SnO_2 POWDERS PREPARED BY WET CHEMISTRY METHODS

Andrei-Dan BUSUIOC[1], Teodor VIŞAN[2]

SnO_2 powders were synthesized by three different wet chemistry methods: precipitation, sol-gel and Pechini, each of these leading to zero dimensional structures, suitable for the development of nanoscale devices. $SnCl_2 \cdot 2H_2O$ was employed as tin precursor, the preparation procedures being conducted in basic or acidic medium. The resulting materials were characterized in terms of composition, structure and morphology with the help of the thermal analysis, X-ray diffraction, scanning electron microscopy and laser granulometry. The final features of the oxide powders were correlated with the processing parameters.

Keywords: tin oxide, precipitation, sol-gel, Pechini, gas sensors

1. Introduction

Based on the ability of changing its electrical conductivity in a measureable and quantifiable way upon exposure to a gaseous specie, a chemical gas sensor is a device which mimics the olfactory discrimination mechanism [1]. Therefore, it is employed in a wide range of industries, on one hand for safety reasons and on the other hand for environmental monitoring, ultimately ensuring the human welfare.

Considering the field of equipments which signal, evaluate and monitor the presence of certain gases, the oxide based sensors play an important role both for the research and fabrication concerns due to their notorious chemical resistance and high operating temperatures [1]. The response of the corresponding devices strongly depends on the composition, crystal structure, size, shape and surface of the active material [2]. In the case of metal oxide sensors, the conductivity is determined by the concentration of carrier electrons, which is subsequently controlled by the surface adsorption sites; the activation energy is correlated with Fermi energy changes [3]. In this context, the shift to low dimensional structures achieved through wet chemistry methods [4-7] offers a solution for tuning the physical and chemical properties. Moreover, this group of

[1] PhD Student, Dept. of Inorganic Chemistry, Physical Chemistry and Electrochemistry, University POLITEHNICA of Bucharest, Romania, e-mail: busu1569@gmail.com
[2] Prof., Dept. of Inorganic Chemistry, Physical Chemistry and Electrochemistry, University POLITEHNICA of Bucharest, Romania, e-mail: t_visan@chim.upb.ro

techniques provides a good control in terms of stoichiometry, purity, homogeneity and morphology, while significantly reducing the processing temperature [8, 9].

In this context, tin oxide (SnO_2) represents an appropriate choice for developing oxide based sensors for selective gas detection, since the material is a well-known *n*-type semiconductor with a wide direct band gap (3.6 eV) [2] and the derived devices are simple to implement and low cost, offering good stability and sensitivity [10]. As well, besides its gas sensing capability [11], SnO_2 is a promising candidate for photocatalysts [12], dye-sensitized solar cells [13], lithium-ion batteries [14], as well as spintronic devices [15].

The aim of the current paper was to synthesize SnO_2 powders by different wet chemistry methods, starting from the same inorganic precursor and focusing on the implication of the processing complexity and calcination temperature on the properties of the resulting zero dimensional oxide structures.

2. Experimental

Precipitation, sol-gel and Pechini techniques were approached for the preparation of SnO_2 powders, all of them employing tin chloride dihydrate ($SnCl_2 \cdot 2H_2O$, Sigma-Aldrich, $\geq$ 98 %) as source of tin cations.

In the first case, the precipitation procedure was conducted in basic conditions, provided by an excess 25 % ammonia solution (3 mL), which led to the precipitation of Sn^{2+} ions from the solution obtained by dissolving the necessary amount of $SnCl_2 \cdot 2H_2O$ (7.49 g) in a minimum volume of distilled water (5 mL). Thus, a white precipitate was formed, namely $Sn(OH)_n$, where n = 2 or 4, the resulting suspension being further filtered and the collected solid being intensively washed with distilled water in order to remove the residual Cl^- ions. Then, the precipitate was dried at 100 °C for 12 h, followed by calcination at 400 °C for 2 h in order to achieve a crystalline oxide phase.

