



ELSEVIER

Available online at [www.sciencedirect.com](http://www.sciencedirect.com)

Journal of Magnetism and Magnetic Materials 320 (2008) e268–e271

[www.elsevier.com/locate/jmmm](http://www.elsevier.com/locate/jmmm)

# Iron oxide nanoparticles and VO<sub>x</sub>/Hexadecylamine nanotubes composite

M.E. Saleta<sup>a</sup>, H.E. Troiani<sup>a</sup>, S. Ribeiro Guevara<sup>a</sup>, R.D. Sánchez<sup>a,\*</sup>, M. Malta<sup>b</sup>, R.M. Torresi<sup>c</sup><sup>a</sup>Centro Atómico Bariloche, CNEA, 8400 S. C. de Bariloche, RN, Argentina<sup>b</sup>Depto. de Ciências Exatas e da Terra, Universidade do Estado da Bahia, Rua Silveira Martins, 2555 Cabula Salvador, BA, Brazil<sup>c</sup>Instituto de Química, Universidade de São Paulo, CP 26077, 05513-970 São Paulo, SP, Brazil

Available online 23 February 2008

## Abstract

In this work, we present the synthesis and characterization of a hybrid nanocomposite constituted by iron oxide nanoparticles and vanadium oxide/Hexadecylamine (VO<sub>x</sub>/Hexa) nanotubes. Transmission Electron Microscopy (TEM) images show small particles (around 20 nm) in contact with the external wall of the multiwall tubes, which consist of alternate layers of VO<sub>x</sub> and Hexa. By Energy Dispersive Spectroscopy (EDS), we detected iron ions within the tube walls and we have also established that the nanoparticles are composed of segregated iron oxide. The samples were studied by Electron Paramagnetic Resonances (EPR) and dc-magnetization as a function of the magnetic field. The analysis of the magnetization and EPR data confirms that a fraction of the V atoms are in the V<sup>4+</sup> electronic state and that the nanoparticles exhibit a superparamagnetic behavior. The percentage of V and Fe present in the nanocomposite was determined using Instrumental Neutron Activation Analysis (INAA).

© 2008 Elsevier B.V. All rights reserved.

PACS: 75.75.+a; 68.37.Lp; 76.30.-v

Keywords: Magnetic properties of nanostructures; Vanadium oxide nanotube; Nanocomposite; EPR; TEM

## 1. Introduction

Bulk vanadium oxides (VO<sub>x</sub>) have been studied for several years. The multivalence of the V (+2, +3, +4 and +5) results in a complex phase diagram [1,2]. Whilst in some of these oxides, the vanadium ions are in a unique oxidation state, in other oxides different magnetic species coexist, increasing the complexity of the phase diagram.

The VO<sub>x</sub> nanotubes (VO<sub>x</sub> NTs) have been studied since the 90s. Nesper and co-workers reported the synthetic method and demonstrated the viability of producing hybrid VO<sub>x</sub>/surfactant NTs [3–5] in which the used surfactant acts as template. Krusin-Elbaum et al. [6] and Vavilova et al. [7] have investigated VO<sub>x</sub> NTs with Dodecylamine as template. Their magnetic measurements are consistent with a higher percentage of V<sup>4+</sup> ions and

that half of these ions are dimers with an antiferromagnetic coupling.

The structural flexibility of these layered oxides allows the partial substitution of template molecules by metallic cations, while preserving the nanotubes morphology. This can be achieved using a chemical exchange reaction.

The Nesper's group studied the effect of cation exchange [3]. According to these authors, some metallic cations such as Sr<sup>2+</sup>, Ag<sup>+</sup>, Ba<sup>2+</sup>, Rb<sup>+</sup> and Cs<sup>+</sup> destroyed the tubular morphology completely. They also found that Pb<sup>2+</sup> is not exchanged. By contrast Ni<sup>2+</sup>, Na<sup>+</sup>, K<sup>+</sup>, Mn<sup>2+</sup>, Ca<sup>2+</sup> and Co<sup>2+</sup> can be easily exchanged with good preservation of tubular morphology. Using the same strategy but with the different template molecules (Hexadecylamine) our group prepared VO<sub>x</sub>/Hexa NTs replacing partially the Hexa surfactant by Ni ions [8]. Azambre and Hudson [9] have succeeded in preparing a composite constituted by copper nanoparticles (NPs) within VO<sub>x</sub>/Dodecylamine NTs.

