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Hydrothermal synthesis of vanadium oxide nanotubes from V_2O_5 gels

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Abstract

Vanadium oxide nanotubes (VO_x-NT) have been synthesized in high yield by adding hexadecylamine to $V_2O_5 \cdot nH_2O$ gels, followed by a hydrothermal treatment (150–180 °C, 2–7 days). Scanning electron microscopy (SEM) and X-ray diffraction analysis have been performed to optimize the temperature and reaction time required for formation of VO_x-NT and the morphology of the nanotubes investigated by transmission electron microscopy (TEM).

Keywords: Vanadium oxide; Hydrothermal synthesis; TEM; SEM

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1. Introduction

Vanadium metal is known to be a catalytically active centre in different molecular complexes and inorganic materials. Vanadium (V) peroxo complexes have been used as catalysts and in stoichiometrically conducted reactions as oxo reagents for alcohols, arenes, alkenes and thioethers [1,2]. The biocatalytic role of vanadium has also been reported in different vanadium-dependent enzymes such as haloperoxydase and nitrogenase [3,4].

Vanadium oxide-based materials including vanadium pentoxide, vanadium phosphates can be used as catalysts for the mild oxidation of hydrocarbons and alcohols [5]. During the last years, an increasing interest has been devoted to hybrid vanadium oxides due to their potential application as catalysts, sensors, electrodes. A large family of hybrid vanadium oxides has been prepared from the combination of the hydrothermal process with the use of organic templates. The crystalline V_2O_5 is currently used as a precursor and several vanadium oxides have been recently synthesized using amines, ammonium cations ($N(CH_3)_4^+$, CH_3NH_2) or diamines $H_2N–(CH_2)_n–NH_2$ ($n = 2, 3, 4$) as organic templates [6–8]. They all exhibit a layered structure in which protonated amines are inserted between negatively charged vanadium oxide planes. In the presence of long chain alkyl amines, mesostructured vanadium oxides with a tubular morphology have been obtained [9,10]. The structure of these compounds is similar to that of carbon nanotubes discovered by Iijima in 1991 [11]. Vanadium oxide nanotubes (VO_x-NT) are made of multilayer scrolls with thick walls built up from several vanadium oxide layers.

This paper deals with the synthesis of vanadium oxide nanotubes starting from vanadium oxide gels, $V_2O_5 \cdot nH_2O$. These gels comprise ribbon-like vanadium oxide particles about 10 nm wide and over 1 μm long. They exhibit a two-dimensional structure closely related to that observed for the *ab* plane

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of orthorhombic V_2O_5 [12]. Intercalation through proton-exchange reactions with the acidic protons of the gels is much easier than in crystalline V_2O_5, and may be a real advantage in the synthesis of VO_x-NT.

2. Experimental

2.1. Synthesis of vanadium oxide nanotubes

The synthesis of VO_x-NT was performed in three stages. The first step consisted of the preparation of $V_2O_5\cdot nH_2O$ gels according to an earlier publication [13]. This synthesis involves on the dissolution of crystalline V_2O_5 (Merck, 1 g) in a solution of hydrogen peroxide (Aldrich, 50 ml, 30%). The exothermic reaction that occurs during synthesis leads to the partial decomposition of hydrogen peroxide that in turn leads the release of oxygen gas and the formation of V(V) peroxo complexes [14]. A clear orange solution is formed after about 10 min (final pH $\approx$ 1.5) that progressively turns into a red gel after ca. 24 h. This gel has been shown to correspond to $V_2O_5\cdot nH_2O$, where the amount of water depends on the experimental conditions. In our case, before drying, it corresponded to $n = 300$.

For the second step, 3 ml of a 0.45 g ml^{-1} solution of hexadecylamine $C_{16}H_{33}NH_2$ (Aldrich) in acetone was added to the $V_2O_5\cdot nH_2O$ gel (molar ratio V/amine = 2:1). The resulting green mixture was stirred for 16 h.