For the sol-gel method, the same initial steps as in the previous case were applied, but the white precipitate consisting of tin hydroxides was dissolved in glacial acetic acid (10 mL) and then ethylene glycol (corresponding to a molar ration between acetic acid and ethylene glycol of 2:1) was added to the solution in order to ensure the formation of tin complexes. Even though the stirring and heating at 100 °C were continued for 12 h, until the acetic acid was completely removed, the solution formed a viscous gel only when a small amount of citric acid (0.1 g) was added, which probably favoured the polycondensation reaction. The resulting gel was aged for 24 h, dried in similar conditions as mentioned earlier and subsequently calcined at 500 °C for 2 h for eliminating the organic part and determining the oxide nucleation and growth.

Finally, the Pechini method was carried out starting from a solution of $SnCl_2 \cdot 2H_2O$ (7.49 g) in ethylene glycol (10 mL), in which a quantity of citric acid

was added, corresponding to a molar ration between $SnCl_2 \cdot 2H_2O$ and citric acid of 1:1. A resin type precursor was obtained by estherification at 140 °C for 6 h, which was further burned at 800 °C for 2 h in order to remove the polymeric matrix and promote the formation of SnO_2 crystalline network.

The as-obtained precipitate, dried gel and resin type precursor were subjected to thermal analysis in air, in the 20 - 1000 °C temperature range, this being performed on a Shimadzu DTG-60 equipment. The phase composition and crystal structure of the powders obtained after calcination were investigated by means of X-ray diffraction (XRD), with a Shimadzu XRD 6000 diffractometer with Ni filtered Cu Kα radiation (λ = 1.5406 Å), 2θ ranging between 20 and 80 °. A Malvern Mastersizer 2000 laser diffraction particle size analyzer was used to evaluate the particle size distribution in liquid suspension, while a FEI Quanta Inspect F scanning electron microscope (SEM) was employed to visualize the morphology of all samples.

3. Results and discussion

The thermal analyses performed on the intermediate materials obtained for the three approached wet chemistry methods are displayed in Fig. 1. The weight loss curves give information about the gravimetric modifications occurred during heating with a constant rate up to 1000 °C. For the precipitation method, the corresponding curve indicates two weight loss steps (with maxima at 187 and 320 °C), but also a significant weight gain step (centred at 266 °C); if the first two can be attributed to the decomposition of different hydrated species emerged in the precipitation process, with water vapour elimination, the third one is related to the oxidation of Sn^{2+} to Sn^{4+}, with oxygen incorporation in the crystalline network. Going to the sol-gel technique, the dried gel suffers a major weight loss process up to 318 °C, followed by a minor one, which ends at 500 °C; both decreases can be assigned to the organic part removal, with the crystalline structure formation. Finally, the Pechini method generates a precursor that displays a continuous multi step weight loss in the 30 - 800 °C temperature range, in correlation with the burning of the resin type precursor and other unreacted excess compounds. Thus, based on the thermal analyses, the calcination temperatures were established, so that the calcined material to contain only crystalline oxide phase. The specific values are as follows: 400 °C for the precipitation method, 500 °C for the sol-gel method and 800 °C for the Pechini method, temperatures over which there are no significant mass losses.

