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Micro-Raman investigation of vanadium-oxide coated tubular carbon nanofibers for gas-sensing applications

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ABSTRACT

Commercial tubular carbon nanofibers were uniformly coated with a 5 nm thick vanadium oxide layer via a modified approach to atomic layer deposition. The composition and microstructure of the resulting hybrid material was analyzed by micro-Raman spectroscopy. The effect of the post-synthesis thermal treatment in air at temperatures in the range of 25–375 °C was investigated in order to more deeply understand the behavior of the hybrid material in gas sensing devices. The obtained results demonstrate that the thermal treatment primarily affects the oxide coating-layer that is responsible for the sensing properties. The best sensor performance was obtained at the temperature at which the oxide layered-structure exhibits the highest structural order.

1. Introduction

Metal oxide (MO_x) coated carbon nanofibers/nanotubes (CNFs/CNTs) hybrids, a new class of materials with promising applications in many technological fields, were successfully utilized as active components in gas-sensing devices.

Atomic layer deposition (ALD) is a quite versatile technique that allows the controlled deposition of thin films on complex-shaped supports. Recently, a modified approach to ALD has been successfully applied to homogeneously coat CNTs/CNFs with nanometer thick films of metal oxide [1]. By using carboxylic acids as oxygen source instead of the more traditionally used ones (e.g. water, ozone, oxygen, etc.) it was shown that several metal oxides such as hafnia, titania or vanadia can be grown from the respective metal alkoxide precursors even at low temperatures. Recently, the coating of CNTs/CNFs with an inorganic layer of controlled thickness, based on the above procedure, has been reported [2]. It was shown that the hybrid sensing devices obtained by ALD of vanadium oxide (VO_x) exhibit interesting sensing properties toward NO_2, with improved performance with respect to uncoated CNT-/CNF-based sensors [2,3].

This work is an extension of the above-cited reports and is focused on a micro-Raman spectroscopic (MRS) study of VO_x-coated tubular CNFs. The occurrence of structural changes that are induced by post-synthesis thermal treatments in air at temperatures in the range between 25 and 375 °C was investigated. The aim of this work is to reveal the phase composition of the VO_x coating and further, to evaluate the influence of microstructural changes on the sensing properties of the hybrids. The obtained results are discussed in the light of the model that is currently adopted for the sensing mechanism of devices based on MO_x/CNTs hybrids [3–5].

2. Experimental

The coating of commercial (Applied Science PR-24-PS) tubular CNFs with a vanadium oxide layer was performed at 200 °C in an ALD reactor working in exposure mode. Vanadium *n*-propoxide and acetic acid were used as precursors. CNFs were pre-treated with concentrated HNO_3 at 100 °C for 2 h. Metal precursor and acetic acid vapors were generated in external reservoirs pre-heated at 80–90 °C and 40 °C, respectively. Pure nitrogen was utilized as carrier and purging gas (the residence and purging periods were 20 s and 15 s, respectively). Under these conditions, uniform oxide layers with the desired thickness were deposited onto the inner and outer surfaces of the tubular CNFs at a rate of ~0.04 nm/cycle. In the following, the case of an initially (after deposition) 5 nm thick vanadium oxide layer is considered.

Sensor devices were fabricated by mixing the as-deposited VO_x/CNFs with ethanol and depositing one drop of the resulting

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suspension onto 3 mm × 6 mm alumina substrates supplied with inter-digitated Pt electrodes and heating elements. Before testing, the sensors were treated in air at different temperatures (150–300 °C). The sensors were then introduced in a stainless-steel test chamber, designed to carry out measurements in a controlled atmosphere. The concentration of NO_2 in air was regulated by mass flow controllers. Electrical measurements were carried out in the temperature range from 50 to 250 °C, with steps of 50 °C, under a dry air total stream of 200 sccm. The sensors resistance data was collected in the four-point mode using an Agilent 34970A multimeter data acquisition unit. Further technical details concerning the coating process, sensing test and instrumentation can be found elsewhere [1–3].

The crystalline structure of pristine and VO_x-coated CNFs was investigated by MRS. Raman spectra were recorded in air at room temperature (RT) using an Ar^+ laser (Coherent Innova 70) operating at 2.41 eV (514.5 nm) and a microscope (Olympus B×40, ×50 objective) coupled to a double monochromator (Jobin Yvon Ramanor U-1000) and a photomultiplier (Hamamatsu R943-02) operating in photon-counting mode. Care has been taken to minimize heating of the sample by choosing a low laser-power (3 mW at the sample surface). In order to reliably describe the sample and to account for possible structural inhomogeneities, several different locations of each specimen were sampled. An acquisition time of 30 s was used in order to obtain a sufficient S/N ratio. Spectra recorded in the range of 100–3000 cm^{-1} were normalized and averaged. Lorentzian bands, superimposed to a constant background, were used to fit the spectra. The center frequency, width (FWHM) and intensity of the bands were chosen by a least-square best-fit method using a commercially available spectroscopic analysis software package. The relative intensities were calculated as integrated-intensity ratios.

3. Results

Fig. 1 displays the Raman spectra of pristine and VO_x-coated tubular CNFs. In the case of the pristine CNFs, only the G-band (1580 cm^{-1}), derived from the graphite-like in-plane optical mode, the D-band (1350 cm^{-1}), originating from lattice defects that break the basic graphene-layer symmetry (i.e. vacancies, pentagons, heptagons…) [6–8] and its overtone, the G′-band (2700 cm^{-1}), which is indicative for long-range graphitic order, are detected.