Finally, the vanadium oxide–amine composite was heated under hydrothermal conditions in a Parr Teflon digestion bomb at 150 or 180 °C for 2–10 days. The resulting black powder was washed with ethanol and cyclohexane and then dried under vacuum at 80 °C for about 5 h. The products obtained, and the synthesis conditions used are given in Table 1.

2.2. Characterization

X-ray powder diffraction patterns were recorded on a Philips PW 1830 diffractometer operating with the Cu Kα radiation ($\lambda = 1.5406$ Å). Scanning electron microscopy (SEM) studies were performed on a Cambridge Stereoscan 120 microscope. Transmission electron microscopy (TEM) investigations were carried out on a JEOL 100 CX II microscope. One droplet of the powder dispersed in $CHCl_3$ was deposited onto a carbon-coated copper grid and left to dry in air.

Table 1
Synthesis condition and layer distances (nm) for the products NT1–NT4

Samples	Hydrothermal process		d_{00l} (nm)
	T (°C)	Time (days)	
NT1	150	2	3.7
NT2	180	2	3.7; 3.2
NT3	180	4	3.2
NT4	180	7	3.2; 3.0
c-V_2O_5-NT[a]	180	7	3.2

[a] Vanadium oxide nanotubes prepared from crystalline V_2O_5 and hexadecylamine according to [10].

3. Results and discussion

$V_2O_5\cdot nH_2O$ gels have been used as vanadium source for the synthesis of vanadium oxide nanotubes. These gels are currently prepared via the acidification of metavanadate $NaVO_3$ aqueous solutions through a proton-exchange resin [12]. However, this method does not provide an accurate control of the vanadium concentration. As the V/amine molar ratio appears to be a crucial parameter for the large scale synthesis of VO_x-NT as previously reported [9,10], an alternative synthesis based on the dissolution of crystalline V_2O_5 in hydrogen peroxide was preferred. A green mixture was obtained when the amine was added to the $V_2O_5\cdot nH_2O$ gels. This mixture was aged for 16 h at room temperature in order to allow the intercalation of the amines between the layers of the vanadium oxide gel. Finally, the hydrothermal treatment of the vanadium oxide–amine composite leads to the formation of a black powder. The black colour of the powder arises from the reduction of some V^{5+} to V^{4+} by decomposition of the organic compounds [15]. It has already been reported that such $V_2O_5\cdot nH_2O$–amine intercalated compounds are not stable beyond 200 °C and some mixed valence vanadium oxides are formed [16].

Various experiments were performed to investigate the effect of modifications to the hydrothermal treatment on the morphology of the final product. Four products (NT1–NT4) were prepared at different temperatures and durations of the hydrothermal process

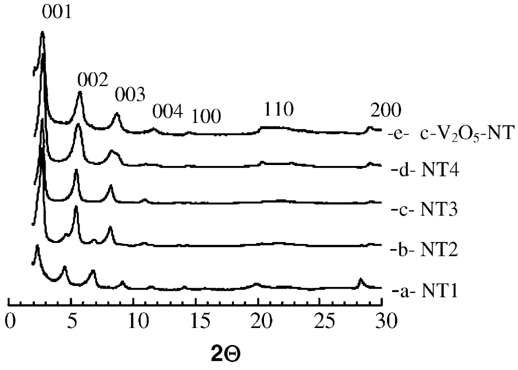

Fig. 1. X-ray diffraction patterns of compounds NT1–NT4 (a–d) obtained under different hydrothermal treatments. The X-ray pattern of c-V_2O_5-NT (e) [10] is also reported.

(see Table 1). They were characterized by powder X-ray diffraction (Fig. 1). As a comparison, vanadium oxide nanotubes were also prepared from crystalline V_2O_5 and hexadecylamine (c-V_2O_5-NT) according to the procedure reported by Niederberger et al. [10].