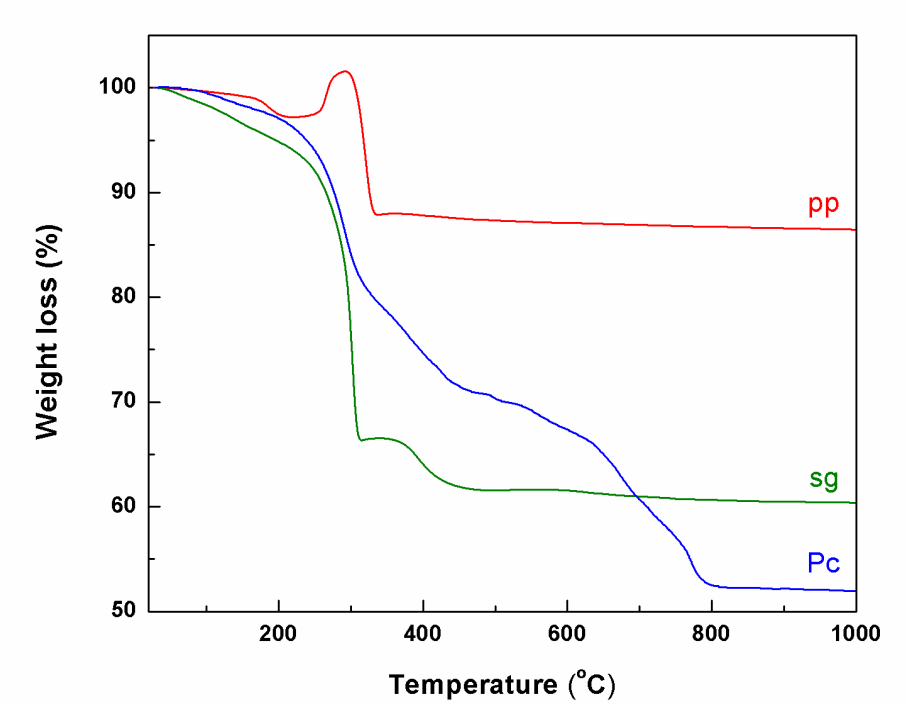

Fig. 1. Weight loss curves for the as-obtained precipitate (pp - precipitation), dried gel (sg - sol-gel) and resin type precursor (Pc - Pechini).

Fig. 2 shows the XRD patterns of the calcined powders synthesized by the three wet chemistry methods. All diffraction peaks are typical of SnO_2 phase with tetragonal symmetry (JCPDS 01-080-6727), except the powder prepared by the Pechini technique, for which a small amount of secondary phase is present alongside the desired oxide phase. Otherwise, the intense and narrow diffraction peaks indicate a high crystallinity for all three cases. Further, the average crystallite size was estimated by using Scherrer equation: $D=K\cdot\lambda/(\beta\cdot\cos\theta)$, where K is a dimensionless shape factor with a typical value of about 0.9, λ is the X-ray wavelength (0.154 nm), β is the full width at half maximum value and θ is Bragg angle. A mediation on the values achieved by employing the first three most intense diffraction peaks ((110), (101) and (211)) was made. The calculated values are as follows: 53 nm for the precipitation method, 56 nm for the sol-gel method and 93 nm for the Pechini method, respectively. As expected, the increase of the calcination temperature led to larger crystallites even if the synthesis procedures showed different peculiarities.

