Study of the morphological evolution of vanadium pentoxide nanostructures under hydrothermal conditions†

W. Avansi,*a C. L. P. Oliveira,b C. Ribeiro,c E. R. Leited and V. R. Mastelaroe

A detailed study on the morphological evolution of one-dimensional (1D) vanadium pentoxide (V2O5) nanostructures was performed. Small-angle X-ray scattering (SAXS) and electron microscopy techniques were used for the analyses of the influence of synthesis parameters on a hydrothermal synthesis method of V2O5 nanostructures based on the degradation of a peroxocomplex precursor. A mechanism that explains the morphological evolution under different experimental conditions is proposed and the role of the dehydration process as well as the importance of the oriented attachment (OA) mechanism is discussed.

Therefore, several methods have been explored to obtain a simple and effective methodology for the synthesis of one-dimensional (1D) morphology V2O5 nanostructures.2,3,5–8,11,12,16–21 As reported by several papers, the hydrothermal method has appeared as a potential candidate, since it provides nanostructured materials of different morphologies, sizes and crystalline structures, which depend only on synthesis parameters.3,9,17,19–21 Li et al. demonstrated that the V2O5 morphology depends mainly on the composition of acids employed for pH control.17 According to the authors, after the formation of V2O5·nH2O nanoribbons, the presence of sulfuric acid leads to the formation of V2O5·nH2O nanobelts. On the other hand, in the presence of acetic acid, relatively larger CH3COOH molecules may intercalate into the V2O5·nH2O interlayers once the weak acetic acid is partially ionized in solution. Such intercalation leads to higher tension that might gradually cause the edges of the nanobelts to roll up, hence, the formation of nanorolls.17 Wei et al. studied a similar synthesis procedure and proposed a hydrating-exfoliating-splitting model to explain the formation of V2O5·0.25H2O nanowires.9

In a previous study, we reported a systematic study on V2O5·nH2O synthesis through a V2O5–H2O2 route (V-peroxo-complex degradation assisted by hydrothermal annealing), whose morphology, crystalline structure and number of water molecules between the layered structures are regulated by strict control of the hydrothermal synthesis variables.21,25 The methodology offers several advantages and has proved to be an easy-handling and environmentally friendly procedure for obtaining nanostructured materials since it prevents the presence of foreign ions or organic ligands and offers an accurate way for controlling the material morphology.26–29

A key factor in the nanostructure formation is the growth mechanism, i.e. the morphological evolution. This is not...
often considered in studies about materials syntheses and can be significantly influenced by the variables employed, such as temperature, precursors and time. Although the Ostwald ripening (OR) model, which is related to dissolution–reprecipitation, has been used for the interpretation of the crystal growth mechanism, the oriented attachment (OA) has been considered an effective mechanism of crystal growth under hydrothermal conditions. Therefore, the morphological evolution during hydrothermal treatment must be known, so that the role of different crystal growth mechanisms can be understood for the control of nanoparticle morphology and size.

This paper demonstrates the morphological evolution of V$_2$O$_5$·nH$_2$O 1D nanostructures obtained by a hydrothermal method based on peroxocomplex degradation. Small-angle X-ray scattering (SAXS), scanning transmission electron microscopy (FE-STEM) and transmission electron microscopy (TEM) techniques were used to study the crystal growth process. The importance of intrinsic parameters, such as synthesis time and temperature, was analyzed and the effect of the dehydration process and the role of growth mechanisms, especially the oriented attachment (OA) mechanism, are discussed.

### 2 Experimental section

The synthesis of V$_2$O$_5$·nH$_2$O 1D nanostructures under hydrothermal conditions is described in detail elsewhere. It is based on the dissolution of 0.06 M V$_2$O$_5$ powder in distilled water and addition of 30% H$_2$O$_2$ to form a V-peroxocomplex, which is the real precursor involved in the synthesis. It is stable at room temperature, can be subjected to hydrothermal treatment under different conditions and generates the desired V$_2$O$_5$·nH$_2$O nanostructures. Table 1 shows the samples of V$_2$O$_5$·nH$_2$O nanostructures designated with sample codes, as well as the temperatures and treatment time used in the hydrothermal synthesis.

