Low-Cost Synthesis of Vanadium Oxide Nanotubes via Two Novel Non-Alkoxide Routes

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The synthesis of vanadium oxide nanotubes (VO_x-NTs) containing primary monoamines with long alkyl chains has been achieved by two new approaches, using either $VOCl_3$ or V_2O_5 as vanadium oxide precursor. The hydrolysis of amine complexes of $VOCl_3$ involves a ligand-assisted templating mechanism as well as the intercalation of amines in layered V_2O_5. Both procedures followed by a hydrothermal treatment lead to VO_x-NTs as the main product. The structure and morphology of the tubes obtained have been investigated and are discussed in terms of comparison with those obtained by the previously reported alkoxide route. Due to its low cost and ease of handling, the synthesis starting from V_2O_5 in particular provides an advantageous access to large quantities of the novel tubular nanomaterial.

Introduction

The outstanding structural versatility of vanadium oxides and derived compounds[1] is receiving significant attention especially with respect to applications in catalysis and as electrochemical devices.[2,3] In recent years, much of the interest was focused on the design of mesostructured vanadium oxides to optimize their chemical and physical properties. Generally, two different strategies are applicable for the preparation of mesoporous oxides: (i) a template approach or (ii) an intercalation route.

(i) Mesoporous silicates were obtained for the first time in 1992 (M41S).[4,5] The synthesis was based on specific interactions between the surfactant and the molecular precursor unit following the so-called liquid crystal templating (LCT) mechanism. After this breakthrough, many attempts have been made to expand this synthesis strategy to the preparation of mesoporous metal oxides. They are difficult to obtain since most of the non-silica-based oxides show a stronger tendency to form lamellar structures rather than mesostructured phases and, thus, collapse upon removal of the surfactant. However, several mesostructured transition metal oxides have been successfully prepared using similar routes.[6−8]

To overcome these problems, Antonelli and Ying developed a novel method, the ligand-assisted templating (LAT) approach. In this case, the surfactant headgroup is covalently bound to the inorganic molecular precursor prior to hydrolysis and polycondensation. Oxides of niobium,[9,10] tantalum,[11] and zirconium[12] with very high surface areas and ordered mesoporous structures are thereby accessible.

(ii) The host/guest chemistry of intercalation systems also provides a highly variable potential for the design of nanostructured functional materials.[13] The pillaring of layered solids with organic molecules, i.e., the controlled intercalation of spacers between the layers of the material,[14] is a promising but rarely investigated approach. In contrast to the hydrothermal synthesis of mesoporous compounds using alkoxide precursors, the intercalation route starts from preformed metal oxide layers. Although the large number of host lattices with layered structure types in conjunction with the multitude of possible guest species formally opens a wide range of synthesis routes to mesoporous materials, no simple way has been found of controlling pore size and pore size distribution until now.

In the past decade, vanadium pentoxide gels have been extensively studied[15] and several approaches to the preparation of mesostructured vanadium oxides have

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been reported, using ammonium vanadate,[16,17] vanadium pentoxide,[18,19] or vanadium alkoxides[20] as precursors.

Recently, we found an alkylamine-containing vanadium oxide with a tubular morphology.[21−24] These vanadium oxide nanotubes (VO_x-NTs) were obtained as the main product of a sol−gel reaction, followed by hydrothermal treatment, from vanadium(V) alkoxide precursors and primary monoamines $C_nH_{2n+1}NH_2$ with $4 \leq n \leq 22$ or α,ω-diamines $H_2N(CH_2)_nNH_2$ with $12 \leq n \leq 20$. The amine molecules act as structure-directing templates. As vanadium alkoxides are expensive, the search for alternative precursors is still important with regard to a cost-saving scale-up.

