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Hydrothermal synthesis of a novel phase of vanadia-based nanowhiskers

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A novel phase of vanadia-based whiskers $Ba_{0.25}V_2O_5 \cdot 1.5H_2O$ with a huge aspect ratio (40000:1), which can be used as conductive reinforcing fibers in electrode composites or as an 'electronic paper', has been synthesized by a hydrothermal method and characterized by XRD, SEM, TEM, SAED, EDX, TG and XPS.

Vanadia-based materials can be applied as catalysts for propane and propene selective oxidations to acrylic acid,[1] sensors for hydrocarbon detection,[2,3] cathode materials in Li-ion batteries[4–11] *etc*.

1D nanomaterials attract much attention abreast of 3D, 2D and 0D. Recently, fibers named as whiskers or nanowires based on analcime zeolite,[12] potassium titanate,[13] hydroxyapatite,[14] molybdenum trioxide,[15] zirconium dioxide[16] have been studied.

1D nanomaterials based on V_2O_5 are widely investigated due to their perspective properties. Vanadia nanotubes are among the most frequently used electrochemical materials for producing new types of electronic devices.[17] Another kinds of 1D materials based on V_2O_5 are nanobelts,[18–20] nanorods,[21,22] and nanofibers.[23,24] However, the objects with a whiskers-like morphology are the most promising in further application among all listed 1D structures of vanadia-based phases.[25–28]

Generally the 1D structures can be obtained by several experimental techniques (*e.g.*, electrospinning,[23,29] calcination,[13] chelate decomposition,[14] *etc.*). Nevertheless, hydrothermal treatment is one of the most powerful and frequently used route.[30] This method allows one to obtain metastable compounds and unique materials. Owing to the hydrothermal treatment, it becomes possible to control the composition, structure and morphology of a product simultaneously.

Here, we report on the hydrothermal synthesis of the new phase $Ba_{0.25}V_2O_5 \cdot 1.5H_2O$ as nanowhiskers with a huge aspect ratio.

The following chemically pure compounds were used for the synthesis: a powder of V_2O_5, a 15% aqueous solution of H_2O_2 and a saturated aqueous solution of $Ba(NO_3)_2$.

At the first stage, 0.5 g of V_2O_5 was added to 30 ml of an H_2O_2 solution in a beaker. After intense exothermal reaction and cooling down to room temperature, a gel-like brown mass was obtained, which was dried at 40–60 °C for 4–6 h to afford a brown film of the xerogel.

At the second stage, the xerogel film was stirred with a $Ba(NO_3)_2$ solution for 48 h at room temperature. The resulting orange precipitate was separated by centrifugation and washed with distilled water.

At the third stage, the precipitate was placed in a Teflon-lined stainless steel autoclave (volume, 50 ml; occupancy, 80–90%). The hydrothermal treatment was carried out for 48 h at 250 °C. The autoclave was cooled to room temperature for 8–12 h. The precipitates were repeatedly washed with distilled water and dried at 60 °C.

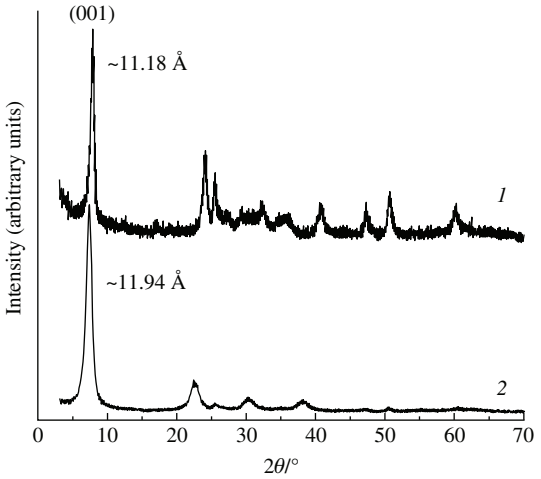

Figure 1 XRD patterns of (*1*) Ba-exchanged and (*2*) as-obtained $V_2O_5 \cdot nH_2O$ xerogels.

The $V_2O_5 \cdot nH_2O$ xerogel with a well-known layer structure forms at the first stage of the synthesis. In this structure, each layer consists of tetragonal VO_5 pyramids connected by edges and water molecules located between layers.[31,32] The typical XRD pattern contains several broad peaks (Figure 1, pattern *2*). The interlayer space of the structure calculated from the (001) peak position is ~11.94 Å. In our case, Ba^{2+} ions are intercalated by the xerogel. The composition of the as-obtained Ba-exchanged xerogel can be described as $Ba_xV_2O_5 \cdot nH_2O$. This crystalline phase (Figure 1, pattern *1*) has a similar layer structure with a space of ~11.18 Å. A slight decrease in this parameter together with significantly changing relative peak intensities indicate the formation of a Ba-exchanged xerogel phase different from $V_2O_5 \cdot nH_2O$.