\*Corresponding author. Tel.: +54 2944 44 5158; fax: +54 2944 44 5299.  
E-mail address: [rodo@cab.cnea.gov.ar](mailto:rodo@cab.cnea.gov.ar) (R.D. Sánchez).

In this work, we present the magnetic and morphological characterization of VO<sub>x</sub> NTs using Hexa as the principal template and partially replaced by Fe cations. The TEM study shows that Fe cations are segregated within NPs. The magnetic characterization was performed using Electronic Paramagnetic Resonances (EPR) and dc-magnetization experiments. The amount of V and Fe in the samples was determined by INAA and the local qualitative composition was investigating using EDS.

## 2. Experimental

Vanadium oxide nanotubes were synthesized following the method described in Ref. [10] (untreated sample). In a subsequent step, the VO<sub>x</sub>/Hexa NTs were immersed during 24 h, at 25 °C, in a saturated solution of Fe(NH<sub>4</sub>)<sub>2</sub>(SO<sub>4</sub>)<sub>2</sub> (treated sample).

The amounts of V and Fe in the samples were determined by INAA. Both samples were irradiated in the RA-6 nuclear reactor, located at Centro Atómico Bariloche (Bariloche Atomic Center, Argentina), inside plastic vials with a disk shape of 1 cm in diameter. The neutron flux at the irradiation position was predominantly thermal ( $\phi_{th} = 8 \times 10^{11} \text{ n cm}^{-2} \text{ s}^{-1}$ ). Vanadium and iron concentrations were determined by comparison with high purity metallic standard materials. Vanadium was measured by evaluating <sup>52</sup>V isotope (half life 3.743 min) while the <sup>59</sup>Fe isotope (half life 44.50 d) was evaluated to measure iron concentration.

The morphological characterization by TEM and the EDS analysis were performed using a CM 200 Philips microscope (LaB<sub>6</sub> cathode, 200 keV).

EPR spectra were taken at X-Band (9.5 GHz) with a Bruker ESP-300 spectrometer, between 115 and 300 K temperature range.

The magnetic measurements were performed in a commercial superconducting quantum interference device magnetometer (Quantum Design MPMS-5S and MPMS-XL), reaching in some cases a maximum field of 70 kOe.

## 3. Results

The INAA data of samples before and after the treatment within the iron solution are presented in Table 1.

The EDS studies confirm the presence of V, O and N (from VO<sub>x</sub> and Hexa: C<sub>16</sub>NH<sub>35</sub>) inside the NT's walls. In the treated sample Fe was detected inside the walls of the nanotube as well as in the form of FeO<sub>y</sub> isolated NPs.

Table 1  
Mass percentage of V and Fe atoms measured by INAA

	V (%)	Fe (%)
VO <sub>x</sub> /Hexa NTs	24.5 ± 0.4	–
FeO <sub>y</sub> –VO <sub>x</sub> /Hexa	26.9 ± 0.4	2.3 ± 0.4

Fig. 1 shows TEM images of treated and untreated samples. In both cases a similar morphology can be observed, which consists of a tubular shape and multiwall layers (around 10) of VO<sub>x</sub> intercalated with layers of Hexa or FeO<sub>y</sub>/Hexa. The presence of FeO<sub>y</sub> in the treated sample has been confirmed by EDS (Fig. 1c). Further evidence for the presence of the intercalated iron between the layers could be the increase in the typical inter-layer distance (*d*). For untreated NTs,  $d = (1.9 \pm 0.2) \text{ nm}$  while for the treated samples the observed separation between layers is  $d = (2.1 \pm 0.3) \text{ nm}$ . The treated sample also contains small particles of FeO<sub>y</sub>, which have been deposited in the walls of the nanotubes.

