub>2</sub>O nanobelts.

average pore size (d<sub>por</sub>) of V<sub>3</sub>O<sub>7</sub>·H<sub>2</sub>O nanobelts were measured by physisorption of nitrogen according to BET. The obtained results are  $S_{BET} = 13 \text{ m}^2 \cdot \text{g}^{-1}$ ,  $V_{por} = 47.10^{-3}$  $cm^3 \cdot g^{-1}$  and  $d_{por} = 141$  Å. Furthermore, the analysis of the N<sub>2</sub> adsorption and desorption isotherms of the sample leads to identification of the isotherm profiles, as type IV in the BDDT system [29] as shown in Figure 7. This profile is typical of mesoporous materials having pore diameter between 2.0 and 50.0 nm. A hysteresis loop is apparent identified as H3 type (IUPAC), which is characteristic of cylindrical pores [29]. H3-type hysteresis loops are usually observed with rigid bulk particles having a uniform sizes [30]. This result is confirmed by the specific surface area and the average pore size values. These materials are promising for chemical and energy-related applications such as catalysts, and electrochemical device.

Although the formation mechanism of  $V_3O_7 \cdot H_2O$ nanobelts remains an open question, experimental data and close investigation of intermediate compounds make it possible to propose a model for the belt formation. To the best of our knowledge and experiments, the whole formation process of  $V_3O_7 \cdot H_2O$  nanobelts under hydrothermal conditions can be described as follows.

To explain the mechanism which controls the morphology of the material after hydrothermal treatment, a possible intermediate process was suggested on the basis of the layered structure of the precursors [31]. Whereas this structure is stabilized by the phenolphthalein molecules, it is sensible that the lamellate structure would break down after displacement of the organic compounds. Through the hydrothermal treatment, it is plausible that the layered precursors would split into nanobelts, and the products obtained would show striated morphologies. However, in the hydrothermal synthesis, the lamellar intermediate product would split later in small stems because of the loss of organic molecules. Indeed, the phenolphthalein molecules make the immobilization of this lamellar structure difficult, resulting in the collapse of the final lamellar precursor, supporting the exfoliation of the precursor and the formation of vanadium oxide belts. We think that the phenolphthalein played a double role of reducing and structuring agent in the formation of  $V_3O_7$ · $H_2O$  nanobelts.

#### 4. Conclusions

In summary, a facile synthetic route to monodisperse crystalline vanadium oxide hydrate ( $V_3O_7$ ·H<sub>2</sub>O) nanobelts has been developed. Indeed, the synthesized  $V_3O_7$ ·H<sub>2</sub>O nanobelts were reported for the first time using phenolphthalein as structure-directing template. The lengths of nanobelts up to several hundreds of nanometers, the widths and thicknesses are 90 and 40 nm, respectively. The phenolphthalein molecules were mainly as reactants in the development of the formation of  $V_3O_7$ ·H<sub>2</sub>O nanobelts. The formation mechanism of  $V_3O_7$ ·H<sub>2</sub>O nanobelts was clearly explained. Finally, the as-obtained  $V_3O_7$ ·H<sub>2</sub>O nanobelts are promising cathode materials in lithium-ion batteries

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