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Structural evolution in crystalline MoO_3 nanoparticles with tunable size

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This paper is dedicated to Professor Yoshitaka Gushikem on the occasion of his 70th anniversary.

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ABSTRACT

In this study MoO_3 nanoparticles were prepared in porous Vycor glass by impregnation–decomposition cycles (IDC) with molybdenum(VI) 2-ethylhexanoate. X-ray diffraction data show that the nanoparticles are crystalline and are in the orthorhombic α-MoO_3 phase. Raman spectroscopy data also indicate the formation of this phase. The profiles in the Raman spectra changed with the number of IDC, indicating a structural evolution of the MoO_3 nanoparticles. The IDC methodology promoted a linear mass increase and allowed tuning the nanoparticle size. Analysis of HRTEM images revealed that for 3, 5 and 7 IDC, the MoO_3 nanoparticle average diameters are 3.2, 3.6 and 4.2 nm. Diffuse reflectance spectroscopy indicates a consistent red shift in the band gap from 3.35 to 3.29 eV as the size increases from 3.2 to 4.2 nm. This observed red shift in the band gap of the MoO_3 nanoparticles is presumably due to quantum confinement effects.

1. Introduction

Recently, the development of new materials has been the goal in both basic and technological research due to their potential application in new devices. Among these materials, there is great interest in the synthesis of semiconductor oxides, such as TiO_2 [1–3], CeO_2 [4], MoO_3 [5,6], and WO_3 [7,8]. These materials are used in many processes, such as catalysis [1,2], gas and humidity sensing [3,4], and photochromic devices [6,8]. In this context, there is interest in the synthesis of materials in the approximate size range of 1–100 nm. These nanomaterials exhibit unique physical and chemical properties that differ from those of the respective bulk materials. When many materials are reduced to nanoscale, novel phenomena can be present. One these effects is related to quantum confinement, which appears due to the fact that the sizes of the particles are on the nanoscale [9,10]. Quantum confinement effects can be observed as an increase in the energy gap and/or shifts in the lattice phonons when the particle size decreases. This effect has been well studied in TiO_2 and CeO_2 nanostructures [9–12]. However, there are few reports on this effect in molybdenum trioxide (MoO_3) nanostructures.

MoO_3 is a large band gap semiconductor (2.90 eV) and, when crystallized, forms hexagonal or rectangular plates, depending on synthesis conditions [13]. Thermodynamically, the stability of the phases follows: amorphous $MoO_3 <$ monoclinic MoO_3 (β, hexagonal) $<$ orthorhombic MoO_3 (α, rectangular) [14]. This oxide is normally found in the orthorhombic phase, which is the main goal of much research due to its many applications [15–19]. This phase can be described as a layered structure formed by covalent double layers of MoO_6 octahedrals [14]. Beyond nanoparticle synthesis [15,16], various other MoO_3 morphologies have been obtained, such as, nanoribbons, nanorods, and nanofibers. The aim of many projects is to control the shape and size of these materials, in order to tune their properties [17–19]. MoO_3 on the nanoscale can exhibit the quantum confinement effect that can lead to changes in optical properties [20–22]. Dhanasankar et al. [21] reported the synthesis of MoO_3 thin films, using different temperatures, in the orthorhombic phase with the size distribution of grains equal to 30 nm. The authors observed a band gap value at 3.65 eV, indicating the quantum confinement effect with size dependence. Bouzidi et al. [22] also observed the quantum confinement effect in MoO_3 thin films. These authors showed different band gap values for monoclinic MoO_3 (3.14 eV) and for orthorhombic MoO_3 (3.34 eV). Despite these reports there is a lack in theoretical information about how these structures and sizes directly affect physical and chemical properties.

Several synthetic methods have been employed in the preparation of nanomaterials, such as hydrothermal synthesis, chemical vapor deposition (CVD), and others [17–19]. These techniques have some limits including, for example, the complexity of the various steps involved and low yields from the synthetic process. For these reasons, the development of

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simple and efficient methods to prepare nanostructures is of practical interest.

The synthesis of oxide semiconductor nanoparticles using metallo-organic decomposition (MOD) has been explored as an efficient methodology for this purpose [23–25]. This method consists in the thermal decomposition of a metallo-organic compound, leading to the formation of the inorganic solid of interest [26,27]. From the experimental point of view, MOD does not require an inert atmosphere or vacuum. Another advantage is the absence of sophisticated apparatus when compared with CVD. Cangussu et al. [25] reported the nanoparticle synthesis of γ-Fe_2O_3 supported in porous Vycor glass (PVG) by MOD. The authors described that using PVG as porous support and the MOD method allowed obtaining nanoparticles with controlled sizes. Corrêa et al. [28] also reported the use of MOD in the synthesis of TiO_2 and CeO_2 core-shell nanoparticles, supported in PVG, with different sizes and shell thicknesses. This was possible since the thermal decomposition of the metallo-organic compound happened inside the PVG pores, obtaining the oxide nanoparticles in situ [28].

In this work, MoO_3 nanoparticles with size control have been synthesized in PVG by metallo-organic decomposition. Cycles of impregnation–decomposition of molybdenum(VI) 2-ethylhexanoate in PVG plates were employed. The material prepared was analyzed by X-ray diffraction using synchrotron radiation (XRD), Raman spectroscopy and high resolution transmission electron microscopy (HRTEM). The quantum confinement effect was analyzed by ultraviolet–visible spectroscopy in the diffuse reflectance mode (DRS).

2. Experimental

Molybdenum(VI) 2-ethylhexanoate, $Mo[OOCCH(C_2H_5)C_4H_9]_6$, denominated $Mo(Hex)_6$, was purchased from Strem Chemicals. This metallo-organic compound was used as source of MoO_3 without further purification.