The EPR spectra collected at 130 K for both samples are shown in Fig. 2. Two lines can be observed in the treated sample. One of them is at low field (LF) while the second one is at high field (HF). The HF resonance has a linewidth of 500 Oe, and it is centered at  $H_0 = 3449 \text{ Oe}$ , which corresponds to a  $g = 1.96$  value. These values together with the independent temperature dependence of  $H_0$  suggest that this line corresponds to paramagnetic V<sup>4+</sup> ions [8]. In addition at low magnetic field in the treated sample, an extra resonance can be detected with a  $g$  between 7 and 9. Following this line with  $T$ , we observe that the  $H_0$  parameter increases when  $T$  is rising (see Fig. 3), but it never reaches the expected paramagnetic value ( $H_0 \sim 3300 \text{ Oe}$ ). This indicates that the resonating ions are magnetically coupled. Taking into account that for the treated sample the TEM microscopy reveals the presence of Fe oxide NPs and that EPR shows a LF magnetic resonance, we conclude that this line is associated with the Fe ions magnetically ordered inside the NPs.

The magnetization as a function of  $H/T$  measured close to the liquid helium temperature is presented in Fig. 4. With the aim of verifying the EPR results we have fitted the experimental data to the following expression:

$$M\left(\frac{H}{T}\right) = M_o^V \times B_{1/2}\left(\frac{H}{T}\right) + M_o^{\text{NP}} \times L\left(\frac{\mu \times H}{T}\right) + \chi_o \times H, \quad (1)$$

where  $M_o^V = N^{V(4+)} g S \mu_B$ ,  $B_{1/2}(H/T)$  is the Brillouin function for  $S = 1/2$  to describe the paramagnetic V<sup>4+</sup> ions and  $L(\mu \times H/T)$  is the Langevine function for superparamagnetic NPs,  $M_o^{\text{NP}} = \mu \times N^{\text{NP}}$ .  $\mu$  is the magnetic moment of the NPs,  $N^{\text{NP}}$  the number of NPs and  $\chi_o$  is a independent temperature term (which describes contributions as the van Vleck, diamagnetism of the cores, of the template, or of the sample holder, etc.) [8]. The contribution of each term of the  $M$  as function of  $H/T$  is present in Fig. 4 inset. Fig. 4 also presents the  $M$  vs.  $H/T$  data for the untreated sample and the fit using only the first term of Eq. (1). In both cases, theoretical expectations are in a very good agreement with the experimental data (see Fig. 4 and Table 2).

In our analysis of the low temperature data, we have neglected the possible contribution of V–V dimers [6,7], because this term only becomes significant at high  $T$ .

