Free-standing SnO_2 nanoparticles synthesized by hydrothermal route

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ABSTRACT

In this contribution we present the obtaining of SnO_2 nanoparticles with average diameters of 5 nm by hydrothermal route from $SnCl_2$ and temperature of 150 C.
The nanostructures were studied by UV-visible electronic absorption and Raman spectroscopy [1], their crystal structure were determined from XRD patterns and by HRTEM images.
XRD showed the presence of single phase of cassiterite structure, as found from XRD line broadening the crystallite sizes of all powders were in the nanometric range.

Keywords: tin oxide, nanoparticles, semiconductors, chemical preparation

1 INTRODUCTION

SnO_2 with a rutile type crystalline structure is an n-type wide band gap (3.5 eV) semiconductor that presents a proper combination of chemical, electronic and optical properties that make it advantageous in several applications. Due to its physical properties, such as transparency and semiconductivity, it is an oxide of great interest from the technological point of view for gas sensors, white pigments for conducting coatings for furnaces and electrodes, ultraviolet optical fibers, dye based solar cells, optoelectronic devices, and catalysts, an increasing interest in the use of anodes of SnO_2 in lithium batteries has been recently noticed [1-4]
One area of primary importance is the field of solid state gas sensors for environmental monitoring, where SnO_2 has been established as the predominant sensing materials.
Tin oxide (SnO_2) has been the material of choice for semiconductor gas sensors, which detect reducing gases in air from a change in electrical resistance. According to research on the sensing mechanism, a reduction in grain size leads to an increase in sensitivity.
The microstructure of SnO_2 could be controlled by temperatures treatment, doping and method of preparation.
Many methods had been developed to synthesize SnO_2 nanoparticles such as homogeneous precipitation, sonochemical, hydrothermal, microemulsion, sol-gel, and polymeric precursor [4-10] methods among others. Even though the development of agglomerates is to be avoieded, their growing is somehow inevitable due to the small diameter of the oxide particles and to the presence of the compounds involved in the mentioned procedures, mainly solvents.
In the present study, had been synthesized free-standing SnO_2 nanoparticles by hydrothermal route using $SnCl_2$ like precursor.

2 EXPERIMENTAL

2.1 Materials

Tin chloride, $SnCl_2.2H_2O$ (98% Aldrich) and Ammonium hydroxide NH_4OH (98% Aldrich) were purchased and used as received, without further purification. Ultra pure water (18 $M\Omega cm^{-1}$) was obtained from a Barnstead E-pure deionization system.

2.2 Preparation of nano-SnO_2

An aqueous solution of 0.163 M $SnCl_2.2H_2O$ was prepared by mixing 2.03g of tin chloride with 30 ml of distilled water, NH_4Cl was added with stirring, a white precipitate was immediately formed, which was then separated from the aqueous solution. To remove the ammonium and chloride ions, the precipitate was washed 4 times with distilled water. The obtained precipitate was dried at room temperature, the dried powder was fired at 150ºC for 2 h in air to finally obtain a pale yellow powder of tin dioxide nanoparticles..
The chemical reaction proceeds according to:

$$SnCl_2.2H_2O + NH_4OH \rightarrow Sn(OH)_2 + 2NH_4^+ + 2Cl^-$$

$$Sn(OH)_2 \xrightarrow[2h]{150^\circ} SnO_2 + H_2$$

3 CHARACTERIZATION

The UV-visible electronic absorption spectra of the powdered samples were obtained by diffuse reflectance technique, with an Ocean Optics HR4000 miniature fiber optic spectrometer. The Raman spectra, from 100 to 900 cm^{-1}, were evaluated using a Nicolet Almega XR Dispersive Raman Spectrometer and detected by a CCD camera, at 25 seconds and a resolution of ~4 cm^{-1}. The excitation beam was a Nd:YVO_4 532 nm laser and the incident power on the sample was ~3 mW. The X-ray

diffraction patterns were performed at room temperature with Cu Kα radiation (λ = 1.5406Å) in a D5000 Siemens diffractometer; diffraction intensity was measured between 2.5° and 70°, with 2θ step of 0.02° for 0.8 s per point. High-resolution transmission electron microphotographs (HR-TEM) were obtained in a JEOL 2010 FasTEM analytical microscope, operating at 200 kV, by deposition of a drop of the powdered transition metal oxide dispersed in N,N'-dimethylformamide (DMF) onto 300 mesh Cu grids coated with a carbon layer.

