



Divanadium Pentoxide Nanorods

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Recently the control of the shape in the production of nanoparticles has become a new and interesting research area. In fact it has been demonstrated that physical properties are strongly related to the nanoparticles shapes. Hence non-spherical metallic nanoparticles such as silver nanorods [1], nanodisks [2], triangular particles [3] and gold nanorods [4] show anisotropic optical properties. In the same way, it was shown that the optical properties of semiconductor particles [5–7] and the magnetization properties of magnetic particles [8, 9] are drastically affected by their shapes. Shape controlled BaCrO₄ nanoparticles have been synthesized in reverse micelles [10].

In the present letter we present a new soft chemistry to synthesize for the first time divanadium pentoxide (V₂O₅) nanorods (Fig. 1).

These nanorods are characterized by several techniques.

EDS [11] shows that the nanorods are made of vanadium oxide, but nothing can be said about the oxidation state of the vanadium by this technique.

To answer the question about oxidation state of the vanadium, XPS measurements were made for the sample aged 24h [12]. The spectra of the V2p_{3/2} (top) and O1s (bottom) core levels are shown in figure 2.

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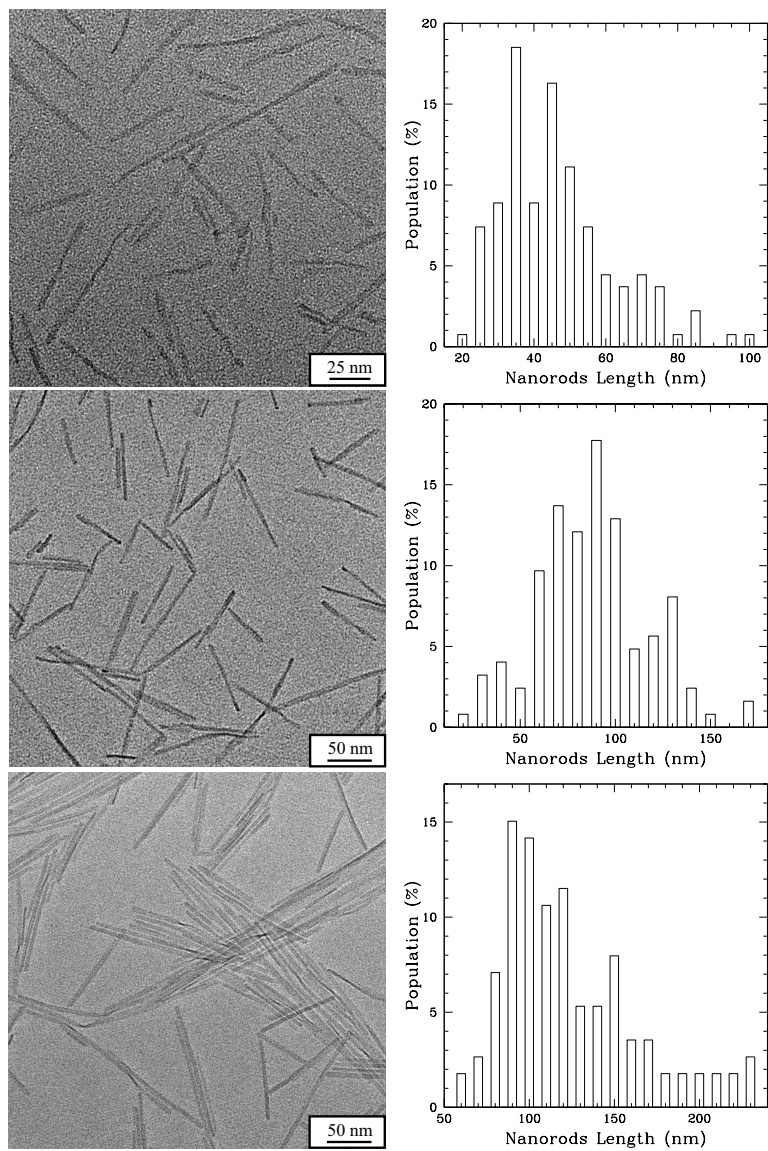


Figure 1: Vanadium oxide nanorods synthesized in reverse micelles. Just after synthesis (top), after 24h in micellar solution (center) and after 4 days in micellar solution (bottom).

The $V2p_{3/2}$ peak is centered at 517.2 eV. This binding energy is characteristic for vanadium at the +5 oxidation state [13, 14]. A small amount (4%) of vanadium at the +4 oxidation state can be seen after interpolation (thin line in Fig. 2) of the $V2p_{3/2}$ peak. During exposition of the sample to the x-ray beam the amount of V^{4+} increases. So the particles are slowly reduced during irradiation. The time of measurement of the XPS spectrum in figure 2 was 5min.