Here, we report two novel non-alkoxide routes to VO_x-NTs using either vanadium(V) oxytrichloride or vanadium(V) pentoxide as vanadium source and primary amines as templates or intercalates, respectively.[25,26] $VOCl_3$ and V_2O_5 represent promising precursors because of their particular properties. $VOCl_3$ readily forms addition compounds with nitrogen donors[27] and condenses in the presence of water to the hydrated oxide in a sol−gel process. The layered structure of V_2O_5 can efficiently be used for host−guest intercalation chemistry: alkylammonium ions and neutral alkylamines have been successfully intercalated into vanadium pentoxide gels.[28]

Experimental Section

Materials. Vanadium(V) oxytrichloride, vanadium(V) pentoxide, and undecyl-, dodecyl-, and hexadecylamine were obtained from Fluka, Switzerland. Vanadium(V) pentoxide and the amines were used without further purification. Vanadium(V) oxytrichloride was distilled under inert atmosphere before use. Eicosylamine was prepared by a well-known procedure.[29] For the hydrothermal treatment we used Parr acid digestion bombs with 23 or 45 mL Teflon cups as autoclaves. To test the scaling up of these procedures, the hydrothermal treatment was carried out in a 750 mL autoclave.

Synthesis. *(a) VO_x-NTs from Vanadium Oxytrichloride.* In a typical preparation, $VOCl_3$ (7 mmol) was mixed with the primary amine $C_nH_{2n+1}NH_2$ ($11 \leq n \leq 16$; molar ratio 2:1) and stirred under inert atmosphere until the template had completely dissolved. The resulting brown viscous solution was hydrolyzed with 30 mL of acetate buffer (1 M, pH 7) at 0 °C under vigorous stirring. A dark green precipitate was formed immediately. After the precipitate was aged for 24 h at room temperature, the brown product was filtered and washed thoroughly with water and ethanol. The resulting powder was suspended in 20 mL of water and 2 mL of 2-propanol, followed by hydrothermal treatment at 180 °C in a Teflon-lined autoclave for 7 days. The black product was filtered, washed with ethanol and hexane, and dried in a vacuum (10^{-3} mbar) at 80 °C.

(b) VO_x-NTs from Vanadium Pentoxide. A suspension of V_2O_5 (15 mmol) and a primary amine $C_nH_{2n+1}NH_2$ ($11 \leq n \leq 20$; molar ratio 1:1, i.e., V:template = 2:1) in 5 mL of ethanol was stirred for 2 h. To this mixture was added 15 mL of water, and stirring was continued for 48 h. The hydrothermal reaction of the resulting composite in an autoclave at 180 °C for 7 days generated a black product which was finally washed with ethanol and hexane and dried in a vacuum (10^{-3} mbar) at 80 °C.

Characterization. The X-ray powder diffraction (XRD) diagrams of all samples were measured in transmission mode (0.3 mm glass capillaries, Cu $K\alpha_1$ radiation) on a STOE STADI-P2 diffractometer equipped with a position sensitive detector (resolution ~0.01° in 2θ).

Transmission electron microscopy (TEM) investigations were performed on a CM30 ST microscope (Philips), operated at 300 kV. For the investigation of the longitudinal shape and structure, the nanotube material was deposited on a perforated carbon foil supported by a copper grid. To observe the structure perpendicular to the tube axis, a cross-sectional preparation technique was applied.[23]

Results and Discussion

Synthesis. $VOCl_3$ and V_2O_5 were successfully tested as new precursors for the low-cost and large-scale synthesis of VO_x-NTs, which can be obtained in excellent yield with primary amines $C_nH_{2n+1}NH_2$ ($11 \leq n \leq 20$). Experimental parameters such as surfactant chain length, pH, temperature, aging time, and vanadium-to-template ratio and the use of cosolvents have an important influence on the formation of the VO_x-NTs and, thus, have been investigated in detail.

In the first step of the synthesis of VO_x-NTs from $VOCl_3$, a dark brown solution formed after the amine surfactant was added to $VOCl_3$. The $VOCl_3$−amine complex was hydrolyzed with 1 M acetate buffer (pH 7), and a lamellar-structured intermediate formed. The influence of the pH is small as long as it is kept below 7. At higher pH values, an amorphous gray gel results.

