



# On the role of hydrodynamic forces in vanadium oxide nanoscroll synthesis

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## ARTICLE INFO

### Article history:

Received 1 September 2011  
Received in revised form 31 January 2012  
Accepted 3 February 2012  
Available online 11 March 2012

### Keywords:

Sol–gel process  
Vanadium oxide  
Nanoscroll  
Hydrodynamic force

## ABSTRACT

Nanostructured vanadium oxides are promising materials for applications as semiconductors, cathode materials in nanoelectronics, in sensor technology and heterogeneous catalysis. Despite the increasing number of publications on nanostructured vanadium oxides, there is still a significant lack of systematic studies focusing on molecular and supramolecular aspects of the material synthesis. In this article, we address the effect of hydrodynamic forces on vanadium oxide gelation and the formation of vanadium oxide lamellar phases and nanoscrolls systematically. Hydrodynamic forces were generated by circulating the reagent mixture in a closed loop. ESR spectra revealed that application of strong hydrodynamic forces resulted in increased V(4+) concentrations in the lamellar material. High V(4+) concentrations are crucial for the defined rolling up of the lamellar, amine-intercalated vanadium oxide layers during hydrothermal treatment to form the nanoscrolls. The electronic properties of the lamellar precursor which are translated into the final nanoscroll product can be controlled by hydrodynamics, thus enabling nanoscroll synthesis with defined physical characteristics and morphology.

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## 1. Introduction

Vanadium oxide (VO<sub>x</sub>) gels have been in the focus of transition metal (“TM”) oxyhydroxide research for the past decades because of their extraordinary physical properties such as proton diffusion and semiconductivity. While the semiconductor properties arise from electron hopping in the mixed V<sup>4+</sup>/V<sup>5+</sup> oxide network, the proton conductivity results from the high acidity of the polymeric vanadates through intercalated water in the layered gels.

Vanadium oxide gels cannot be obtained through the traditional high temperature TM oxide synthesis methods. Therefore, synthesis of these peculiar phases occurs through sol–gel processes and solution-based synthesis approaches, commonly referred to as “chimie douce”, that provide access to transition metal oxyhydroxides, glasses and ceramics which are attained only with difficulty through traditional high temperature synthesis methods [1–6].

In typical research-focused syntheses, VO<sub>x</sub> gels are obtained by hydrolysis and subsequent polymerization of metal alkoxide precursors in aqueous conditions near the point of zero charge (pH 2). More economical routes, alternative to the rather expensive alkoxide approach, include the acidification of dissolved vanadate salts,

hydration of amorphous V<sub>2</sub>O<sub>5</sub>, gelation of V<sub>2</sub>O<sub>5</sub> with hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) or quenching of molten V<sub>2</sub>O<sub>5</sub> in aqueous solution [4,7].

In all synthesis strategies, polymerization of dissolved VO<sub>x</sub> molecular precursors through gelation and oxolation reactions commonly yields highly condensed oxide particles containing penta-coordinated vanadium atoms. This coordination is similar to the vanadium environment found in V<sub>2</sub>O<sub>5</sub> where V atoms are surrounded by oxygen in a square-pyramidal coordination sphere [8]. In the presence of excess water and at vanadium concentrations larger than 0.1 M, the color of the synthesis mixture changes from (light) orange to wine red as function of progressing gel formation and the associated increasing viscosity. It has been reported that the relative concentration of V(4+) in the oxide network can be influenced and increased up to 20% when the polymerization is performed in the presence of an organic solvent [7].

