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Electron energy-loss spectroscopy of V_2O_5 nanofibers synthesized by electro-spinning

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ABSTRACT

The dielectric properties of V_2O_5 nanofibers, synthesized by the electrospinning method, are studied by analyzing the low-loss region of the electron energy loss spectroscopy (EELS) in a transmission electron microscope. A comparison of experimental EELS spectra and *ab initio* density-functional theory calculations (WIEN2k code) within the Generalized Gradient Approximation (GGA) is presented, having found an excellent agreement between them. Although the experimental EELS has been acquired for the nanoparticles composing the fibers, and numerical calculations were carried out for bulk material, agreement between experimental and calculated results shows that no difference exists between the electronic structure in calculated bulk material and the nanoparticles. Furthermore, our results from EELS confirm that we accomplished the expected crystalline phase. The origins of interband transitions are identified in the electronic band structure by calculating the partial imaginary part of the dielectric function and the partial density of states.

1. Introduction

Vanadium oxides are of great interest in multiple applications, mainly because of the wide range of valency exhibited by V, which affects the physical and chemical properties of the oxides (Katzke et al., 2003; Schwingenschlögl and Eyert, 2004). Vanadium oxides can be used as catalysts (Gellings, 1985), e.g. for partial or selective oxidation reactions. Furthermore, transition-metal oxides, containing active sites able to adsorb gas molecules and catalyze reactions, are widely utilized as sensing elements in resistive gas sensors, especially those with d^0 (e.g. V_2O_5) electron configurations (Wang and Chen, 2010; Shimizu et al., 2009). On the other hand, in commercial sensor devices, high gas sensitivity frequently requires high operating temperatures, which actually constitutes a significant drawback in terms of power consumption, cost and thermal stability (Wei et al., 2004; Santangelo et al., 2010; Ban and Whittingham, 2008; Wee et al., 2010). Therefore, great efforts are presently addressed to the development of materials allowing better sensor performances. For these purposes, divanadium pentoxide (V_2O_5) has attracted great interest for its potential applications in numerous technological areas such as gas sensing, catalysis and electronics. V_2O_5 is an n-type semiconducting oxide whose electric conductivity increases when part of the V^{5+} species are reduced to V^{4+} because of the formation of oxygen vacancies. The sensing mechanism of most of the sensors for reducing gases exploits this property (Shimizu et al., 2009).

Nanotubes, nanowires, nanorods and nanobelts of V_2O_5 have been synthesized by different methods to maximize its surface area and to improve the sensing efficiency, such as sol–gel (Muster et al., 2000), reverse micelle (Pinna et al., 2003) and chemical vapor deposition (Wang et al., 2010). Recently, electro-spinning has been proposed as a novel technique for the low-cost preparation of one-dimensional transition-metal oxide based nanostructures (Viswanathamurthi et al., 2001; Guan et al., 2003; Kim et al., 2003; Faggio et al., 2011; Mai et al., 2010).

From a theoretical point of view, a number of first principles calculations have been carried out for V_2O_5, including electronic and mechanical properties (Reeswinkel et al., 2009; Brázdová et al., 2004; Hébert et al., 2002; Eyert and Höck, 1998).

On the other hand, electron energy-loss spectroscopy (EELS) has been widely used in the study of materials composition and electronic structure (Egerton, 1996; Ahn, 2004; Brockt and Lakner, 2000). The interactions of fast electrons with the specimen result in electrons being excited into unoccupied energy levels within the conduction band, as well as collective excitation of valence electrons. In the high-loss region, analysis of the first 10 eV of the spectra after the ionization edge (ELNES) can give information about the oxidation state, absolute energy position, and local symmetry via d level splittings in transition metal elements and orbital hybridization. The low-loss region can provide information

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about composition and electronic structure, and also the optical properties, although it has not been as widely applied as ELNES. This is due to the well-known fact that low-losses are caused by all possible transitions between the valence band and the conduction band. The valence band is made up of dispersed levels as opposed to almost flat core levels, and the interpretation of EELS is a priori more difficult.

From the dielectric theory, it is possible to relate the experimental single scattering distribution $S(E)$, to the energy-loss function $\mathrm{Im}(-1/\varepsilon)$ (Egerton, 1996), by:

$$S(E) = \frac{I_0 t}{\pi a_0 m_0 v^2}\, Im\left[-\frac{1}{\varepsilon(q,E)}\right] \ln\left[1+\left(\frac{\beta}{\theta_E}\right)^2\right] \tag{1}$$

where $\varepsilon(q,E) = \varepsilon_1 + i\varepsilon_2$ is the complex dielectric function at energy-loss E and momentum transfer q, a_0 the Bohr radius, m_0 the electron rest mass, v the electron beam velocity, θ the scattering angle and $\theta_E = E/(\gamma m_0 v^2)$ is the characteristic scattering angle, γ is the relativistic factor, I_0 is the zero-loss intensity, t the specimen thickness, and β is the collection semi-angle. The real and imaginary parts of the dielectric function can be obtained from the energy-loss function through Kramers–Kronig analysis.

In this work, we studied the electronic structure of V_2O_5 nanofibers with both EELS, in the transmission electron microscope, and *ab initio* calculations with the FLAPW method, as implemented in WIEN2K code (Blaha et al., 1990, 2001). The aim is to determine the dielectric properties of V_2O_5 nanofibers, via valence electron energy-loss spectroscopy (VEELS) and to compare with *ab initio* calculations. Even though there are many articles studying the high energy-loss EELS of V_2O_5 (Pinna et al., 2003; Su et al., 2001; Ding et al., 2008; Grogger et al., 2008; Mitterbauer et al., 2003) in the literature, we were not able to find any references addressing low energy-loss EELS. Our focus rests on the electronic structure of V_2O_5 nanoparticles composing the fibers.

