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Comparative structural-vibrational study of nano-urchin and nanorods of vanadium oxide

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We present a comparative structural-vibrational study of nanostructured systems of V_2O_5: nano-urchin (VONURs) which are spherical structures composed of a radially oriented arrays of VOx nanotubes (VOx-NTs) with a volumetric density of ~40 sr^{-1}, and vanadium oxide nanorods (VOx-NRDs) with an average length of ~100 nm. The Raman scattering of the nano-urchin exhibits a band at 1014 cm^{-1} related to the distorted gamma conformation of the vanadium pentoxide (γ-V^{5+}). The infrared vibrational spectra of the nanorods sample also exhibit a distorted laminar V_2O_5 structure with evidence observed for quadravalent V^{4+} species at 921 cm^{-1}.

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1 Introduction

One-dimensional nanomaterials, such as nanotubes [1,2], nanowires [3], and nanobelts or nanoribbons [4-6] have attracted considerable attention in the past decade because of their novel and useful physical properties leading to numerous potential applications. Although the majority of research and development has been based on carbon nanotubes, considerable attention is now being directed to transition metal nanostructures based on their metal oxides which, due to their versatile chemical properties often modulable by changes in the oxidation state of in the metal coordination sphere, may lead to a variety of products and tunable materials [7,8].

Vanadium oxide-based low dimensional products have been studied extensively. Starting from the laminar V_2O_5 xerogel [7] numerous two dimensional organic-inorganic intercalation products have been obtained [9]. Many of these V_2O_5 based nanostructures may be obtained in quantities of the order of grams [10]. With the electrical and optical properties of vanadium oxide derivatives [11], this yield has encouraged its study as a potential new functional material. The possibility of synthesizing new varieties of shapes and sizes will encourage their potential application in new kinds of optical and electrical devices.

In this work, we present a comparative structural-vibrational study of nano-urchin (VONURs) and nanorods (VOx-NRDs) of vanadium oxide recently reported by our group [10,11]. The products are characterized by TEM, electron diffraction (ED), Raman scattering and infrared spectroscopies.

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2 Experimental

2.1 Synthesis of vanadium oxide nanourchin

The method employed for the synthesis of vanadium pentoxide nano-urchin was essentially the same as described in Refs. [10,11]. The preparation of the vanadium oxide nanorods can be found in Ref. [11]. Briefly, the nanocomposite consists of a solution mixture of 10^{-3} mol dm^{-3} of hexadecylamine (HDA) in 10 ml of pure ethanol and 2×10^{-3} mol dm^{-3} vanadium (V) tri-isopropoxide (VOTPP) that underwent hydrothermal treatment at 180^{o} C for 7 days. The final product has the composition $V_2O_5(HDA)_{0.83} \cdot 1.8H_2O$. Analysis: Exp. (calculated for $C_{13.28}H_{32.65}N_{0.83}O_{6.8}V_2$), C: 39.06 (38.32); H: 8.05 (7.89); N: 2.56 (2.79).

2.2 Sample characterization methods

The morphological characterization of the nanostructured products was performed by field emission scanning electron microscopy (FESEM) using a JEOL JSM-6700F operating at beam voltages between 1 and 10 kV. Electron transparent specimens were prepared by ion-milling techniques and placed on a holey carbon support. Transmission electron microscopy (TEM) and electron diffraction (ED) were conducted using a JEOL 2000FX operating at 200 kV. The FTIR spectra were recorded using a Perkin-Elmer series 2000 apparatus in the region 4000-450 cm^{-1}. Raman spectroscopy was conducted using a Jobin Yvon XY 800 spectrometer equipped with a cooled charge coupled device (CCD) detector. The spectral excitation was provided by an argon ion laser, using a 514.5 nm laser line (2.41 eV) with a variable laser power density. The chemical composition of the samples was determined by elemental chemical analysis using a SISONS model EA-1108 analyzer.

3 Results and discussion

Figure 1a shows an FESEM micrograph of a spherical vanadium oxide nanourchin (VONUR) synthesized using the hydrothermal treatment (HT) outlined in Section 2.1. The nanourchin contain a relatively high volume of vanadium oxide nanotubes (VOx-NTs) with a volumetric density of ~40 sr^{-1}. The tubes are approximately 9 – 12 μm in length with internal hollow diameters of 100 – 200 nm. The HRTEM (Fig. 1a) of the nanourchin tubes show an interlamellar distance of 2.85 nm [10], and we have determined that the organic surfactant used during synthesis of the nanostructure is in an *all-trans* configuration between successive vanadate atomic layers [11].