4 RESULTS AND DISCUSSION

The powders were analysed by X-ray powder diffraction. XRD pattern (Fig.1) reveals the formation of a single nanocrystallyne product, which was identified as cassiterite, all diffractions peaks can be perfectly indexed to the rutile type structure (JCPDS card 21-1250), with a unit cell described by the space group P42/mnm and lattice parameters a = 4.738 and c = 3.188 Å.
These results are consistent with those of the bulk. In order to determine the average crystallite size, a peak broadening method was applied using the classical equation over all reflections, finding out to be of 5.74 nm

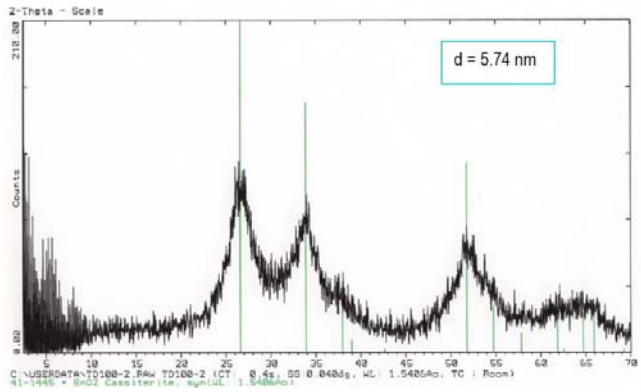

Figure 1 XRD pattern of SnO_2 nanoparticles. All peaks can be indexed to SnO_2 cassiterite, card 21-1250

The optical response of SnO_2 Nps was evaluated by UV-Visible electronic absorption spectra, obtained by DRS. As shown in figure 2, the spectra exhibits one broad absorption band, centered at 630 nm for the SnO_2 Nps.

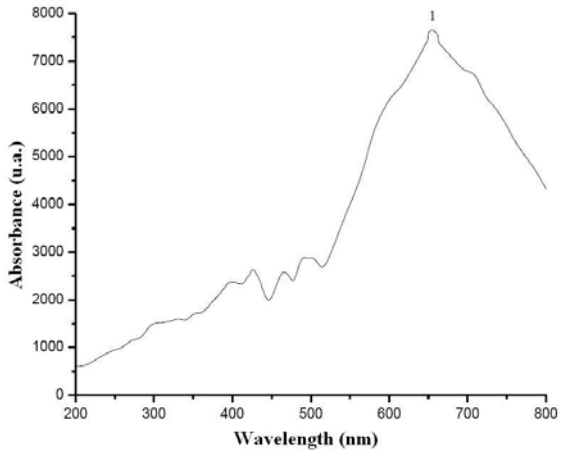

Figure 2. UV-visible spectra of SnO_2 Nps

Moreover, since the Raman spectroscopy is a nondestructive technique which in the last years has been extensively used in nanostructure characterization, we obtained the corresponding SnO_2 Nps Raman spectra, as shown in figure 3. These spectra clearly exhibit five well-defined peaks at 230, 472, 630, and 773 cm^{-1}, assigned to the Raman-active modes of the SnO_2 with B_{2g}, E_g and A_{1g} symmetries, respectively. In the SnO_2 Nps Raman spectrum, the peaks appear broadened and additionally a little red shift is observed. This behavior has been observed by other authors, and related to size effect.

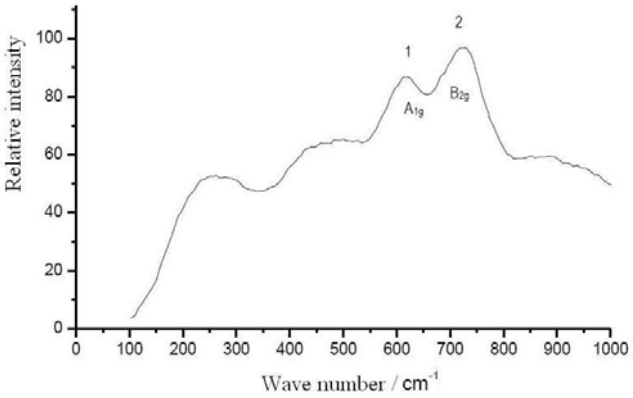

Fig 3 Raman spectra SnO_2 Nps

The HR-TEM micrographs corroborate the formation of small nanocrystals with dimensions close to those determined by X-ray diffraction patterns (figure 4). These nanocrystals have dimensions of 4.7 nm X 4.3 nm (the smallest one) and 6.2 nm X 5 nm (the largest one). While figure 5 shows a nanocrystal with dimensions of 5.4 nm X 4.7 nm;