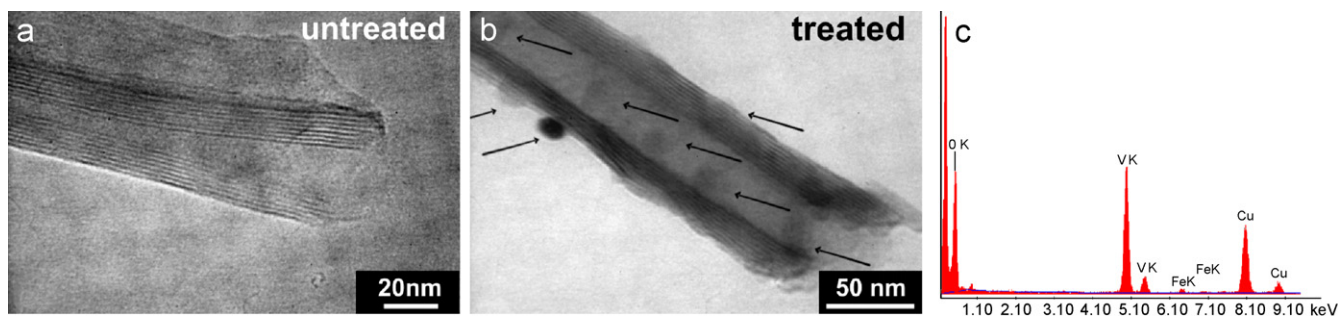


Fig. 1. TEM images of (a) untreated  $\text{VO}_x/\text{Hexa}$  NTs showing the multiwall tubular shape. (b)  $\text{FeO}_y-\text{VO}_x/\text{Hexa}$  NTs showing the coexistence of  $\text{FeO}_y-\text{VO}_x/\text{Hexa}$  NTs and segregated  $\text{FeO}_y$  NPs (see arrows). In both cases, the presence of Fe was confirmed by EDS. (c) EDS spectrum of a treated NT in a region without segregated  $\text{FeO}_y$  NPs, the contribution of Cu come from the copper grid.

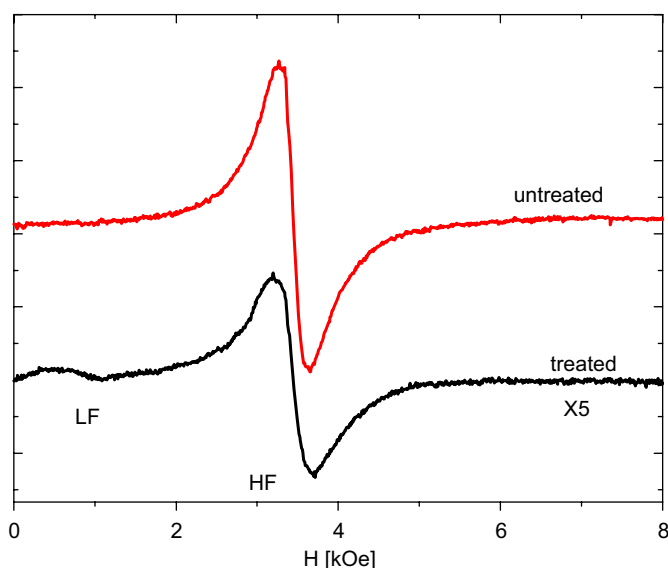


Fig. 2. EPR spectra measured at 130 K.

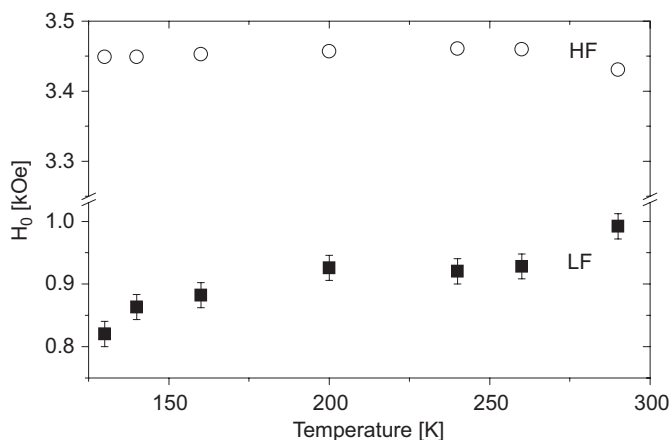


Fig. 3. EPR resonance field ( $H_0$ ) as function of temperature for the HF and LF lines observed in the treated sample.

In summary, the TEM images and the EDS microanalysis demonstrate that the treated sample is a nanocomposite where some iron has been incorporated inside the walls of the

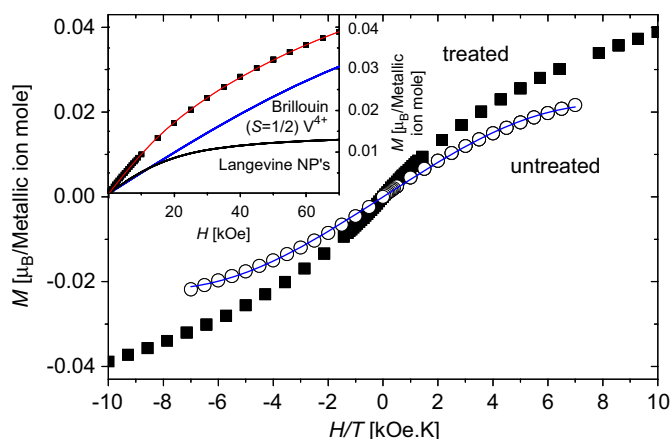


Fig. 4. Magnetization as function of  $H/T$  for treated and untreated samples. The solid lines are the fit using Eq. (1) (untreated without the Langevine term). Inset shows a detail of the  $M$  components for the treated sample.