2. Experimental

The synthesis of the V_2O_5 nanofibers was carried out by the electro-spinning method. A detailed description of the procedure can be found in the literature (Faggio et al., 2011; Li and Xia, 2004; Chronakis, 2005). In this work, the precursor solution was composed of poly(vinylpyrrolidone) (PVP), with molecular weight M_W 1,300,000, and vanadyl sulfate ($VOSO_4$), dissolved in ethanol. The solution was heated at 60 °C with vigorous stirring for 4 h and then delivered into a metallic needle at a constant flow rate of 0.3 mL/h by a syringe pump. The metallic needle was connected to a high-voltage power supply and a grounded aluminum foil was placed 15 cm from the needle tip. With an applied high-voltage of 15 kV, the precursor solution jet was accelerated toward the aluminum foil, leading to the formation of $VOSO_4$/PVP fiber composite, together with a rapid evaporation of the ethanol. The composite nanofibers were then annealed at 600 °C for 1 h, with a slope of 3 °C/min to obtain V_2O_5 nanofibers.

The thermal stability of as-spun and calcined PVP-$VOSO_4$ fibers was analyzed by thermogravimetry–differential scanning calorimetry (TG–DSC) using a TA Instruments Q600 thermal analyzer at a heating rate of 3 °C/min under inert atmosphere with 50 cm^3/min of argon flux.

X-ray diffraction (XRD) measurements were performed in a Panalytical diffractometer with Cu Kα radiation(1.54060). For XRD measurements, the nanofibers were separated from the aluminum foil and then slightly pressed on a glass slide to form a dense film.

Field-emision scanning electron microscopy (FESEM) images were acquired with a JEOL JSM-7401F at an accelerating voltage of 10 kV. High-resolution transmission electron microscopy (HRTEM) images were recorded by using a JEOL JEM-2200FS microscope.

Electron energy-loss spectra were obtained using a Gatan parallel electron energy-loss spectrometer (PEELS model 766) attached to a transmission electron microscope (TEM) Philips CM200. Spectra were acquired in diffraction mode with 0.2 eV/channel dispersion, an aperture of 2 mm, and a collection semi-angle of about 4 mrad. The resolution of the spectra was determined by measuring the full-width at half-maximum (FWHM) of the zero-loss peak, and this was typically close to 1.0 eV, when the TEM was operated at 120 kV. EELS spectra were corrected for dark current and readout noise. The channel to channel gain variation was minimized by normalizing the experimental spectrum with independently obtained gain spectrum from the spectrometer. Next, spectra were Fourier-log deconvoluted to have the single scattering distributions $S(E)$, by using the program FLOG (Egerton, 1996). The real and imaginary parts of the dielectric function can be obtained from the energy-loss function $\mathrm{Im}(-1/\varepsilon)$ (Eq. (1)) through the Kramers–Kronig analysis. Theoretically, by measuring the absolute cross section and the thickness of the sample, we can obtain the value of the energy-loss function. However, this approach is usually not practically feasible. In order to obtain the absolute value of the energy-loss function for semiconductor materials, the refractive index at one point is needed to normalize the energy-loss spectra. We have used the value of 2.28, taken from the literature (Kaid, 2006) and then the program KRAKRO (Egerton, 1996) to obtain the dielectric function.

3. Calculation details

Self-consistent band structure calculations were performed using density-functional theory (DFT) with the full-potential linearized augmented plane-wave (FLAPW) method, using the WIEN2k code (Blaha et al., 2001). Exchange and correlation were treated using the generalized gradient approximation (GGA) for the potential. The core states were treated in a fully relativistic fashion. The wave functions within the muffin-tin spheres were expanded in spherical harmonics with an angular momentum up to $l = 10$. Additional local orbital extensions were used to avoid linearization errors. Nonspherical contributions to the charge density and the potential within the muffin-tin spheres were considered up to $l_{\max} = 4$. In the interstitial region, plane waves with reciprocal lattice vectors up to $G = 10$ were included, and the plane-wave cut-off (RMTKmax) was set to 7. Self-consistency was considered to be achieved when the total energy variation from iteration to iteration did not exceed 10^{-6} Ry, on a mesh containing 396 k-points in the irreducible Brillouin zone (IBZ).

The dielectric function can be obtained from the Optic Program of the WIEN2k code (Ambrosch-Draxl and Soto, 2006), allowing for comparison with experiment:

$$\varepsilon_{2ii}(\omega) = \frac{4\pi^2 e^2}{m^2\omega^2 V}\sum_{v,c,k} |\langle \psi_k^v \left| p_i \right| \psi_k^c \rangle|^2 \times \delta(E_{\psi_k^c} - E_{\psi_k^v} - \hbar\omega) \tag{2}$$

Matrix elements are calculated from the electron states and integration over the irreducible Brillouin zone is performed to calculate the imaginary part of the dielectric function. Then a Kramers–Kronig analysis is performed to obtain the real part of the dielectric function ε_1, and finally, the energy-loss function $\mathrm{Im}(-1/\varepsilon)$.

The crystal structure of V_2O_5 has been widely studied experimentally. The structure belongs to the space group Pmmn. The lattice constants are $a = 11.5219$, $b = 3.5667$, $c = 4.3751$ Å, taken from the experimental results (Haas et al., 2003). The atomic positions are: V at (0.1010, 0.250, 0.8967) and three non-equivalent oxygen atoms at (0.1077, 0.250, 0.5333), (0.9297, 0.250, 0.5333) and (0.250, 0.250, 0.9920). The optical properties were calculated on a mesh containing 1920 k-points in the irreducible part of the Brillouin zone, as many points are needed for optical calculations.