The shape of the O1s peak is very broad and looks more complicate. In general there are at least five possible contributions to the O1s peak: V-O due to the vanadium oxide and C-O-C, C=O and S-O due to the residual AOT and water. To separate the different contributions of the O1s peak from each other, the O1s spectrum of the Na(AOT) (Fig. 2, bottom) was subtracted from that of the vanadium oxide nanorods after normalization procedure [15]. The resulting spectrum is characterized by two contributions. The most pronounced, centered at 530 eV, is due to V-O stretch. The contribution centered at 531.5 eV is very weak and can be due to a normalization problem or to alkoxy ligands not completely removed from the surface of the nanorods [16] or some water contained in the structure or absorbed to the surface of the nanorods..

In conclusion, the oxidation state of the vanadium of the nanorods is +5 like in V_2O_5 and the contribution of the oxygen in the nanorods is estimated principally due to the V-O stretch.

X-ray diffraction [17] has been performed on the sample aged for 24h. The experimental spectrum is shown in figure 3 (full line). Principally only 3 diffraction peaks can be distinguished. The peak at $b = 0.56 \text{ \AA}^{-1}$ is the most intense and the most sharp. The peaks at $b = 0.29$ and $b = 0.326 \text{ \AA}^{-1}$ are very broad.

This diffraction pattern is very different from that of the bulk V_2O_5 because the particles are small and the non spherical shape induce a modification of the intensity and the width of the diffraction peaks. Hence the structure cannot be determined from such a broad spectrum

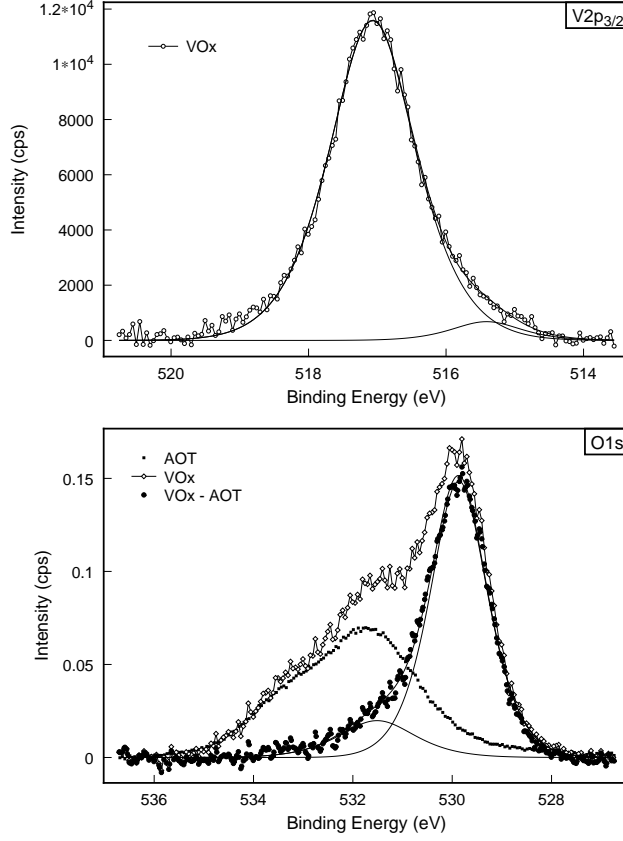


Figure 2: XPS core level spectra of the sample aged of 24h for the vanadium $2p_{3/2}$ and the oxygen $1s$

without the calculation of the diffraction pattern for model particles of the two V_2O_5 structures [18].

So the Debye functions (eq 1) of different sizes, shapes and structures of V_2O_5 are calculated [19].

$$I_N(b) = \sum_{n,m \neq n}^N f_n f_m \frac{\sin(2\pi b r_{nm})}{2\pi b r_{nm}} \quad (1)$$

The sum runs over all pair distances r_{nm} of atoms labeled by n, m with scattering amplitudes f_n, f_m in a nanoparticle of N atoms ($b = \frac{2\sin\vartheta}{\lambda}$; 2ϑ scattering angle; λ : wavelength).

The best fit for V_2O_5 structure is for a nanorod of $1.1 \times 20 \times 0.9$ nm (Fig 3 dashed line) and for γ - V_2O_5 structure [18] is for a nanorod of $2 \times 20 \times 1$ nm (Fig 3 dotted line). The peak at $b = 0.56$