Table 2

Fit parameters of the experimental magnetization curve

	$\text{VO}_x/\text{Hexa}$	$\text{FeO}_y-\text{VO}_x/\text{Hexa}$
$M_0^V$ ( $\mu_B$ metallic ion $\text{mol}^{-1}$ )	0.267 (9)	0.0512 (3)
$M_0^{\text{NP}}$ ( $\mu_B$ metallic ion $\text{mol}^{-1}$ )	0	0.0148 (2)
$\mu$ ( $\mu_B$ )	0	11.8 (2)

$\text{VO}_x/\text{Hexa}$  multiwall NTs and the rest of the iron has segregated into  $\text{FeO}_y$  NPs. This could be a consequence of the high thermodynamical stability of iron oxides.

The EPR data and the dc-magnetization experiments indicate that the magnetic behavior of the  $\text{FeO}_y-\text{VO}_x/\text{Hexa}$  nanocomposite, at low temperatures, can be described by taking into account the coexistence of paramagnetic  $\text{V}^{4+}$  ions and superparamagnetic nanoparticles of iron oxide with magnetic moment of  $\sim 10 \mu_B$ .

In addition, we have established that the incorporation of Fe into the tube structure reduces the amount of  $\text{V}^{4+}$  ions. This value is around 17–25% in the untreated NTs

while in the treated sample this decreases to only 4–6%. A similar behavior has also been observed by us in other exchanged NTs, such as the Ni doped VO<sub>x</sub>/Hexa [8].

### Acknowledgments

MES acknowledges to CONICET for the studentship, and HET and RDS are members of CONICET. This work was partially funded by the following projects: in Argentina by U.N. Cuyo 06/C203; ANPCyT (PICT-2004 21372, PAV and RN3M); PIP-CONICET 5250 and Fundación Antorchas; in Brazil by FAPESP (Proc. 03/10015-3).

### References

- [1] K. Kosuge, J. Phys. Chem. Solids 28 (1967) 1613.
- [2] H. Katzke, P. Toledano, W. Depmeier, Phys. Rev. B 68 (2003) 024109.
- [3] J.M. Reinoso, H.-J. Muhr, F. Krumeich, F. Bieri, R. Nesper, Helv. Chim. Acta 83 (2000) 1724.
- [4] M. Niederberger, H.-J. Muhr, F. Krumeich, F. Bieri, D. Günther, R. Nesper, Chem. Mater. 12 (2000) 1995.
- [5] F. Krumeich, H.-J. Muhr, M. Niederberger, F. Bieri, B. Schnyder, R. Nesper, J. Am. Chem. Soc. 121 (1999) 8324.
- [6] L. Krusin-Elbaum, D.M. Newns, H. Zeng, V. Derycke, J.Z. Sun, R. Sandstrom, Nature 43 (2004) 672.
- [7] E. Vavilova, I. Hellmann, V. Ketev, C. Täschner, B. Büchner, R. Klingeler, Phys. Rev. B 73 (2006) 144417.
- [8] M.E. Saleta, J. Curiale, H.E. Troiani, S. Ribeiro Guevara, R.D. Sánchez, M. Malta, R.M. Torresi, Physica B 398 (2007) 333.
- [9] A. Azambre, M.J. Hudson, Mater. Lett. 57 (2003) 3005.
- [10] M. Niederberger, H.-J. Muhr, F. Krumeich, F. Bieri, D. Günther, R. Nesper, Chem. Mater. 12 (2000) 1995.