In the spectrum of the as prepared VO_x-coated CNFs, recorded after storage at ambient temperature, a lot of narrow spectral features are observed in the range between 100 and 1000 cm^{-1}. Some of them are partially superimposed to the laser tail. Their frequency-positions are reported in Table 1. No relevant changes are observed in the region of the Csp^2 vibration modes.

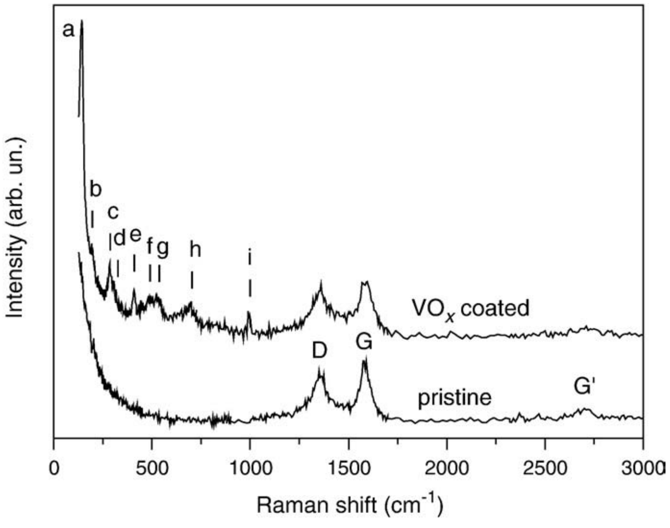

Fig. 1. As-measured Raman spectra of pristine and VO_x-coated CNFs.

Fig. 2 shows the effect induced by the thermal treatment of the VO_x/CNFs hybrids in air: the shape evolution of the Raman spectra reflects the structural modifications promoted by the heating process. The frequency-positions of the features arising from both VO_x (100−1000 cm^{-1}) and CNFs (above 1000 cm^{-1}) appear to be substantially insensitive to the thermal treatment. The D/G intensity ratio, providing a measure for the extent of lattice defects within the graphene layers [6–8], remains nearly constant since the heating temperature (T_H) is too low to heal the structural defects of the graphitic matrix. Instead, the intensities of the peaks in the region between 100 and 1000 cm^{-1} undergo evident changes with respect to the G-band of the CNFs.

Fig. 3 displays the dependence of the main descriptive parameters derived from the quantitative analysis of the Raman spectra on T_H. The sensing response to NO_2 of the device fabricated by the use of the VO_x/CNFs hybrid as active material [3] is also shown for comparison. It is defined as $S = [(R - R_0)/R_0 \cdot 100]$ (where R_0 and R are the values of the sensors electrical resistance measured in dry air, before and during exposure to gas, respectively). The relative intensities of the VO_x peaks at 284 cm^{-1}, 407 cm^{-1}, 693 cm^{-1} and 995 cm^{-1} (features *c*, *e*, *h* and *i* in Fig. 2) exhibit non-monotonic trends, roughly replicating the dependence of S on T_H [compare Fig. 3(a) and (c)]. The effect is by far more pronounced for the sharp feature at 142 cm^{-1} [Fig. 3(b)], whose relative intensity increases with T_H up to a value that is higher by more than a factor of 10, with respect to the one measured in the case of an untreated sample. This value is reached at the temperature at which the highest sensor response is obtained. The FWHM of this peak, instead, shows an opposite trend.

4. Discussion

4.1. Microstructure of the VO_x coating layer

In a previous work, electron energy loss spectroscopic (EELS) investigations were performed over the energy region of the V 2*p* and O 1s ionization edges in order to obtain information about oxidation state and elemental ratio of the VO_x coating [2,3]. The comparison of EELS spectra recorded from as-deposited VO_x films with those of various binary vanadium oxides revealed that the energy-positions and intensity ratios of the vanadium L_{III} and L_{II} edges, as well as the fine structure of the oxygen K edge closely resemble the one obtained for V_2O_4. Although the stoichiometry was found to correspond to V_2O_4, high-resolution transmission electron microscopy (HRTEM) and

Table 1
Assignation and center frequencies (in cm^{-1}) of the spectral features arising from vanadium oxide (*b* and *s* stand for bending- and stretching-vibration mode, respectively). The center frequencies measured in V_2O_5 single crystal, V_2O_5 thin film and V_2O_5 nanotubes are also reported for comparison.

Spectral feature	Vibrating group	VO_x/CNFs$^{(a)}$	V_2O_5 single crystal [12,13]	V_2O_5 thin film [9]	V_2O_5 nanotubes [10–12]
a	$(V_2O_2)_n$, *b*	142	146	145	138–143
b	$(V_2O_2)_n$, *b*	195	198	195	186–194
c	V O, *b*	284	285	282	278–286
d	V_3–O, *b*	304	305	303	303
e	V O, *b*	407	406	403	405
f	V–O–V, *b*	483	483	483	482–484
g	V_3–O, *s*	529	528	529	519
h	V_2–O, *s*	693	702	700	694
i	V O, *s*	995	996	992	992–999

(a) Present work.