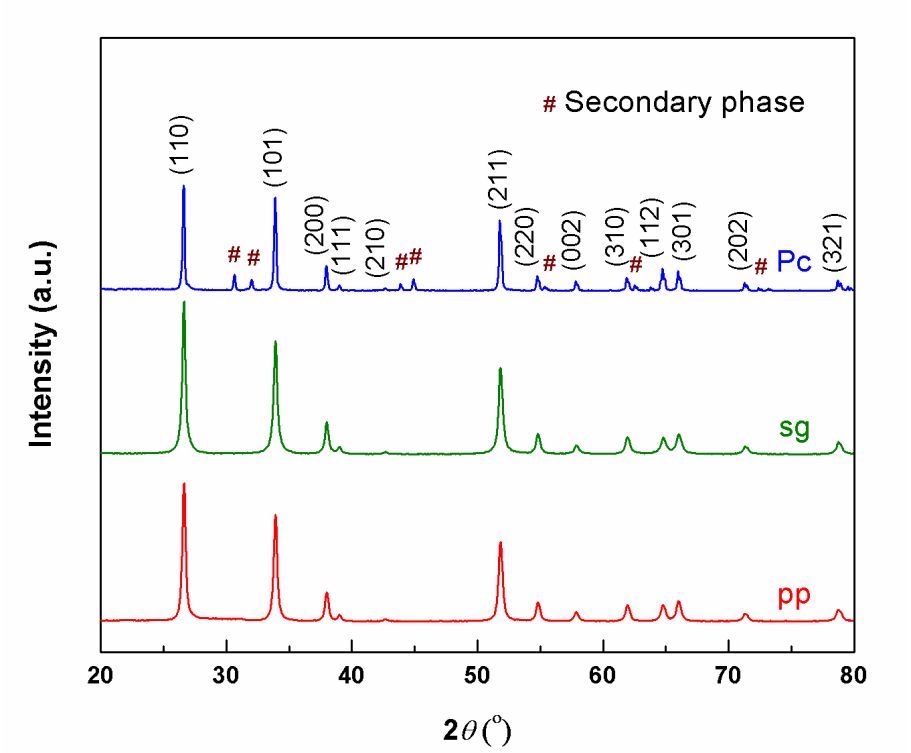

Fig. 2. XRD patterns of SnO_2 powders synthesized by different wet chemistry methods (pp - precipitation, sg - sol-gel, Pc - Pechini).

Fig. 3 exhibits the morphological properties of SnO_2 powders through the SEM images captured on representative samples. Thus, in the case of the precipitation method, the calcined powder consists of quasi spherical or polyhedral particles with dimensions from several nanometers to tens of nanometers, but also few particles with prismatic shape, a peculiarity of the synthesis procedure (Figs. 3 a and a'). The gel derived powder presents particles with a large dimensional range: fine spherical particles with sizes below 10 nm, medium quasi spherical or polyhedral particles with dimensions below 1 μm and large irregular micro sized particles (Figs. 3 b and b'). In the third case, the particles from the calcined powder are more rounded and uniform in dimension, with an average diameter of 80 nm, while the minor, soft and laced phase can be associated with the secondary phase revealed by the XRD investigation (Figs. 3 c and c').