Initially, the size and morphology of the as-prepared nanostructures were determined under a Zeiss VP Supra 35 field emission scanning transmission electron microscope (FE-STEM). Selected samples were also characterized by transmission electron microscopy (TEM) using a JEOL JEM 2010 URP and a FEI-Tecnai F20 operating at 200 kV. The samples were deposited on a copper grid covered with a thin layer of carbon for the electron microscopy studies.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Temperature of synthesis (°C)</th>
<th>Time of synthesis (h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SAM01</td>
<td>60</td>
<td>6</td>
</tr>
<tr>
<td>SAM02</td>
<td>120</td>
<td>24</td>
</tr>
<tr>
<td>SAM03</td>
<td>160</td>
<td>24</td>
</tr>
<tr>
<td>SAM04</td>
<td>180</td>
<td>6</td>
</tr>
<tr>
<td>SAM05</td>
<td>180</td>
<td>24</td>
</tr>
<tr>
<td>SAM06</td>
<td>200</td>
<td>24</td>
</tr>
</tbody>
</table>

A cross-sectional preparation technique used by Krumieich et al. was applied for the analysis of the morphology perpendicular to the V$_2$O$_5$·nH$_2$O nanorod axis. The V$_2$O$_5$·nH$_2$O nanorods were deposited on a Si wafer coated with an epoxy resin and then covered with a second Si wafer. This sandwich was placed into a copper tube (3 mm outer diameter) filled with epoxy. After the resin hardening, the resulting cylinder was cut into slices (with a thickness of 300 µm) which were then mechanically abraded on both sides until a thickness of around 80 µm was achieved. Subsequently, dimples of approximately 15 µm were produced on one side of the slice by using a dimple grinder (Gatan model 656). In the final step of the sample preparation, the specimen was etched on both sides with ion beams (PIMS, Gatan, argon (Ar) ions, 4.5 keV with an incidence angle of 80°) until a hole was created in the central area of the support that contains the nanorods. The beam energy and incidence angle were then decreased to 3 keV and 4°, respectively. In this step, the temperature was controlled with liquid N$_2$, in order to avoid damaging the sample. The nanorods were observed under a JEOL microscope (JEM 2010 UR) operated at 200 keV that focused on the specimen close to the hole to investigate the sample orientation along their axis. The mean width distribution of the nanoparticles was estimated according to the measurements of at least 350 nanostructures observed in the FE-STEM images of distribution fitted by a Gaussian function.

The morphology and overall size of the nanoparticles in the as-prepared suspension were determined by small-angle X-ray scattering (SAXS) experiments carried out on the LNLS (National Synchrotron Light Laboratory, Campinas, Brasil) synchrotron D02A-SAXS2 beam line. The distance from the sample to the detector was set to 2019 mm. The experimental data were normalized with respect to the incident beam intensity, and the background scattering of the solvent buffer was subtracted. The data to be analyzed were displayed as a function of the modulus of the scattering vector, $q = (4\pi/\lambda)\sin \theta$, where $\lambda = 1.488$ Å is the X-ray wavelength and $2\theta$ is the angle between the incident and scattered X-rays.

### 3 Results and discussion

X-ray diffraction (XRD) (see Fig. S1†) shows the XRD patterns of SAM01, SAM02 and SAM03 samples that were indexed as the monoclinic phase of V$_2$O$_5$·nH$_2$O. Such patterns displayed a series of 00l diffraction peaks, indicating a preferential orientation in the c direction. The interlayer spacing $d$, whose value is related to the hydrated form of the V$_2$O$_5$·nH$_2$O sample, shows a slight variation with the hydrothermal temperature.

The XRD pattern of the SAM04 sample also shows peaks related to the monoclinic phase, although a peak associated with the orthorhombic phase was also observed at around 20°, indicating the beginning of a structural phase transition. This behavior is expected based on our previous results. Indeed, for samples such as SAM05 and SAM06 subjected to hydrothermal treatment at 180 °C and 200 °C
for 24 hours, respectively, the XRD patterns are characteristic of the orthorhombic phase of V₂O₅, which is a dehydrated and more stable crystalline V₂O₅ phase.²¹