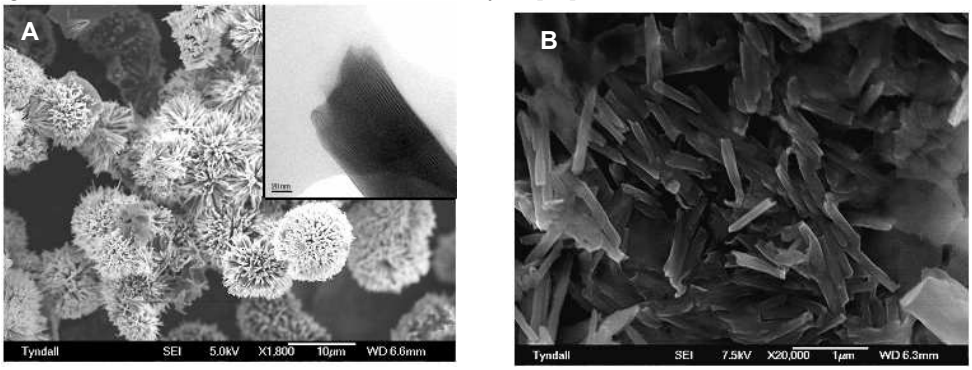


Fig. 1 (a) FESEM image of the nano-urchin of vanadium oxide (inset) HRTEM image of a nano-urchin tube with uniform hollow core and open ended. (b) FESEM image of nanorods of vanadium oxide.

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The HRTEM image inset to Fig. 1a shows a uniform and open-ended nanotube tip found in the nanourchin. The inner hollow core is straight and maintains a constant diameter surrounded by an equal number of alternating contrast lines resulting from diffraction from similarly spaced vanadate atomic layers. The vanadium oxide nanorods (VOx-NRDs), on the other hand, have a length of typically ~1 μm, and a diameter in the range of 100 – 200 nm. A typical FESEM image of a group of nanorods can be seen in Fig. 1b.

The Raman scattering spectrum for the nano-urchin and nanorods are reproduced in Fig. 2. In the case of the Raman signal of the VOx-NRDs, shown in Fig. 2a, we observed signals that correspond to the bending mode of the vanadyl group at 400 cm^{-1}. The stretching vibrational mode of the doubly coordinated oxygen (V_2-O) was also observed at 683 cm^{-1}. For the nanorods, the Raman scattering signal exhibits a medium intensity band at 986 cm^{-1} corresponding to the vanadyl group. By applying the empirical equation and the relation for the different vanadium conformations from Ref. [12], the value for the length of the V-O bond is estimated to be 0.155 nm. This value corresponds to presence of the α-V^{5+} species, see Table 1.

The spectrum for the nano-urchin in Fig. 2b exhibits a band at 504 cm^{-1} that is assigned to the triply coordinated oxygen (V_3-O) mode in pure V_2O_5 [13]. It arises from the stretching mode from edged-shared oxygen atoms in common to three pyramids in the oxide structure. The doubly coordinated vanadium-oxygen signal is observed at 643 cm^{-1}, slightly shifted compared to that observed in the VOx-NRDs.

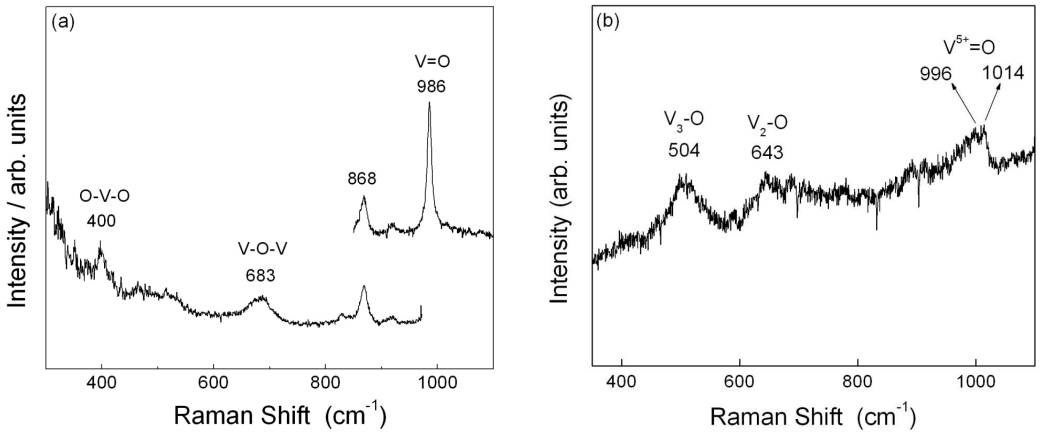


Fig. 2 Raman scattering spectrum of the (a) nanorods and (b) vanadium pentoxide nano-urchin acquired with a laser power density at 291 μW $μm^{-2}$.