The color of the hydrolyzed product, a vanadium oxide−surfactant composite, varies among yellow, orange, and green, mainly depending on the pH and the amount of water. After being aged at room temperature, all gels were brown. The final hydrothermal treatment of the thoroughly washed gel yields VO_x-NTs as the main product. The washing is necessary since the direct hydrothermal treatment of the intermediate product always resulted in lamellar composites and not in VO_x-NTs. Most likely, the large amount of different ions, the chlorine ions in particular, inhibits the nanotube formation.[30]

The duration of both processes, the aging at room temperature as well as the hydrothermal treatment, during the VO_x-NTs synthesis is crucial. Aging at room temperature has to be long enough (between 1 and 3 days), so that the vanadium oxide−surfactant composite develops a lamellar structure, which can be monitored

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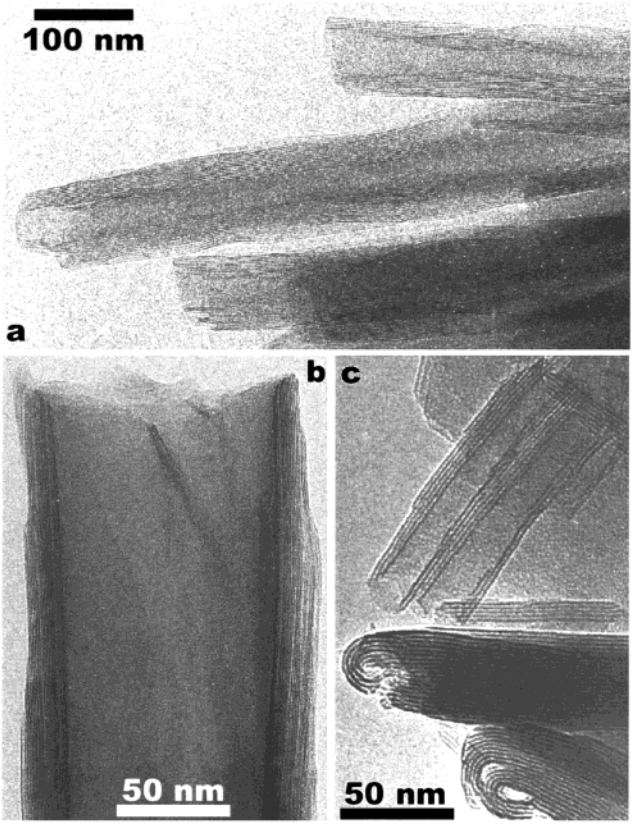

Figure 1. (a) TEM image of typical nanotubes, synthesized from $VOCl_3$ and hexadecylamine. The inner (23−33 nm) and outer (75−100 nm) diameters are average values of the tube dimensions. The multilayered walls of the tubes consist of a parallel arrangement of vanadium oxide layers with the template molecules intercalated between them. (b) A single nanotube, prepared from $VOCl_3$ and undecylamine, shows an exceptionally large inner diameter of almost 100 nm and a disordered wall structure. (c) Rarely, separated packs of vanadium oxide layers are observed in addition to the nanotubes. These layers started to roll but have not formed tubes yet.

by powder X-ray diffraction and TEM. The formation of this intermediate is essential. All experiments have clearly revealed that, only after a prestructuring of the gel during the aging period, the following hydrothermal treatment yields nanotubes.

For the hydrothermal treatment, the washed vanadium oxide−amine composite is suspended either in water or in a water−2-propanol mixture. However, the presence of alcohol is not necessary for the nanotube formation. The relative yield of nanotubes was monitored by transmission electron microscopy (Figure 1), showing that the as-synthesized sample consists almost entirely of nanotubes.

Various experiments investigating the influence of the temperature and the duration of the hydrothermal treatment provide evidence that the reaction in the autoclave has to be conducted at 180 °C for at least 7 days to obtain well-developed VO_x-NTs. Lower synthesis temperatures as well as a shorter duration of the hydrothermal treatment always resulted in lamellar structured composites. Although the lamellar arrangement of vanadium oxide layers started to bend, the formation of the VO_x-NTs was interrupted at this stage (Figure 2).

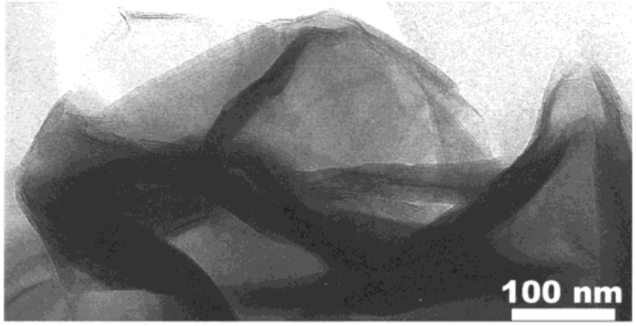

Figure 2. TEM image of the product obtained from $VOCl_3$ and dodecylamine. Without washing, the gel was hydrothermally treated at 180 °C for 3 days. The lamellar arrangement of vanadium oxide layers started to bend, but then the tube formation stopped.