In the nanoparticle synthesis porous Vycor® glass 7030 (PVG) was used as substrate, cut into plates of $0.8 \times 0.8 \times 0.1\ cm^3$. MoO_3 nanoparticles were synthesized by means of impregnation of the PVG plates with $Mo(Hex)_6$ ($0.05\ mol/dm^3$) in hexane. After impregnation, the PVG plates were submitted to thermal treatment for 8 h under static air at 550 °C. This procedure was named one impregnation–decomposition cycle (IDC). The solids obtained are PVG/$x$$MoO_3$, where x corresponds to the number of IDC (x=3, 5 or 7). All the samples, independent of the number of IDC, were submitted to the same total thermal treatment time.

High-intensity synchrotron X-ray powder diffraction (XRD) data were collected at the D10B-XPD beamline of the LNLS (Brazilian Synchrotron Light Laboratory), placed after a dipolar source. X-rays of λ=1.24 Å wavelength were selected by a double-bounce Si (1 1 1) monochromator. The diffracted beam was analyzed with pyrolytic graphite HOPG (0 0 2) and detected with a Na(Tl)I scintillation counter with a pulse-height discriminator in the counting chain. The nanoparticles were characterized by Raman spectroscopy in a Renishaw Raman Microprobe Imaging System 3000 coupled to an optical microscope with spatial resolution of 1.5 μm and spectral resolution of $2\ cm^{-1}$. The He–Ne laser (λ=632.8 nm) power was estimated to be 8 mW. The laser light was focused onto the sample using a 50 × objective lens (Olympus). Diffuse reflection (DRS) UV/Vis spectra were recorded on a Cary 5G UV–Vis spectrophotometer. The PVG/$x$$MoO_3$ plates were ground, and the powdered samples were smoothly compacted into a quartz sample holder which was mounted in an integrating sphere spectral collector. The data were collected between 800 and 200 nm with a 2 nm spectral bandwidth. $BaSO_4$ powder was used as standard for instrumental background correction. The HRTEM images were obtained using a JEOL JEM-3010 microscope (300 kV, 1.7 Å point resolution) at the LNLS. The samples were prepared by suspending the powders in isopropanol and placing a drop of the solution on a holey carbon coated Cu grid.

3. Results and discussion

Successive impregnation–decomposition cycles with the MoO_3 metallo-organic precursor resulted in a mass increase (Fig. 1), which was estimated from differences in PVG plate weights before and after each IDC. The linear cumulative mass gain (CMG) observed was about 3% for ten IDC. Mazali et al. [23] reported that the linear CMG with the number of IDC is associated with growth in crystallite size. In that paper the authors prepared particules with different size distributions as functions of the number of IDC for the system PVG/TiO_2. In the present work, the particle size distribution was obtained by counting particle diameters in several HRTEM images (supplementary data). We observed an increase in the size distribution (Fig. 2 (d)) with the number of IDC for the system PVG/xMoO_3 (3 IDC=3.2 nm with 1.0–5.5 nm variation, 5 IDC=3.6 nm with 2.3–6.0 nm variation, and 7 IDC=4.2 nm with 2.3–10 nm variation), corroborating results already published for the other systems [23,24].

All the samples of the system PVG/xMoO_3 are formed of nanoparticles with sphere-like shapes. The particles grow in a dispersed way in the PVG pores, indicating that the porous structure prevents growth by coalescence (Fig. 2). These results showed that the IDC methodology associated with the metallo-organic decomposition process allows particle size control. This phenomenon occurs because the growth of the MoO_3 nanoparticles happens through layer-by-layer deposition in each IDC.

Fig. 3 shows the XRD pattern for the sample PVG/5MoO_3 used as representative of the system PVG/$x$$MoO_3$. The difference in the peak positions in the XRD pattern, compared to bulk MoO_3 XRD, is related to the wavelength used (1.24 Å from synchrotron radiation source). The peaks indicated, with their respective lattice plane, are attributed to the α-MoO_3 orthorhombic phase (JCPDF2 file 050508). This phase is a typical metastable MoO_3 polymorph, commonly formed at temperatures above 400 °C [29–31]. The broad peak between 10° and 30° 2θ is related to the PVG structure. It is difficult to identify other MoO_3 phases based on the XRD pattern. The broad peak related to the PVG structure

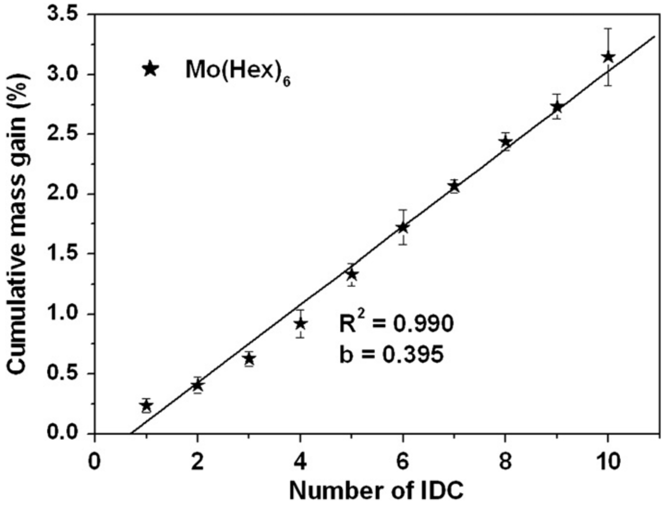

Fig. 1. Cumulative mass gain of MoO_3 after each IDC.