



Tuning physical surface properties of tin dioxide nanopowders using zinc oxide as template

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ABSTRACT

With a view to energetic and (opto)electronic applications, tin (IV) oxide (SnO₂) nanoparticles have been successfully prepared at the nanoscale by a templating approach based on the use of zinc (II) oxide (ZnO) as template. The procedure consisted in preparing a mixture of tin precursor and template, subsequently calcined at 650 °C under air to lead to the formation of a SnO₂/ZnO composite material. Finally, the material was washed with an alkali solution to remove the template. The template/tin precursor mass ratio was varied in order to tailor the tin (IV) oxide material, especially with a view to main particle size. The resulting SnO₂ nanomaterials were characterized by X-ray diffraction, Fourier transform infrared spectroscopy, nitrogen adsorption and electron microscopy. The tin (IV) oxide nanomaterial exhibited enhanced textural and physical surface properties (particle size, surface area, pore size) correlated to an increasing template/tin precursor mass ratio. For instance, from optimized experimental conditions, the specific surface area and pore volume were heightened twofold, reaching values of 49 m²/g and 0.32 cm³/g, respectively.

1. Introduction

Tin (IV) oxide (stannic oxide, SnO₂), a ceramic material and oxygen-deficient n-type semiconductor with a direct wide band gap of 3.6 eV (at 300 K) [1,2], is doubtlessly one of the most scrutinized transition metal oxides and under intensive research by the scientific community. The material represents promising capabilities in many emerging fields, harnessing both the bulk and the surface properties of the tin-based ceramic, such as in the domain of solar energy conversion [1], heterogeneous catalysis (oxidation of carbon monoxide (CO), reduction of nitrogen oxides (NO_x) etc.) [3–5], electrochemistry (for Li- and Na-ion batteries, electrode materials) [6–8] and gas sensors (hydrogen (H₂), formaldehyde (HCOH), triethylamine ((C₂H₅)₃N), carbon monoxide, hydrogen sulphide (H₂S) etc.) [9–13]. Moreover, the transparency in the visible spectrum of tin dioxide is specifically predestined for optoelectronic applications like flat panel displays [1]. Further niche applications were suggested as for instance the preparation of aluminothermic mixtures, which are a class of energetic composites characterized by high exothermicity and flame temperatures [14,15]. In order to have a competitive and performing tin (IV) oxide (nano)material for diverse applications as those above-mentioned, the designing of tailored SnO₂ materials exhibiting zero-to three-dimensional (0D–3D)

structures; i.e. increase the surface to volume ratio, became fundamental and essential. For that, a huge amount of synthetic methods were employed and are described in the literature. Among them, techniques including precipitation [16], sol-gel [17,18], solvothermal routes [19,20], thermal decomposition in liquid phase [21], thermal evaporation [22], combustion [23], microwave technique [24], mechanochemical [25] and electrospinning methods [26,27] were performed for the elaboration of nanosized tin (IV) oxide material. In parallel to these methods, another route implementing the use of sacrificial hard templates is suggested to nanostructure tin (IV) oxide. This approach gives the possibility of synthesizing well-defined tin (IV) oxide nanostructures in terms of physical surface properties (particle size, specific surface area, porosity, pore size) from a judicious choice of the mould. For instance, following this strategy, 0D and 3D carbon templates [6,8,11,28,29], mesoporous silica templates [30], anodic alumina oxide membranes [31], polymethyl methacrylate microspheres [32], silica colloidal [33], calcium-based mineral [29] or biotemplates such as pollen grains of *Peltophorum pterocarpum* [34], cotton fibers [35], grapefruit peel [36] were proved and tested to be efficient in the fabrication of hierarchical pore structure SnO₂ nanomaterials. The low yields in nanostructured SnO₂ material by using templates such as alumina membranes and silica- or carbon-based mesoporous materials,

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and the fact that these templates are either expensive or synthesized in laboratory via sophisticated procedures, may be major drawbacks when up-scaling such approaches.

To this end, in this paper, a simple and versatile process for the synthesis of nanosized tin (IV) oxide material is described. The process consists in a templating approach whereupon a spherical zinc oxide particles dispersion is used as hard template. In the literature, zinc oxide nanorods and nanowires were already tested as suitable templates to nanostructure tin (IV) oxide [37–39]; however, in the context of manufacturing advanced nanotube arrays [37,38]. Here, the surface properties of the SnO₂ material were successfully tailored by adjusting the template to the tin precursor weight ratio. Additional characteristics of the tin (IV) oxide ceramic, like structure and morphology, are also presented and discussed. As mentioned above, nanostructured tin (IV) oxide has already been synthesized by means of zinc oxide templates [37–39] but those authors have worked with laboratory-made ZnO templates (nanorods and nanowires) whose cost are high owing to the equipment used [37,38] and the total removal of the ZnO template cannot be reached [39]. These criterions may represent real disadvantages for the significant production of enhanced surface properties pure SnO₂ nanomaterials.

2. Experimental section

2.1. Tin (IV) oxide material synthesis

The experimental procedure was achieved by means of commercially available reagents without further purification. Tin (II) chloride dihydrate (SnCl₂·2H₂O - 99%) and ethyl alcohol (C₂H₅OH - 98%) were purchased from VWR International LLC. Zinc (II) oxide suspension (ZnO, < 130 nm particle size (Dynamic Light Scattering, DLS), 40 wt % in ethanol) and sodium hydroxide (NaOH - 99%) were obtained from Sigma Aldrich Co. and Carl Roth GmbH + Co. KG, respectively.