Different hydrothermal treatment regimes were tested (Table 1). Only condition regime 'iii' leads to the whiskers with a maximal length.

According to SEM and TEM data (Figure 2),[†] the whiskers have a diameter of 50–150 nm and a length of up to 5 mm. The

[†] Microstructure of the whiskers was observed by TEM [JEOL JEM-2000FX (II) (Japan), an accelerating voltage was 200 kV], and SEM [Leo Supra 50 VP (Germany) with an EDX analyzer 'INCA Energy +' (Oxford, England)].

Table 1 Conditions of the hydrothermal synthesis and morphology of obtained whiskers.

Regime	Temperature of the hydrothermal treatment	Duration of the hydrothermal treatment	Morphology of the product	Maximal length of whiskers according to SEM
i	200°C	10 h	No whiskers	—
ii	250°C	24 h	Short whiskers	~50–500 μm
iii	250°C	48 h	Long whiskers	~500 μm–5 mm

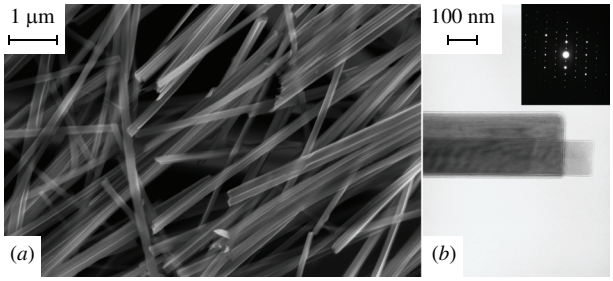

Figure 2 (*a*) SEM and (*b*) TEM microphotographs and an SAED image (inset) of the obtained whiskers.

SAED image [Figure 2(*b*), inset] shows that the whiskers are monocrystalline. Note that, upon completion of the synthesis, the product sometimes included aggregates of thinner whiskers. The estimated aspect ratio of the prepared whiskers was about 40000:1, which is an extremely huge for inorganic materials.

According to XRD data (Figure 3),‡ the phase obtained is not present in the JCPDS PDF-2 database. It permits us to conclude that this phase is novel.

Both XRD patterns contain strong (00*l*) peaks due to the texturing of samples. The (001) peak corresponds to the interlayer space in the structure of the compound. The refined distance is 10.7222(18) Å. In the grinded sample (type *2*), the texturing effects are negligible. Therefore, the relative intensities of (00*l*) peaks are lower than those for type *1*. Unfortunately, we are not able to index the XRD data exhaustively due to possible impurity phases.

Initially, the composition of the synthesized phase can be written as $Ba_xV^{IV}_yV^{V}_{2-y}O_z{\cdot}mH_2O$. According to EDX data, the Ba:V ratio is about 1:8.

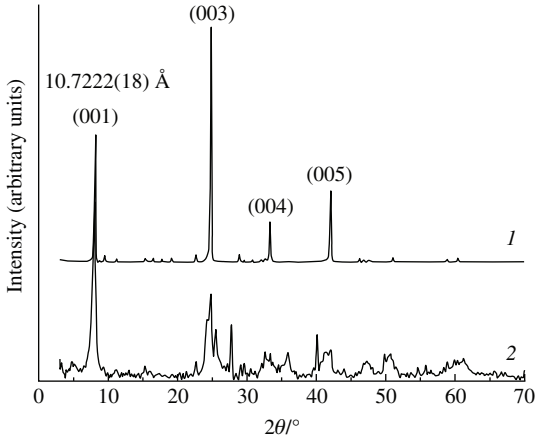

Figure 3 XRD patterns of (*1*) initially textured and (*2*) grinded powder samples of V_2O_5-based whiskers.

‡ XRD analysis of prepared compounds was carried out using a Rigaku D/MAX 2500 diffractometer (Japan) [2θ range, 5–75°; step, 0.02°, radiation, $Cu_{K\alpha1,2}$ (average λ = 1.54176 Å, graphite monocromator)]. Two kinds of samples were investigated by XRD analysis: (1) textured whiskers plate 'as is' (Figure 3, pattern *1*), (2) powder prepared by grinding of whiskers and mixed with the pyrex glass (Figure 3, pattern *2*) to avoid the preferred orientation.

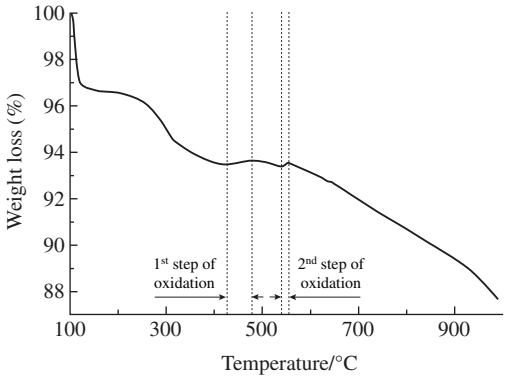

Figure 4 Weight loss in the whiskers sample.