The alternative synthetic method for the VO_x-NTs starts with V_2O_5 and is advantageous because of the precursor's air and moisture stability. Therefore, it can easily be handled without special precautions. The oxide is mixed with either a solution of the amine in ethanol or with the amine in pure, liquid form. The addition of alcohol does not influence the intercalation of the amine and is not necessary for the formation of the VO_x-NTs. After hydrolysis, the yellow-brown suspension is aged at room temperature for 1−3 days. The aging time depends on the chain length of the template: e.g., undecylamine apparently intercalates faster into the vanadium oxide layers than hexadecylamine. Generally, after 1 h, the XRD pattern already shows the characteristic 001 reflection at low diffraction angles, which is typical for layered materials. The corresponding interlayer distance is similar to that determined for the final tubes. After 24 h, the 002 reflection has also appeared, indicating an increased crystallinity of the composite. Similar to the $VOCl_3$ route, it is essential that the vanadium oxide−template composite forms a lamellar structure prior to the hydrothermal treatment.

The whole aging process at room temperature takes place at a neutral pH. During the aging procedure no change of pH was observed. After hydrothermal treatment (180 °C, 7 days) of the hydrolyzed material, the pH of the reaction mixture increased to 8.4, indicating that the amine template molecules became protonated during this process. The reaction yield is nearly quantitative, and the entire sample consists of VO_x-NTs with almost no byproducts according to TEM investigations (Figure 3).

The synthesis of VO_x-NTs using V_2O_5 as precursor material can easily be scaled up. Using a large autoclave (750 mL) for the hydrothermal treatment, a production of several tens of grams of VO_x-NTs can be accomplished. For this scaleup synthesis procedure, the aging time at 180 °C has to be increased from 7 to 14 days. In the case of a shorter duration of the hydrothermal treatment, the tubular material produced contains a large amount of lamellar byproduct.

Our studies revealed some general trends in the formation of VO_x-NTs that are independent of the applied vanadium oxide precursor (V_2O_5, $VOCl_3$, or vanadium(V) alkoxides): (i) Nanotubes of highest quality are always formed if the molar ratio metal:surfactant is 2. (ii) In contrast to the formation of mesoporous transition-metal oxides, there is no distinct effect of the

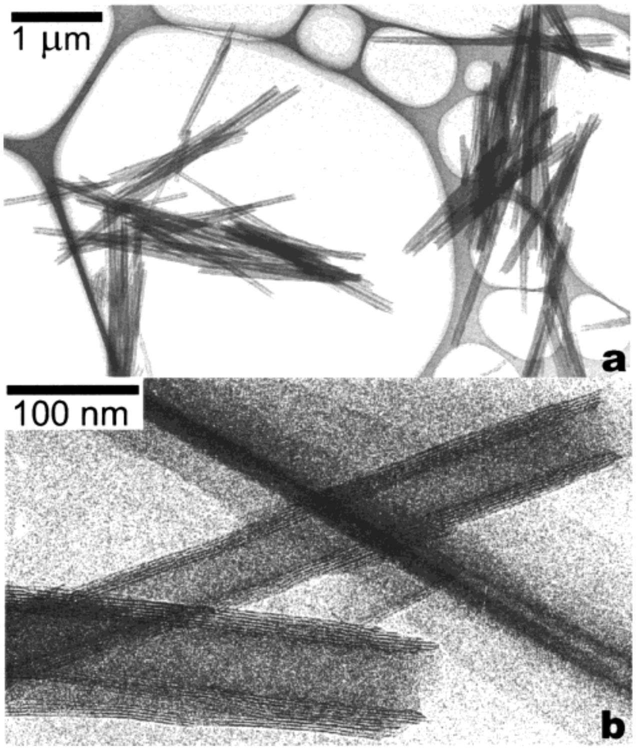

Figure 3. (a) Representative TEM image of VO_x-NTs obtained from V_2O_5 and eicosylamine as template. The tube length ranges from 1 to 3 μm. The product consists of isolated tubes with hardly any byproduct. (b) Representative VO_x-NTs obtained from V_2O_5 and eicosylamine with typical inner diameters of 32 and 45 nm and outer diameters of 65 and 85 nm. The number of layers varies from six to nine layers.

surfactant chain length on the vanadium oxide phase obtained, other than variation of the distances between the layers in the tube walls. The products always consist of VO_x-NTs within a size range of the alkylamine template from 4 to 22 carbon atoms. (iii) The alcohol is not an essential agent in the synthesis of VO_x-NTs.