Hardcastle and Wachs [12] have proposed an empirical equation to relate the highest V-O stretching mode frequency observed in the spectra with the V-O bond length in vanadium-based oxides. Thus, the peaks that we observe in the region around 1000 cm^{-1} (996 cm^{-1} and 1014 cm^{-1}) in the nano-urchin correspond to the estimated V=O lengths of 0.155 nm and 0.154 nm (medium intensity), respectively. These observations are in good agreement with previously reported data for VOx-NT structures [14-16]. These two signals infer that the nano-urchin does not contain divalent vanadium as V^{5+}/V^{4+}. Furthermore, since the V^{4+}=O bond (bond length of 0.160 nm [16]) contributes to a medium intensity band by comparison to the pentavalent V=O bond, it is possible to propose that the predominant vanadium in this nanostructure is present as V^{5+}, see Table 1.

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Table 1 VOx nanostructures: Raman scattering results.

	Wavenumber (cm^{-1})		
Nano-urchin	1014	996	-
Nanorods	-	-	986
Vanadium valency	γ-V^{5+}	V^{5+}	α-V^{5+}

Figure 3 shows the infrared vibrational spectra acquired for the nano-urchin and nanorods. The infrared signals for the nano-urchin exhibit different kinds of vibrational modes. In the region below 1000 cm^{-1}, specifically in the region of the vanadyl group vibrational modes, we observe three distinct bands at 997, 954 and 944 cm^{-1}. In the case of the VOx-NRDs, also in the area corresponding to the vanadyl group vibrational modes, characteristics vibrational modes at 998, 983, 957 and 921 cm^{-1} were also observed.

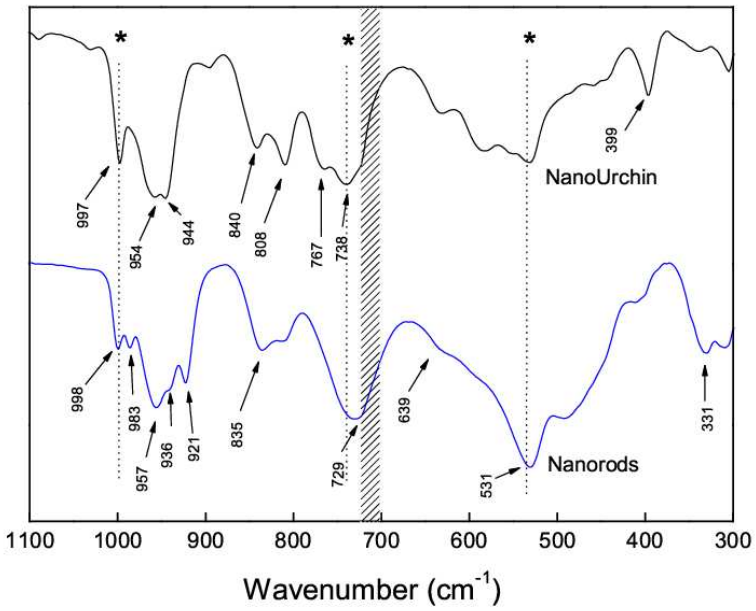


Fig. 3 Infrared spectra of the nano-urchin and nanorods of vanadium oxide. The (*) signals correspond to the bands of V_2O_5 xerogel and the shaded area corresponds to the spectral range of the surfactant vibrational modes.

By employing the empirical equations proposed in Refs [12,16], the vibrational signals of the nano-urchin exhibit the presence of the V^{5+} species represented by the spectral bands at 997 and 954 cm^{-1}, seen in Fig. 3 and outlined in Table 2. The signal at 944 cm^{-1} corresponds to the γ conformation of V_2O_5 [16]. In the case of the VOx-NRDs, the bands at 998, 983 and 957 cm^{-1} correspond to vibrational modes of the V^{5+} species in the vanadyl group. At 921 cm^{-1}, we observe a band due to the presence of V^{4+} species, outlined in Table 2. The other bands shown in Fig. 3 correspond to contributions from the surfactant used during synthesis and have not yet been accurately assigned.

Table 2 VOx nanostructures: Infrared scattering results.

	Wavenumber (cm^{-1})					
Nano-urchin	997	-	954	944	-	-
Nanorods	998	983	957	-	936	921
Vanadium valency	γ -V^{5+}	V^{5+}	α-V^{5+}	V^{5+}	V^{5+}	V^{4+}

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4 Conclusions

Both Raman scattering and infrared spectroscopies of the nanotube-containing nanourchin have shown that the vanadate layers in the nanotubes are in a distorted γ-V^{5+} conformation. The vibrational infrared spectra of the nanorods, by comparison, show evidence for V^{5+} species-containing ordered VOx lamina. Detailed FESEM and HRTEM studies have highlighted their novel structure and the quantity of yields through the synthesis methods involved could permit their application in the field of functional materials in optical and electrical charge storage devices.

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