The X-ray diffraction pattern of NT1 (Fig. 1a) was typical of a layered compound. It displayed two series of reflections: a $0\,0\,l$ set of reflections with high intensity corresponding to the stacking of the layers along a direction perpendicular to the substrate and a $h\,k\,0$ set of reflections with lower intensity corresponding to the two-dimensional structure of the layers. The $0\,0\,l$ series provided the distance between the vanadium oxide layers (e.g. $d_{0\,0\,l} = 3.7$ nm for NT1). Intercalated long chain alkylamines (number of carbon atoms >12) lay perpendicular to the oxide planes and the basal distance should be close to the length of the amine chain ($d_{\mathrm{calc}}(C_{16}H_{33}NH_2) = 3.3$ nm) [16]. The d value observed for NT1 nanotubes was larger than 3.3 nm and also larger than the basal distance reported for c-V_2O_5-NT (3.2 nm). Water molecules could be intercalated together with the protonated amines thereby increasing the basal distance. However, the presence of another vanadium oxide mesophase is also possible as this basal distance is quite high compared to that of vanadium oxide nanotubes. Moreover, as the $h\,k\,0$ set of reflections for NT1 did not correspond to that of c-V_2O_5-NT, it should be assumed that the structure of the vanadium oxide layers are different for the two products.

When the hydrothermal treatment was performed at 180 °C, the X-ray diffraction pattern of the resulting compound NT2 (Fig. 1b) displayed two series of $0\,0\,l$ reflections: a first set of reflections identical to that of NT1 and a second one corresponding to another lamellar compound. The basal distance of this second series (3.2 nm) was close to the length of hexadecylamine molecule and is identical to that of c-V_2O_5-NT. When the gel was heated for 4 days at 180 °C, the X-ray pattern of the resulting material NT3 (Fig. 1c) exhibited one series of $0\,0\,l$ reflections (3.2 nm) identical to that of c-V_2O_5-NT. For both compounds NT2 and NT3, the $h\,k\,0$ series of reflections were different from that of c-V_2O_5-NT.

The reaction in the autoclave had to be performed for at least 7 days at 180 °C in order to obtain nanotubes NT4 (Fig. 1d) giving the same X-ray pattern as c-V_2O_5-NT (Fig. 1e). The $0\,0\,l$ and $h\,k\,0$ series of reflections for c-V_2O_5-NT were present together on diffractogram arising from NT4. However, it was possible to distinguish an additional $0\,0\,l$ series of reflections whose basal distance was close to 3.0 nm. This second series may be assigned to another lamellar compound whose structure could be close to that of c-V_2O_5-NT. However, the SEM image (Fig. 2) of the NT4 sample showed that it was made almost entirely of nanotubes whose size lay between 1 and 10 μm.

This observation was confirmed by TEM. A TEM image of NT4 lying in an longitudinal projection direction is presented in Fig. 3. The nanotubes exhibit a multilayered wall structure made of parallel vanadium oxide layers that are apparent due to the good contrast present between the layers.

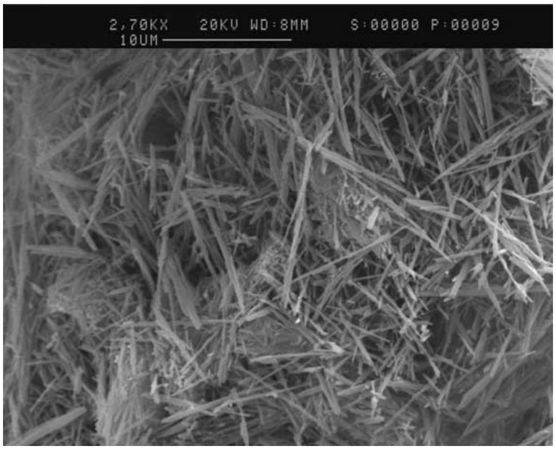

Fig. 2. SEM image of NT4 material (scale bar represents 10 μm).