Characterization of the VO_x-NTs. Starting from vanadium(V) alkoxides, vanadium(V) oxytrichloride, or vanadium(V) pentoxide, the morphology and the composition of the obtained nanotubes are quite similar. TEM, XRD, electron diffraction, and elemental analysis have been used to characterize the various samples and to elucidate the difference in the inner and outer diameters, length, and number of layers of the VO_x-NTs.

Different samples of VO_x-NTs were selected for comparative studies by TEM. Although all of the samples exhibit a tubular morphology, slightly different features can be distinguished. Figure 1 represents selected TEM images of various samples of VO_x-NTs synthesized from $VOCl_3$. These images in longitudinal projection direction demonstrate that the multilayered wall structure of the VO_x-NTs consists of parallel vanadium oxide layers, which appear with dark contrast. The template molecules are intercalated between the vanadium oxide layers, as proved by the dependence of the layer distance on the alkyl chain length of the amines. In Figure 1a, rather well-developed VO_x-NTs are shown with inner diameters of about 30 nm and outer diameters between 75 and 100 nm. The number of layers varies from 10 to 13. All these values are quite typical for VO_x-NTs obtained from $VOCl_3$. Figure 1b presents a tube with an exceptionally large inner diameter of almost 100 nm. Different morphological features are shown in Figure 1c: together with well-developed tubes, lamellar arrangements of rolled vanadium oxide layers are also observed.

Table 1. Morphological Characteristics of the Vanadium Oxide Nanotubes, Depending on the Precursor and Template

precursor	template $C_nH_{2n+1}NH_2$ n	outer diameter (nm)	inner diameter (nm)	number of layers	length (μm)
$VO(O^iPr)_3$[23]	$4 \le n \le 22$	15−150	5−50	2−30	1−15
$VOCl_3$	11	50−100	15−35	10−20	1.5−5
$VOCl_3$	16	80−100	20−35	11−14	0.8−1.5
V_2O_5	11	70−140	20−35	9−13	2−12
V_2O_5	12	50−90	15−35	7−13	1−3
V_2O_5	16	70−100	20−45	6−11	1−2
V_2O_5	20	60−90	20−45	6−10	1−3

The reaction procedure starting from V_2O_5 yields VO_x-NTs in good yield and quality (Figure 3a). The product consists of isolated tubes of 1−3 μm length. The tube openings vary from 30 to 40 nm, while the outer diameters range from 60 to 100 nm (Figure 3b). Both the number of layers (6−9) and the above-mentioned tube dimensions are representative values for VO_x-NTs synthesized from V_2O_5.

Table 1 gives an overview of the different characteristics of the VO_x-NTs depending on the precursor and template. In general, the inner diameter varies between 15 and 50 nm in all samples, independent of the precursor used. Also the outer diameters in all samples are quite similar, generally between 50 and 150 nm. On the other hand, a wide range of tube lengths has been observed. Starting from the alkoxides, the tube length varies from 1 to 15 μm, while the typical length is about 3−4 μm. In the samples starting from $VOCl_3$ and V_2O_5, the average length of the tubes is smaller (1−3 μm). The distributions of the number of layers are similar in all tubes, generally between 6 and 15 layers.

Assuming an average morphology of inner (ϕ_i) and outer (ϕ_o) diameters of 32.5 and 100 nm, respectively, 11 layers, and a length of 4 μm, one calculates nearly the same layer dimensions along the tube axis and in the scroll direction (m): $m =$ (number of layers)$2\pi[(\phi_o - \phi_i)/2]$. Introducing average values, a ratio of length $l{:}m$ of about 2:1 is yielded. This would imply that the layers are mainly preformed in the lamellar phase and just rolled up during autoclave treatment, because the tetragonal structure of the layers (cf. below) should give rise to a more or less square-shaped growth. However, if one considers that many scrolls consist of multiple independent layers and that the maximum length approaches 15 μm without significant change of ϕ_i and ϕ_o, a growth along the tube axis in the autoclave seems to be quite likely as well.