As expected, investigation of the morphologies of the samples by field emission scanning transmission electron microscopy (FE-STEM) (Fig. 1a) shows that SAM01 is composed of nanoribbons.²¹,³⁰ Interactions between nanoribbons governed by the OA mechanism in solution can promote the formation of nanoparticle of exotic shapes, probably due to random collisions during hydrothermal treatment.³⁰ Nevertheless, an increase in the average width value can be observed from (30 ± 1) to (44 ± 1) nm for SAM02 and SAM03, respectively, as the treatment temperature increases. At 180 °C and for 6 h of treatment (sample SAM04), the FE-STEM image revealed the presence of two morphologies, namely, nanoribbons and nanowires (Fig. 1b), which is consistent with the two crystalline phases detected by XRD.²¹ The nanostructure of SAM05 (180 °C, 24h) is composed only of nanowires with an average width of (14 ± 1) nm (Fig. 1c). Finally, in SAM06 (200 °C, 24h), the nanoparticles exhibit a rod morphology with an average width of (29 ± 1) nm (Fig. 1d). Elevation of the hydrothermal temperature causes an increase in the coalescence degree of nanoparticles, which is in good agreement with the results of Lee et al.³⁶

Measurements of the small angle X-ray scattering (SAXS) curves of the as-obtained suspensions, i.e., after the hydrothermal treatment, were obtained for the characterization of the nanostructure morphology in suspension in comparison with the results from FE-STEM analysis. The behavior of SAM01 and SAM02 SAXS curves (Fig. S3†) is similar to that reported by Pelletier et al. in a study of V₂O₅·nH₂O nanoribbons,³⁷ and the difference in the intensities of the scattering curves of such samples is attributed to nanoparticle size variation. Fig. 2 shows the scattering patterns of SAM03, SAM05 and SAM06, whose difference may be due to the different nanoparticle morphologies. The SAXS curves were fitted for the determination of the nanoparticle morphology in the as-prepared solution.

Several models, such as square long prisms, rectangular long prisms and long cylinders, were used for the fitting of the SAXS curves, however, the best fitting was obtained when polydispersed long cylinders (with radius R, length L and relative radial polydispersity σ) were considered. In all cases, the cylinder length was fixed to 1000 nm, which is larger than the resolution of the SAXS technique. Below is the expression used for the modeling of the SAXS curves:

\[ I(q) = Sc P(q) + \text{Back} \]  

where Sc is a scale factor, Back is the background constant and \( P(q) \) is the normalized form factor.³⁸ Assuming the cylinder lengths are much larger than the cross-sectional size, the decoupling approximation³⁹ can be used and the normalized form factor can be written as

\[ P(q) = P_{\text{ROD}}(q)/F_{\text{CS}}(q) \]  

where \( F_{\text{CS}}(q) \) is the scattering amplitude for the particle cross section and \( P_{\text{ROD}}(q) \) is the scattering form factor for an infinitely thin rod.⁴⁰

\[ P_{\text{ROD}}(q, L) = 2\sin(qL)/(qL) - 4\sin^2(qL/2)/(q^2L^2) \]  

For cylinders, \( F_{\text{CS}}(q) \) is given by

\[ F_{\text{CS}}(q) = \left(\frac{2J_1(qR)}{qR}\right)^2 \]  

where \( J_1(x) \) is a Bessel function of first order and first type.

The polydispersity parameter is included in the Schulz–Zimm distribution given by

\[ \langle F_{\text{CS}}(q) \rangle = \frac{\int_0^\infty D(r)F_{\text{CS}}(q,r)dr}{\int_0^\infty D(r)dr} \]
where $\Gamma(x)$ is a real Gamma function, $x_0$ is the distribution of the mass center and $z$ is related to the relative polydispersity in the $\sigma_R/R$ radius by the $z = 1/(\sigma_R/R)^2 - 1$ relation. The data were fitted by least squares procedures.38,41

Fig. 3a and b show the SAXS and fitting curves of SAM05 and SAM06, respectively. At low angles, the experimental and fitting curves of SAM05 show certain disagreement, probably due to a preferential orientation or some type of aggregation of the nanoparticles, which was not considered in our fitting model. The cylindrical morphology assumed in the model shows a radius value of $(5.5 \pm 0.5) \text{ nm}$ for SAM05, which may be interpreted as the average size for the colloidal particles. For SAM06, the radius was equal to $(12.3 \pm 0.5) \text{ nm}$. In both cases, the overall diameter obtained from SAXS is similar to those observed in FE-STEM images.

Even though the best fitting of the SAM05 and SAM06 SAXS curves was obtained when a cylindrical morphology for the nanoparticles was considered, the cross-sectional TEM images of SAM06 in Fig. 4 show that the nanoparticles display a rectangular cross section (nanorods). Aiming to confirm the composition of the material, an EDS spectrum was obtained from the same region as that in Fig. 4 (Fig. S2†). The X-ray emission peaks at around 0.5, 4.9 and 5.4 keV, which are related to V (see Fig. S2†) and confirm the composition of the analyzed nanostructure, can be seen. The presence of peaks at around 1.8 keV (attributed to Si), 0.5 keV (O), 0.25 keV (C) and 8 keV (Cu),42 attributed to the materials used for sample preparation, can also be observed. Additionally, the cross-sectional HRTEM image together with its respective fast Fourier transform (FFT) of an individual nanoparticle confirms the single crystalline nature (Fig. 4b), despite the procedure employed to prepare the sample, which also confirms the preservation of nanoparticle characteristics.