In a typical experiment, loosely inspired by a previous work of the authors [40], 2 g of tin (II) chloride dihydrate was dissolved in 25 mL of ethanol under stirring in a round-bottomed flask. After complete dissolution, a precise volume of zinc (II) oxide suspension was added and the resulting mixture was vigorously stirred for 1 h to form a homogeneous solution/suspension. To break possible ZnO agglomerates, brief ultrasound sequences (2 × 3 min) were undertaken during stirring. The mixture was poured into an evaporating dish and kept overnight at room temperature under a fume hood to finally evaporate the solvent. The coarse powder was placed in a mortar and calcined in air (5 °C/min, 1 h) to prepare an off-white ZnO/SnO₂ composite material. The composite was treated three times with NaOH alkali solution (5 M, 50 mL–30 min) to remove the ZnO template. The resulting powder was centrifuged and washed with demineralized water (until a pH of 7 within the supernatant) and once with acetone. Finally, the white powder was dried at 80 °C and 250 mbar for a period of 3 h.

In order to tailor surface properties of the SnO₂ tin (IV) oxide nanomaterial, the amount of ZnO template within the ZnO/SnO₂ composite material was varied. For that purpose, the volume of ZnO suspension, which was added to the tin (II) chloride-based ethanol solution, was varied in order to have a ZnO/SnCl₂·2H₂O mass ratio (x) of 0.05, 0.25, 0.50, 1 and 1.5. The different as-synthesized SnO₂ materials were termed as SnO₂-Zn_x where Zn and index x represent the ZnO template and the ZnO/SnCl₂·2H₂O mass ratio, respectively. A reference sample (SnO₂-Zn₀) was prepared following the same procedure except the use of ZnO template particles. In every case the tin (IV) oxide phase yield is 36%.

2.2. Characterization techniques

The thermal behaviour of the tin precursor/ZnO template mixture (x = 1) was examined between 25 and 900 °C under air (5 °C/min) by means of a TA Instrument SDT Q600 device allowing a simultaneous

thermogravimetric (TG) and differential scanning calorimetric (DSC) analysis. The X-ray powder diffraction (XRD) was conducted on a Bruker D8 Advance diffractometer (40 kV–40 mA, Cu K_α radiation, λ_{Kα} = 1.54 Å) equipped with a Lynxeye detector. Diffractograms were recorded in the range of 2θ = 10°–80° with a step size of 0.02°. Fourier transform infrared (FTIR) spectroscopy was carried out on a Bruker Tensor 27 spectrophotometer by means of the KBr disk method. Spectra were recorded in transmission mode in the 4000–450 cm⁻¹ wavenumber domain (superposition of 16 scans, definition of 4 cm⁻¹). Nitrogen adsorption/desorption measurements at 77 K were performed on a Micromeritics ASAP 2020 apparatus on samples heated at 473 K for 6 h under vacuum. The specific surface area (S_{BET}) were determined according to the Brunauer-Emmet-Teller (BET) method in the 0.05–0.25 relative pressure (P/P₀) range. The pore volumes and the pore size distributions were determined at a P/P₀ relative pressure of 0.99 and by using the Barrett-Joyner-Halenda (BJH) approach, respectively. Scanning electron microscopy (SEM) images were recorded taking a FEI™ Nova Nano-SEM 450 microscope operating at 10 kV from samples sputtered with a thin layer of gold.

3. Results and discussion

3.1. Tin (IV) oxide material synthesis

Fig. 1 shows the mass evolution and the differential heat flow on the ZnO/Sn-based precursor composite material (x = 1) recorded from room temperature to 800 °C under air. Four major mass losses were observed on the thermogravimetric analysis (TG) curve which fit well with the peaks derived from the differential scanning calorimetric analysis (DSC) curve. From the plot of the first derivative of the thermogravimetric curve (DTG), four main mass changes were recorded between 25 and 140 °C (i), 140–240 °C (ii), 240–350 °C (iii), and 350–650 °C (iv) with corresponding mass losses of -7%, -4.6%, -4.7% and -17.4%, respectively. An attempt to interpret the thermal phenomena, based on the thermal analyses of the SnCl₂·2H₂O (previously dissolved in ethanol) and the ZnO particles (Supporting Information 1), is suggests the following: (i) removal of residual solvent at the surface of the powdered precursor, (ii) release of structural water molecules, (iii) calcination of the ZnO template particles surface groups and finally (iv) conversion of the tin source/ZnO mixture into tin oxide/ZnO composite. Above this last temperature range, no mass change was recorded suggesting that the total decomposition of the ZnO/Sn-based precursor composite material was achieved at around 650 °C. According to the TG and DSC profiles, the temperature of 650 °C (1 h) has been selected as optimal heating temperature to converse the ZnO/tin-based precursor composite material into ZnO/SnO₂ material.

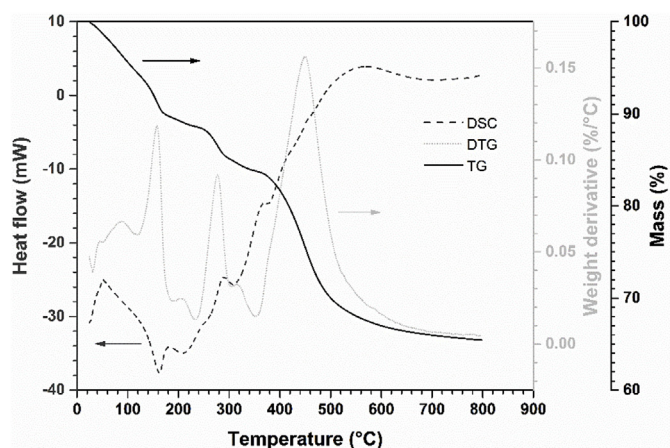


Fig. 1. Simultaneous TG and DSC curves (5 °C/min., air) of the ZnO/Sn-based precursor composite material with a ZnO/SnCl₂·2H₂O mass ratio (x) of 1.

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