The tips of the tubes obtained from $VOCl_3$ and V_2O_5 are open. Cross-sections of tubular V_2O_5 materials (Figure 4) reveal that the tubes are not built up of concentric, closed cylinders—but have a multiwalled morphology consisting of scrolls of vanadium oxide layers. Many tube walls comprise defects and dislocations. In addition, the tubes are not rotationally symmetric; they are oval with small depressions in the tube walls. Since the VO_x-NTs decompose above 250 °C, removal of the template molecules by calcination is not possible. Instead, the highly flexible, scroll-like tube structure allows for functionalization of the tube walls

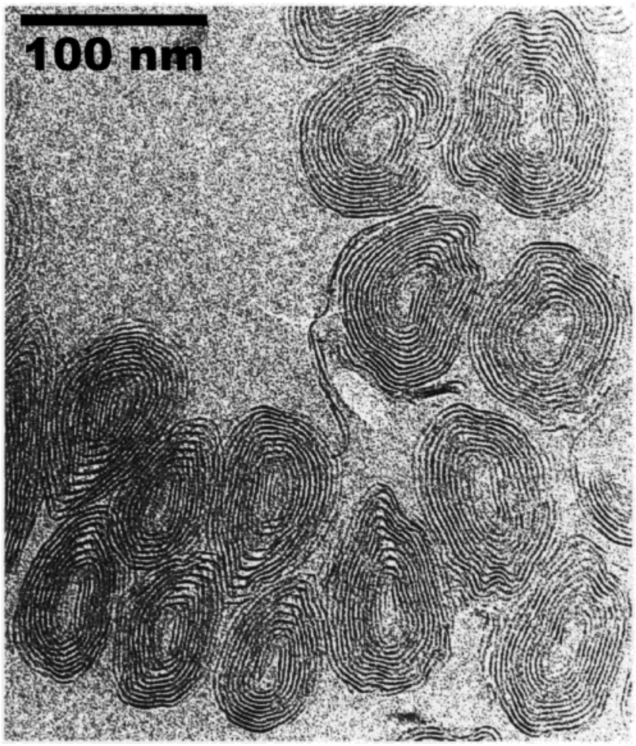

Figure 4. Cross-sectional TEM image of VO_x-NTs obtained from V_2O_5 and dodecylamine. Here, the outer diameters and the numbers of layers are nearly the same for all tubes. Tubes consisting of concentric closed layers have not been found in this sample.

by substitution of the intercalated template molecules via proton exchange against neutral α,ω-alkyldiamines[31] or by cation exchange against the involved metal cations.[32]

Figure 5 shows a typical X-ray powder diffraction pattern of V_2O_5-made VO_x-NTs. The peak with the highest intensity at low diffraction angle reflects the distance between the vanadium oxide layers. The d values of the 001 peak vary between 2.66 and 3.44 nm (Table 2), and are proportional to the alkyl chain length of the amine template. The less intense peaks at smaller d values correspond to the structure within the layers and can be indexed by a square lattice with $a = 0.61$ nm.[23,33] These $hk0$ reflections are independent of the template used, indicating that the wall structure is not affected by different templates. A certain difference between the d values of the $00l$ reflection from the XRD data and those determined by electron diffraction is probably due to a partial rearrangement of the flexible, paraffin-like arrangement of template molecules between the layers under the influence of the special conditions in the electron microscope, as discussed earlier.[23]

Table 2 lists the compositions of different VO_x-NTs. According to elemental analysis, the composition of the VO_x-NTs from $VOCl_3$ can be expressed in a general formula $VO_{2.45\pm0.05}(C_nH_{2n+4}N)_{0.27\pm0.01}$ with $11 \leq n \leq 16$. The average composition of the V_2O_5-synthesized material is $VO_{2.43\pm0.03}(C_nH_{2n+4}N)_{0.27\pm0.01}$ with $11 \leq n \leq 20$. The amount of oxygen has been calculated.[23] This compares well to that of the VO_x-NTs synthesized from the alkoxide precursor, for which the average elemental composition $VO_{2.43\pm0.06}(C_nH_{2n+4}N)_{0.27\pm0.01}$ ($12 \leq n \leq 22$) has been determined.