This morphology difference can be related to the polydispersity in the cross section dimensions (between 30% and 40%) determined from SAXS analysis. Additionally, the image showed some cracks in the nanorods, probably caused by the sample procedure for the TEM analysis.

Fig. 5 shows the SAM06 HRTEM data of two attached nanorods. The HRTEM images of the attached nanorods denoted as NP1 and NP2 (Fig. 5a) and their respective FFT illustrated in Fig. 5b and c, respectively, clearly show the single crystalline nature of the nanorods, as expected.21 Additionally, the FFT results confirmed the nanoparticle attachment in the [001] plane direction, with a small misalignment indicated by arrows in Fig. 5c. The FFT also suggests a stacking planar nanostructure growth mechanism in the [001] direction.23

The morphological evolution from nanoribbons to nanowires occurs via monoclinic to orthorhombic $\text{V}_2\text{O}_5$ structural phase transformation. It is well known that surface energy
Fig. 6 Schematic description of the proposed mechanism for the morphological evolution of V$_2$O$_5$·nH$_2$O nanofibers from nanoribbons to nanorods under hydrothermal conditions.

depends on the crystal structure, therefore, preferential growth in a given direction can occur.\textsuperscript{31,43,44} According to Sayle \textit{et al.}, the (001) plane has the lowest surface energy\textsuperscript{45} for the V$_2$O$_5$ orthorhombic phase, \textit{i.e.} nanoparticles that exhibit such a crystalline structure and growth direction will show a lower total surface energy. This growth process in the [001] direction can occur by either recrystallization or stacking planar nanostructures in the [001] direction.\textsuperscript{23} As our results confirmed that the nanostructures are relatively dense, no splitting\textsuperscript{17} or rolling\textsuperscript{9} of the nanostructures is expected. On the other hand, as the temperature increases, a continuous dehydration process of the nanostructures occurs and leads to tension in the structure that forms the nanorods. Based on our results, a mechanism of morphological evolution (Fig. 6) is proposed. Livage \textit{et al.}\textsuperscript{22} described in detail the V$_2$O$_5$·nH$_2$O nanoribbon formation. By increasing the temperature from 60 $^\circ$C to 160 $^\circ$C, the width of the nanoribbons increased according to the OA crystal growth mechanism (step 1).\textsuperscript{30} The dehydration process starts at above 180 $^\circ$C (step 2), and due to the high tension it caused in the structure, the nanoribbons may crack. At 180 $^\circ$C and upon increasing the hydrothermal treatment time to 24 h, growth along the (001) plane occurs and causes the formation of nanowires of a rectangular cross section (step 3). At 200 $^\circ$C and a hydrothermal treatment time of 24 h, as the viscosity of the suspension decreased and continuous dehydration occurred, the increased tension in the nanoparticles induced the nanorod formation (step 4). The nanorods are also wider in comparison with the nanowires due to crystal growth caused by the OA mechanism. The shorter nanorod lengths may be also attributed to the lower hydration state at that temperature.\textsuperscript{21}

Conclusions

This paper has presented a detailed study on the morphological evolution of V$_2$O$_5$·nH$_2$O 1D nanostructures obtained in a controlled way by hydrothermal treatment based on peroxo-complex degradation. The SAXS results, which were in good agreement with those of TEM, showed that the nanoparticles formed in the suspension remain stable after being removed from the solution. The morphological evolution of the nanoparticles from nanoribbons to nanorods was explained according to a structural phase transition, the tension caused by the dehydration process and the crystal growth based on the oriented attachment (OA) mechanism.

Acknowledgements

The authors gratefully acknowledge the financial support from Brazilian research funding Agencies FAPESP (Process No 2013/07296-2, 2013/17639-4 and No 06/07220-2) and CNPq. SAXS measurements and HRTEM microscopy facilities were provided, respectively, by LNLS (Research proposal SAXS 8055) and LNNano (Research proposal TEM-HR - 7902), Campinas, SP, Brazil.

Notes and references