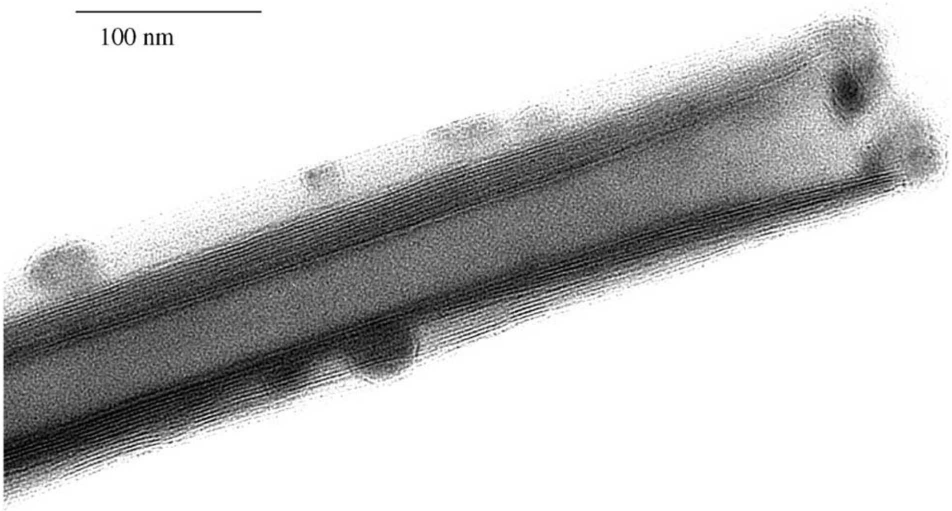

Fig. 3. TEM image of typical nanotubes of NT4 material (scale bar represents 100 nm).

Nanotubes may exhibit slightly different morphologies. Inner diameters range between 30 and 40 nm and outer diameters between 50 and 130 nm. The number of layers varies from 5 to 25.

At lower temperature (150 °C) and shorter duration of the hydrothermal treatment, amorphous compounds together with nanotubes were observed by SEM in agreement with X-ray diffraction measurements. The starting mixture has to be heated at 180 °C for 7 days to obtain quantitatively vanadium oxide nanotubes without other by-products.

4. Conclusion

Vanadium oxide nanotubes starting from $V_2O_5{\cdot}n\,H_2O$ gel precursors were reproducibly prepared. The formation of vanadium oxide nanotubes requires two steps once the initial gel has been formed: first, the room temperature intercalation of long chain amines between the oxide layers of the gel followed by an hydrothermal treatment whose duration and temperature are critical for the crystallization of vanadium oxide nanotubes. The hydrothermal treatment has to be performed at 180 °C for at least 7 days to obtain solely vanadium oxide nanotubes.

Recently, vanadium oxide foams whose morphology is strongly different from those of vanadium oxide nanotubes were obtained by another chemical route using the same precursors: the hexadecylamine was added to the crystalline V_2O_5 followed by the addition of hydrogen peroxide [17]. Both gelation process and intercalation of hexadecylamine between the vanadium oxide layers occur simultaneously when the hexadecylamine and hydrogen peroxide solutions are added to the vanadium pentoxide. The decomposition of hydrogen peroxide in the presence of vanadium oxide leads to a release of oxygen gas through the viscous gel. This approach leads to a macroporous vanadium oxide whose porosity is arranged as an irregular honeycomb-like morphology [17]. In contrast to the vanadium oxide nanotubes, the foams are yellow suggesting that all the vanadium atoms remain in their highest oxidation state V^{5+}. These results show how the hydrothermal treatment is important in the formation of vanadium oxide nanotubes as the thermal decomposition of amines promotes the reduction of some V^{5+} species to V^{4+} species. The presence of V^{4+} in the vanadium oxide framework may lead to a curvature of the inorganic structure as it was evidenced for mixed valence vanadium oxide clusters [18,19].

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