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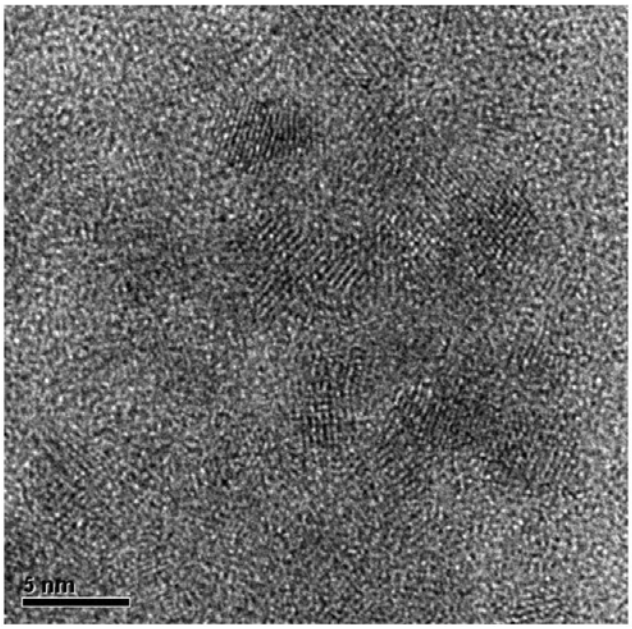

Figure 4 HR-TEM micrograph of SnO_2 Nps

The interplanar distances determined from their corresponding electron diffraction patterns confirm that the nanocrystals are composed of SnO_2. (Fig.5 and Fig.6)

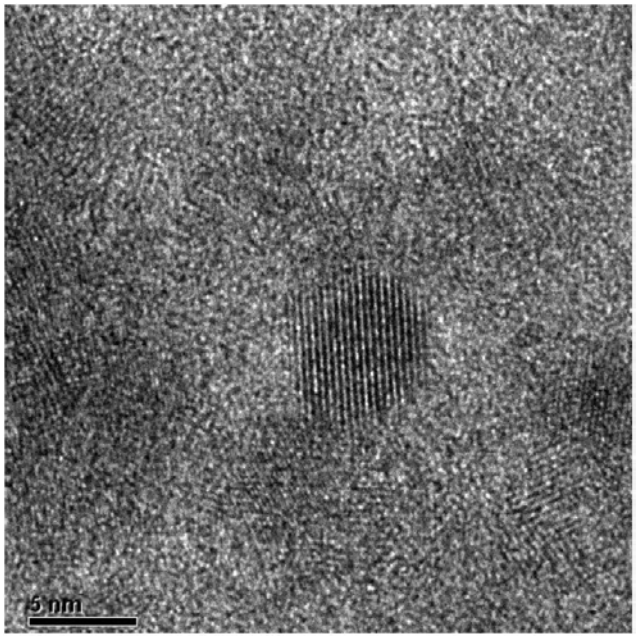

Figure 5. HR-TEM Micrograph of SnO_2 Nps

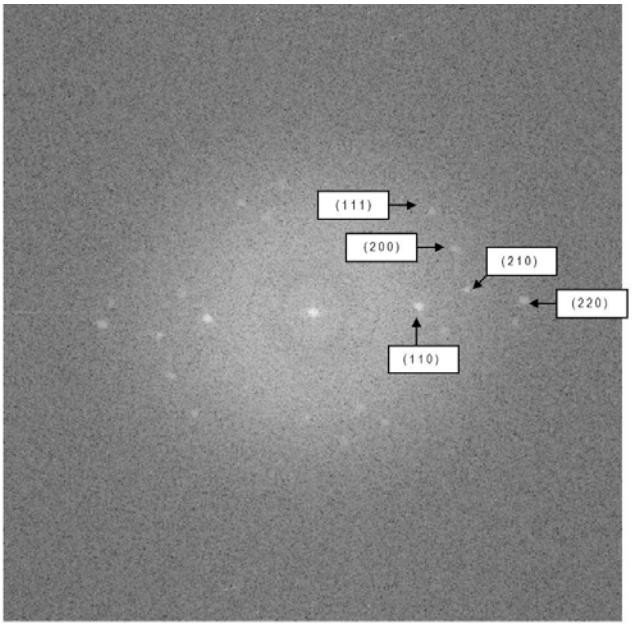

Figure 6. Electron diffraction pattern of SnO_2 Nps

5 CONCLUSION

Free-standing single nanocrystalline SnO_2 have been synthesized by the coprecipitation method and posterior thermal treatment, at temperature of 150°C, from the tin chloride and ammonium hidroxide. The average crystal size of the nanoparticles varies from 4.7 to 5.3 nm. The approach described in this study can be readily scaled up to fabricate large quantities of these nanocrystals.

Acknowledgments

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