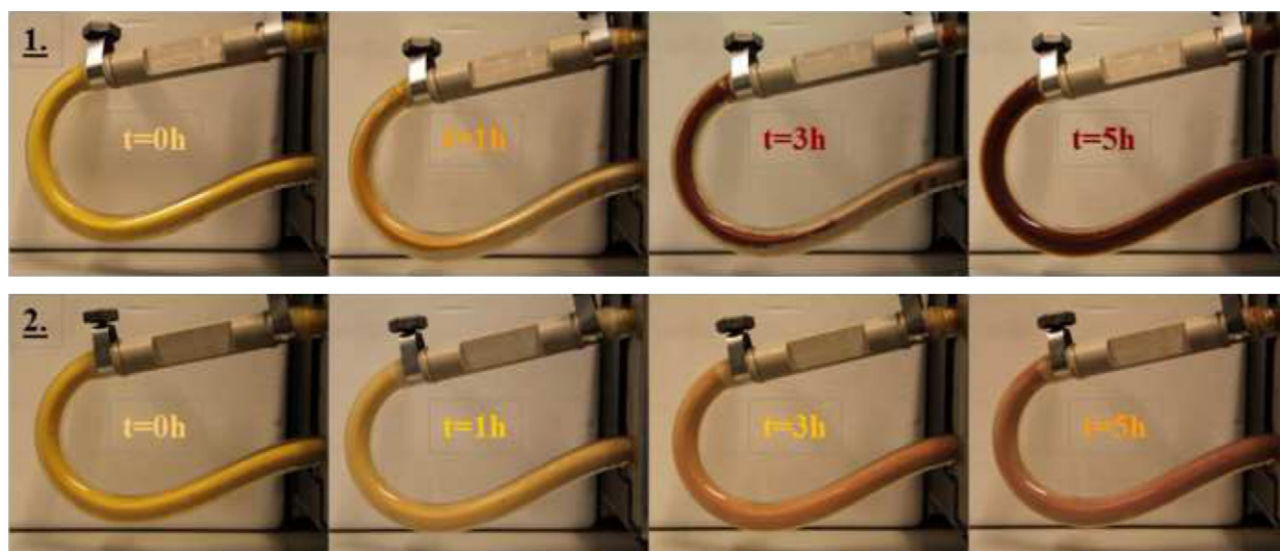
At high vanadium concentration, the development of a lamellar phase consisting of anisotropic layers has been described. This lamellar phase is characterized by a typical set of 00*l* and *hk*0 X-ray diffraction patterns which can be attributed to the 1D stacking (00*l*) and the 2D structure (*hk*0) of VO<sub>x</sub> ribbons, the building unit of the layers. Upon progressing polymerization, metastable, flexible (nanosized) lamellar phases with open lattice structures are obtained which can either be used directly or be treated hydrothermally [6,9–12].

One of the technologically more interesting materials that can be obtained by hydrothermal transformation of amine-intercalated, lamellar VO<sub>x</sub> gels are vanadium oxide nanoscrolls [13–15]. Amine

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**Fig. 1.** Evolution of the  $\text{VO}_x$  gelation at 4 L/min flow rate (Reynolds number ( $\text{Re}$ )  $\approx$  5,000, upper series of pictures, no. 1) compared to the same reaction at 2 L/min flow rate ( $\text{Re} \approx$  2,300, lower series of pictures, no. 2). At a flow of 4 L/min, starting from a pale yellow suspension (0 h), the reaction mixture turns increasingly orange (1 h) before the wine-red precursor gel is obtained (5 h). Compared to experiments at low flow rate, the hydrodynamic forces are much stronger, allowing for efficient mixing of the reactants, thus reducing the aging time. (For interpretation of the references to color in figure legend, the reader is referred to the web version of the article.)

surfactants can reversibly be intercalated into the 2D anisotropic  $\text{VO}_x$  host material via proton transfer from the acidic metal oxide network to the amine base, stabilizing mixed valence polyoxovanadate lamellae around neutral pH. The  $\text{V}(4+)/\text{V}(5+)$  ratio typically is smaller than 1/7 [1]. In analogy to water intercalation into  $\text{VO}_x$  gels and clays, the alkyl chain length and its orientation toward the  $\text{VO}_x$  layer defines the interlayer spacing between the layers while the basic lamellar structure is not affected [4,7]. Starting from this 2D organic–inorganic hybrid material,  $\text{VO}_x$  scrolls are obtained by hydrothermal transformation of the gel under autogeneous pressure for several days.