The total content of water in the phase of whiskers was calculated from TG data (Figure 4).§ The curve contains two stages of intense weight loss at ~98–120 and ~250–300 °C. The first stage can be referred to as the evaporation of water molecules located in the interlayer spaces. The second stage can occur because of the elimination of chemically bound water located in structural layers. The total weight loss at these two stages (6.5%) corresponds to $m \approx 1.5$.

At ~430–560 °C, the weight increased owing to the oxidation of V^{4+} ions. Note that the oxidation proceeds in two stages. The first stage takes place at 430–480 °C, and the second one, at 540–560 °C. Total amount of weight increasing corresponds to $y \approx 0.5$.

Vanadium(V) oxide is formed at 560 °C (proved by XRD, not presented here). Subsequent weight loss at > 560 °C is explained by the isolation of oxygen due to decomposition of V_2O_5.

The partial reduction of V^{5+} to V^{4+} compensates the positive charge abundance of intercalated Ba^{2+}. Thus, the quantity of V^{4+} ions in whiskers should be two times greater than that of Ba^{2+}. Indeed, the Ba:V and V^{4+}:V^{5+} ratios are in good agreement.

Moreover, the XPS data¶ show three main emission peaks at 530 (O_{1s}), 518 (V_{2p}) and 780 eV (Ba_{3d}); thus, Ba^{2+} ions are present in the structure. The profile analysis of V_{2p} peak (Figure 5) shows its splitting into two peaks with binding energies of 518 and 517 eV corresponding to V^{5+} and V^{4+}, respectively. The O_{1s} peak is also complex and consists of O^{2-} (530 eV) and H_2O (532 eV) oxygen peaks. The V^{4+}:V^{5+} and H_2O:O^{2-} ratios calculated on the basis of EDX and TG data were fixed and fitted peak profile demonstrates satisfactory agreement with experimental one.

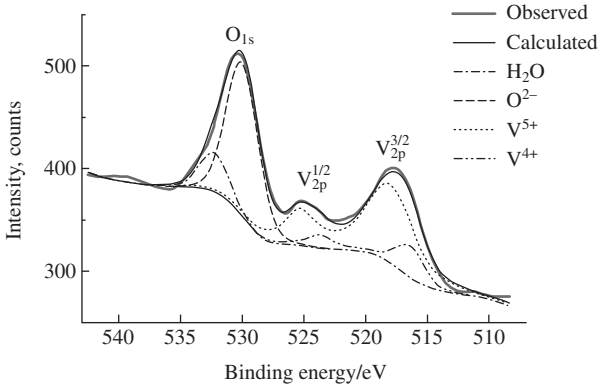

Figure 5 XPS spectrum of V_2O_5-based whiskers.

§ TG analysis in air was performed using Perkin Elmer PYRIS Diamond TG-DTA (heating rate, 10 K min^{-1}; working temperature range, 97–1000 °C).

¶ The XPS measurements were carried out on XSAM 800 (Mg_K radiation, 1253.6 eV; residual pressure, 10^{-9} Torr). Binding energies were corrected using the energy values for C_{1s} of carbon fixed at 284.8 eV. Profile fitting was carried out in Unifit-2006.[33]

According to the EDX, TG and XPS data, the formula of whiskers can be written as $Ba_{0.25}V_2O_5 \cdot 1.5H_2O$.

The relative ohmic resistance of whiskers was estimated by a two-probe method. For this experiment, the whisker was attached to the gold substrate by a silver paste. The relative resistance along the whisker axis (measured on the wisp with a cross section area of ~0.25 mm^2) was ~ 1 Ohm cm.

The detailed investigation of the electrochemical properties of the prepared material was published previously.[34] Note that the discharge capacity of the given material is ~145 mAh g^{-1}. Moreover, this value is practically constant during many charge-discharge cycles. Thus, the material can be successfully used as a cathode of Li-ion batteries.

Finally, we can conclude that the novel phase of vanadia-based whiskers $Ba_{0.25}V_2O_5 \cdot 1.5H_2O$ can be synthesized by a hydrothermal method using a Ba-exchanged $V_2O_5 \cdot nH_2O$ xerogel as the precursor. The composition was determined from EDX, TG and XPS results. Synthesized whiskers possess unique morphology with a very large aspect ratio (up to 40000:1). Unique morphological and electrochemical properties of the material enable one to use it in composites as reinforcing fibers or as 'electronic paper' for the creation of new types of flexible cathodes for Li-ion batteries.

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