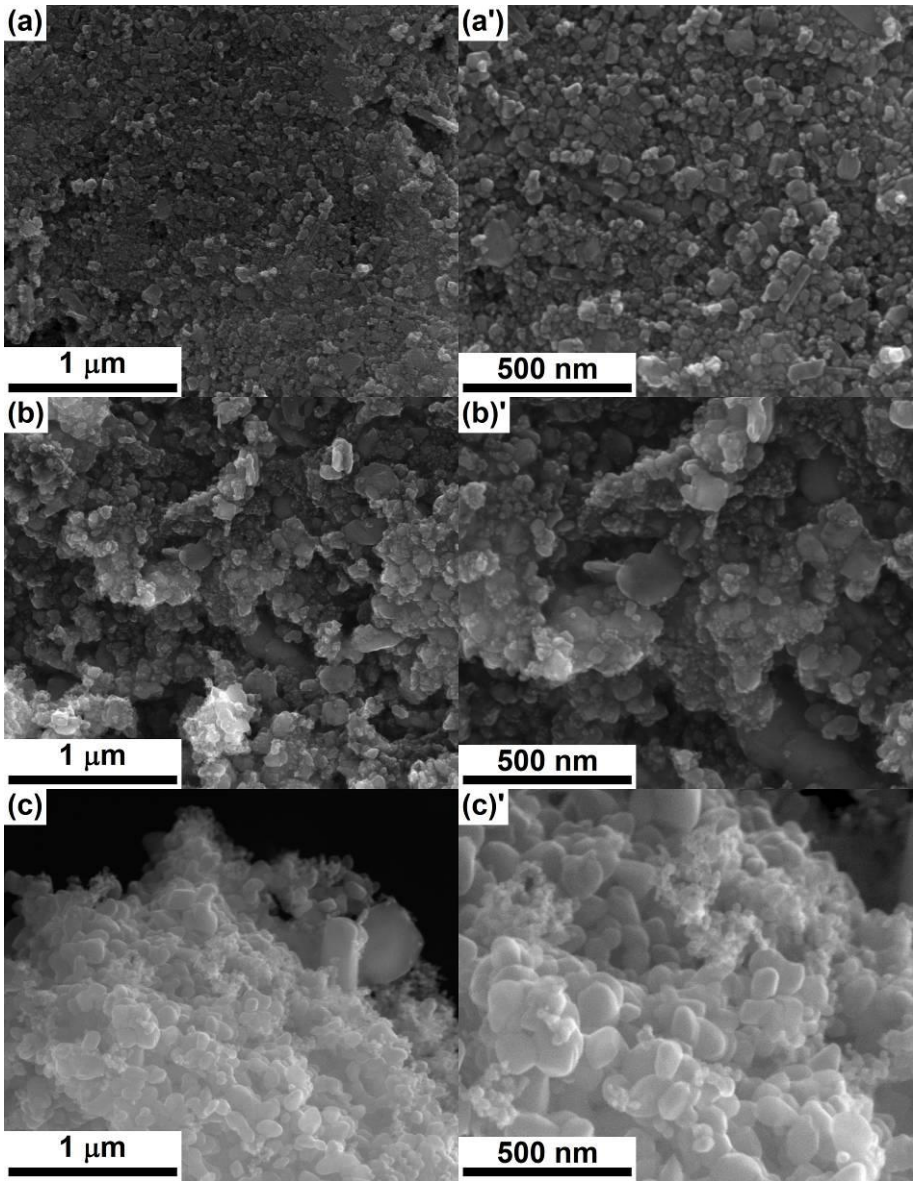

Fig. 3. SEM images of SnO_2 powders synthesized by different wet chemistry methods: (a and a') precipitation, (b and b') sol-gel and (c and c') Pechini.

In order to get more information about the particle size distribution features of SnO_2 powders synthesized by different wet chemistry methods, Fig. 4 presents the specific curves recorded with the help of a laser granulometer, using water as dispersion medium. The fine granulometric fraction, with dimensions below 1 μm, is evidenced for both precipitation and sol-gel methods, whereas the bands located at larger particle sizes can be attributed to the presence of aggregates that could not be separated by ultrasonication. Going to the Pechini

technique, the majority of the particles seems to be placed at around 100 μm, fact that is not sustained by the previous investigation method (SEM); this means that the individual particles are strongly gathered as compact bunches, as a consequence of the high calcination temperature (800 °C).

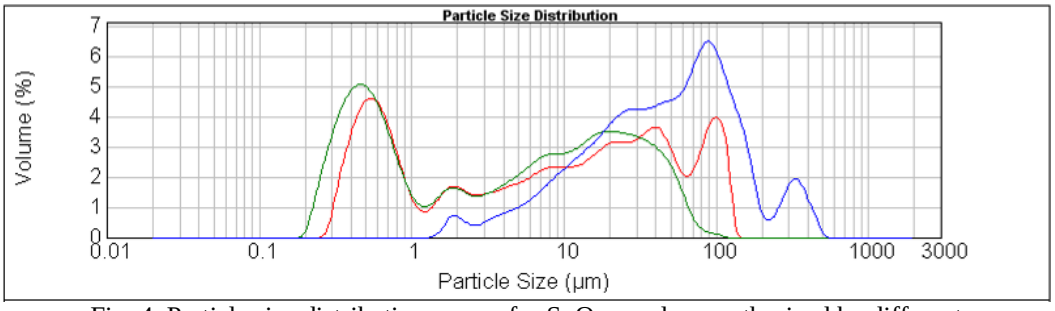

Fig. 4. Particle size distribution curves for SnO_2 powders synthesized by different wet chemistry methods (red - precipitation, green - sol-gel, blue - Pechini).

4. Conclusions

SnO_2 powders were successfully prepared by three wet chemistry methods (precipitation, sol-gel and Pechini) by starting from the same precursor. The intermediates were calcined at different temperatures in order to obtain single phase oxide materials. All powders consist of tetragonal SnO_2 with high crystallinity, except for the Pechini technique, when a small amount of secondary phase was evidenced. The morphological investigation revealed particles with dimensions from several nanometers to tens of nanometers in the case of the precipitation method, a large dimensional range for the sol-gel technique and more rounded, uniform in size and tight agglomerated particles for the Pechini method.

Such zero dimensional structures can be easily integrated in nanoscale devices for the gas sensors field, the functional properties being directly determined by the material properties, which can be tuned in the desired way via adequate processing parameters.

R E F E R E N C E S

[1] *G. Eranna*, Metal oxide nanostructures as gas sensing devices, CRC Press, Boca Raton, 2012.