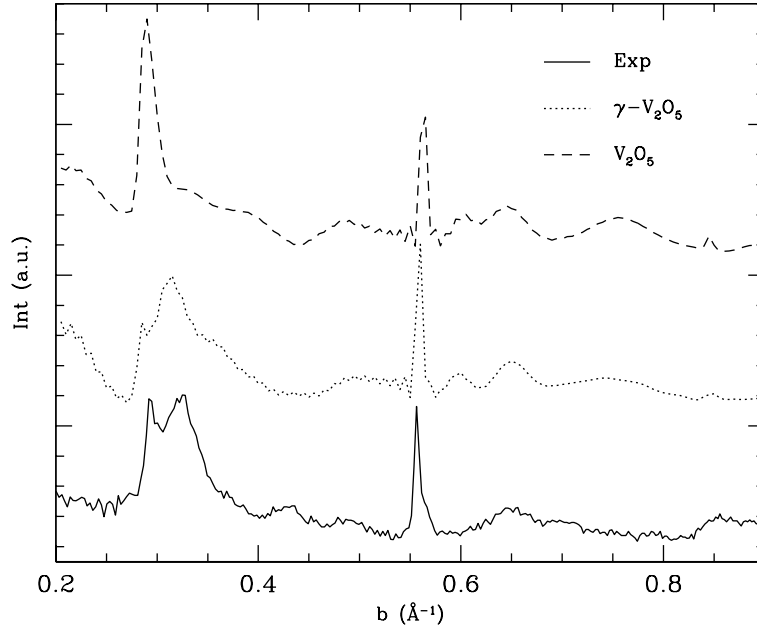


Figure 3: X-ray diffraction pattern of the sample aged of 24h and calculation of the two structures of V_2O_5

\AA^{-1} is well reproduced by both models. From this it is clear that the particles are growing along the b axis because the diffraction peak at $b = 0.56 \text{ \AA}^{-1}$ corresponds to the 020 diffraction and this peak is the most intense. The two peaks at $b = 0.29$ and $b = 0.326 \text{ \AA}^{-1}$ cannot be taken into account by the calculations for the "standard" V_2O_5 structure (Fig 3 dashed line). On the other hand they are well reproduced by the γ - V_2O_5 structure (Fig 3 dotted line).

In conclusion the structure of the nanorods is γ - V_2O_5 including some stacking faults because the model particle used to fit the diffraction pattern is smaller than the size deduced by transmission electron microscopy measurements.

In the present communication we describe for the first time that γ - V_2O_5 nanorods can be produced by the reverse micelle technique and that the size of these nanorods can be tuned

easily by keeping the fresh made nanorods in the micellar solution.

In another article we show that the vanadium surrounding of the nanorods is dramatically different from bulk V_2O_5 [20]. These findings are very important to understand the catalytic activity that we will investigate in further studies.

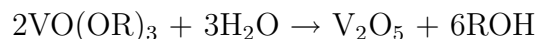
Acknowledgments

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Experimental

Divanadium pentoxide nanorods have been synthesized by colloidal self assembly made of Sodium bis(ethyl-2-hexyl)sulfosuccinate/Isooctane/ H_2O [21]. The water content (w) defined as the ratio of water to surfactant concentrations $w = \frac{[H_2O]}{[AOT]}$ is kept constant $w = 10$. Under such experimental conditions reverse micelles are formed. A solution of the alkoxide $VO(OR)_3$ with $R=CH(CH_3)_2$, in isooctane is then rapidly added to the micellar solution. The nanocrystals are formed instantaneously. The solution takes a brown color. The alkoxide concentration is kept constant at $[VO(OR)_3] = 5 \cdot 10^{-3}M$. The stoichiometric hydrolysis of the vanadium alkoxide [16] would correspond to a ratio $h=(H_2O)/(V_2O_5)=3$:



In our case $h=400$, if h is larger, no formation of V_2O_5 nanorods takes place.

One drop of this solution is then deposited on a carbon film. The TEM pattern [22] (Fig.

1 top) shows that the nanocrystals are characterized by an elongated shape: their average length is 47 nm and their width is 3 nm.

The nanorods are then kept in micellar solution for 24 hours or 4 days and then, like previously, deposited on a carbon film. The TEM patterns and histograms (Fig. 1 left and right respectively) show that the nanorods are growing in the micellar solution. After 24 h the average length is 90 nm and after 4 days is 128 nm.

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- [12] The spectroscopic investigations were carried out in a modified LHS/SPECS EA200 MCD system equipped with facilities for XPS (Mg $K\alpha$ 1253.6 eV, 168 W power). For the XPS measurements a fixed analyzer pass energy of 48 eV was used resulting in a resolution of 0.9 eV FWHM. The binding energy scale was calibrated using Au $4f_{7/2}$ = 84.0 eV and Cu $2p_{3/2}$ = 932.67 eV. The base pressure of the UHV analysis chamber was 1.10^{-10} mbar. Quantitative data analysis was performed by subtracting stepped backgrounds. For XPS measurements the nanorods are extracted from micellar solution by centrifugation and washed several times by isoctane to remove the residual AOT. The washed nanorod solution was then deposited on a stainless steel substrate.

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