These scrolls are particularly interesting for applications in electrochemistry and sensor devices due to their open structure and electronic properties. They also provide unique opportunities for heterogeneous catalysis due to the combined presence of  $\text{V}^{4+}$  and  $\text{V}^{5+}$  species which may enable a combination of high selectivity and activity for specific reactions. Although it has been demonstrated that the microscopic properties of the final  $\text{VO}_x$  nanoscrolls and hence the rigorous control of the synthesis conditions is essential with respect to application of these materials (e.g. as cathode material in lithium ion batteries), the effect of the synthesis conditions on the morphology and crystal structure of the final product has not yet been investigated systematically [16–21].

In this work, the effect of the synthesis conditions during the formation of the initial lamellar gel phase on the final nanoscroll properties has been investigated. An elegant and very reproducible approach for controlling the hydrodynamic conditions during the gel phase synthesis is presented along with examples that demonstrate how tailored control of hydrodynamic conditions allows to tune the final nanoscroll properties toward specific applications. First, the close relation between the hydrodynamic forces and polymerization kinetics during the gel-phase is documented. Furthermore, the impact of these early stage processes on the final relative concentration of  $\text{V}(4+)$  could be demonstrated. As a final example, the tunable control over the magnetic properties, the crystallinity and morphology of the final nanoscrolls is shown. Mastering the nanoscroll formation process enabling to synthesize  $\text{VO}_x$  nanoscrolls with tunable electronic properties is a major step forward toward their application in electrochemistry and heterogeneous catalysis.

## 2. Experimental

Vanadium oxide nanoscrolls were synthesized using a modification of the procedure described by Niederberger et al. [15]. In a typical reaction, 6.68 g of  $\text{V}_2\text{O}_5$  (36.73 mmol) and 4.92 g of dodecylamine (26.54 mmol), corresponding to a surfactant-to-vanadium ratio of 0.36, were added to a transparent tube (Masterflex High-Performance Precision Tygon® Lab tubing, R-3603,  $\phi = 8$  mm, total volume: 50 mL) together with 42 mL solvent ( $\text{EtOH}/\text{H}_2\text{O} = 1/2$ , v/v). The tubing entirely filled with the synthesis mixture was then fitted inside the casing of a peristaltic pump (Masterflex I/P High Performance Pump) and gelation was performed by aging the mixture at 30 °C for 6–24 h at two different flow rates (2 and 4 L/min.). Viscosity measurements on as-synthesized gels for calculating Reynolds ( $\text{Re}$ ) numbers were performed on a MCR rheometer (Anton Paar, model SN935302). The remaining fractions of the resulting gels were split: one part was filtered, consecutively washed with EtOH and hexane and then dried in a vacuum oven (40 °C) before being sent for further analysis. The other part was transferred into a Teflon-lined autoclave (23 mL volume) and treated hydrothermally for 3 days at 180 °C. The as-synthesized nanotubes were filtered, washed with EtOH and hexane and also dried under vacuum overnight (40 °C). Finally, both the gels and the nanotubes were characterized by ESR, XRD and SEM. Diffuse reflectance UV–vis spectroscopy was performed on a Cary 5000 UV–vis–NIR Spectrophotometer (Agilent Technologies).

## 3. Results and discussion

In literature, the experimental description for the preparation of vanadium oxide ( $\text{VO}_x$ ) precursor gels is rather vague. Only few authors report detailed information on the stirring speed, solution pH and color of the final precursor gel that is transferred into the Teflon-lined autoclave for hydrothermal nanoscroll synthesis [15]. Most of the presented experimental data are based on *ex situ* FT-IR and XRD analysis providing information on evolving physical properties [22,23]. This complicates the direct comparison of experimental data as the color range from orange to wine-red, mentioned in the original publications clearly indicates that the degree of polymerization changes upon aging [7,14,15].

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