[2] *S. Das, V. Jayarman*, SnO_2: A comprehensive review on structures and gas sensors, Progress in Materials Science, **vol. 66**, Oct. 2014, pp. 112-255.

[3] *M Ippommatsu, H. Sasaki, H. Yanagida*, Sensing mechanism of SnO_2 gas sensors, Journal of Materials Science, **vol. 25**, Jan. 1990, pp. 259-262.

[4] *K. Anandan, V. Rajendran*, Influence of dopant concentrations (Mn = 1, 2 and 3 mol%) on the structural, magnetic and optical properties and photocatalytic activities of SnO_2

nanoparticles synthesized via the simple precipitation process, Superlattices and Microstructures, **vol. 85**, Sept. 2015, pp. 185-197.

[5] *W. Luo, J. Deng, Q. Fu, D. Zhou, Y. Hu, S. Gong, Z. Zheng*, Nanocrystalline SnO_2 film prepared by the aqueous sol-gel method and its application as sensing films of the resistance and SAW H_2S sensor, Sensors and Actuators B: Chemical, **vol. 217**, Oct. 2015, pp. 119-128.

[6] *Q. Wang, N. Yao, D. An, Y. Li, Y. Zou, X. Lian, X. Tong*, Enhanced gas sensing properties of hierarchical SnO_2 nanoflower assembled from nanorods via a one-pot template-free hydrothermal method, Ceramics International, **vol. 42**, Nov. 2016, pp. 15889-15896.

[7] *E. Drzymala, G. Gruzel, J. Depciuch, A. Budziak, A. Kowal, M. Parlinska-Wojtan*, Structural, chemical and optical properties of SnO_2 NPs obtained by three different synthesis routes, Journal of Physics and Chemistry of Solids, **vol. 107**, Aug. 2017, pp. 100-107.

[8] *C. Jinga, D. Berger, C. Matei, S. Jinga, E. Andronescu*, Characterization of $BaMg_{1/3}(Ta_{1-x}Nb_x)_{2/3}O_3$ ceramics obtained by a modified Pechini method, Journal of Alloys and Compounds, **vol. 497**, May 2010, pp. 239-243.

[9] *G. Voicu, V.L. Ene, D.F. Sava, V.A. Surdu, C. Busuioc*, Sol-gel derived vitroceramic materials for biomedical applications, Journal of Non-Crystalline Solids, **vol. 449**, Oct. 2016, 75-82.

[10] *G. Velmathi, S. Mohan, R. Henry*, Analysis and review of tin oxide-based chemoresistive gas sensor, IETE Technical Review, **vol. 32**, Sept. 2015, pp. 323-331.

[11] *X. Kuang, T. Liu, D. Shi, W. Wang, M. Yang, S. Hussain, X. Peng, F. Pan*, Hydrothermal synthesis of hierarchical SnO_2 nanostructures made of superfine nanorods for smart gas sensor, Applied Surface Science, **vol. 364**, Feb. 2016, pp. 371-377.

[12] *X. Jia, Y. Liu, X. Wu, Z. Zhang*, A low temperature situ precipitation route to designing Zn-doped SnO_2 photocatalyst with enhanced photocatalytic performance, Applied Surface Science, **vol. 311**, Aug. 2014, pp. 609-613.

[13] *M. Peng, X. Cai, Y. Fu, X. Yu, S. Liu, B. Deng, K. Hany, D. Zou*, Facial synthesis of SnO_2 nanoparticle film for efficient fiber-shaped dye-sensitized solar cells, Journal of Power Sources, **vol. 247**, Feb. 2014, pp. 249-255.

[14] *W. Wei, P. Du, D. Liu, H. Wang, P. Liu*, Facile mass production of porous SnO_2 hollow nanospheres as high performance anode material in lithium-ion batteries, Materials Letters, **vol. 196**, June 2017, pp. 191-193.

[15] *J. Wang, D. Zhou, Y. Li, P. Wu*, Experimental and first-principle studies of ferromagnetism in Na-doped SnO_2 nanoparticles, Vacuum, **vol. 141**, July 2017, pp. 62-67.