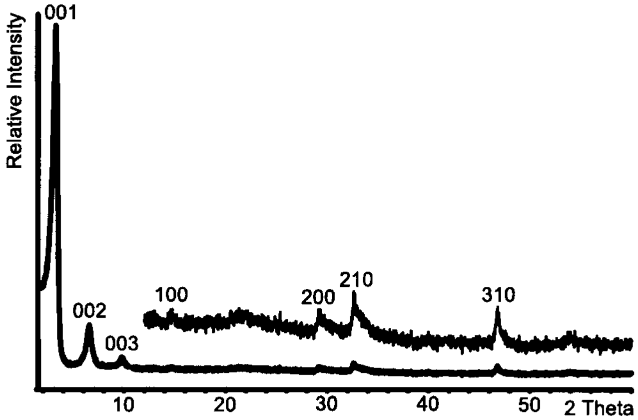

Figure 5. X-ray powder diffraction pattern of VO_x-NTs prepared from V_2O_5 and undecylamine. XRD patterns of VO_x-NTs are the same for all vanadium oxide precursors. The enlarged section shows the characteristic reflections $hk0$ generated by the structure within the layers, indexed on the basis of a two-dimensional square lattice with $a = 0.61$ nm. These reflections appear at the same 2θ values independent of the template used. In contrast to that, the $00l$ reflections, representing the distance between the vanadium oxide layers, change position with the length of the alkylamine template (cf. Table 2).

Table 2. Elemental Composition and Layer Distances of As-Synthesized VO_x-NTs Obtained from Different Precursors and Primary Alkylamine Templates

			interlayer distance (nm)	
precursor	template	composition	XRD	ED
$VO(O^iPr)_3$[23]	dodecylamine	$VO_{2.40}(C_{12}H_{28}N)_{0.26}$	2.77	2.21
$VOCl_3$	undecylamine	$VO_{2.43}(C_{11}H_{26}N)_{0.27}$	2.66	1.94
V_2O_5	undecylamine	$VO_{2.40}(C_{11}H_{26}N)_{0.28}$	2.68	2.13
V_2O_5	dodecylamine	$VO_{2.40}(C_{12}H_{28}N)_{0.27}$	2.74	2.19
V_2O_5	hexadecylamine	$VO_{2.46}(C_{16}H_{36}N)_{0.26}$	3.44	2.88

[a] The initial vanadium to template ratio was always 2. The amount of oxygen was calculated from the elemental analysis with respect to 100%.[23] The layer distances are determined from the d values of the 001 reflection in X-ray (XRD) and electron diffraction (ED) patterns.

Conclusions

In addition to the well-known synthesis of VO_x-NTs starting with a vanadium(V) alkoxide, two alternative routes have been found, which utilize either $VOCl_3$ or V_2O_5 as vanadium source. The results of our investigations strongly indicate that in each case a new mechanism is operative in the formation of the VO_x-NTs and that a liquid crystal templating mechanism similar to the one proposed for the formation of MCM-41-like materials can be excluded. In the synthesis of VO_x-NTs from V_2O_5, the amine is directly intercalated into the vanadium pentoxide layers, forming van der Waals interactions between the noncharged organic surfactant and the inorganic species. With $VOCl_3$, the first step is similar to the ligand-assisted templating mechanism. The amine surfactant is added prior to the hydrolysis,

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thus leading to a coordinative interaction between the amine headgroup and the vanadium atom. The fact that only the hydrothermal treatment of thoroughly washed lamellar intermediates leads to VO_x-NTs strongly supports a new mechanism without a liquid crystal phase or preformed micelles, respectively. Although we have three different reaction pathways, the resulting VO_x-NTs are astonishingly similar concerning morphology, structure, and composition. Since the hydrothermal treatment is performed in the same way for all precursors, the intermediate vanadium oxide−template composite apparently always has a similar lamellar structure. Further evidence for this is given by the experimental observation that in all cases the initial vanadium-to-template ratio has to be 2.

The use of $VOCl_3$ and V_2O_5 as precursors provides the possibility of a cost-saving scaling up of the nanotube preparation procedure. V_2O_5 is the most suitable precursor for this purpose not only because it is cheaper and easier to handle than $VOCl_3$ or vanadium alkoxides, but also because the synthesis is even less sensitive to variations of the reaction parameters in this case.

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