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Sensing behavior to ethanol of tin oxide nanoparticles prepared by microwave synthesis with different irradiation time

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ABSTRACT

Crystalline tin oxide nanoparticles were successfully synthesized by microwave-assisted technique without any post annealing process. The morphology, microstructure and phase composition of the products obtained applying microwave irradiation for different time intervals were examined by XRD, FT-IR, SEM-EDX, TEM and HRTEM. Characterization results indicated that microwave irradiated products are composed of crystalline SnO_2 nanoparticles which exhibit the cassiterite-type tetragonal crystal structure.

The sensing properties of as-prepared SnO_2 nanoparticles towards ethanol at low operating temperature were investigated. Such sensor devices exhibited good response to low concentrations of ethanol at temperature below 100 °C. An abnormal sensing behavior was registered, that is the sensor resistance increases in the presence of ethanol maintaining, at the same time, the usual n-type behavior with other reducing gases such as CO. In contrast, after annealing the SnO_2 nanoparticles at 400 °C, the sensors show the expected regular behavior in all range of operating temperature investigated. A plausible mechanism, linked to a specific interaction between the surface of SnO_2 and ethanol molecule through its hydroxyl group, was suggested in order to describe the unusual sensing behavior observed.

1. Introduction

Metal oxide nanocrystals provide ideal systems not only for understanding nanoscale effects in a nanostructured system, but can effectively be used in practical solid state devices. A specific parameter displayed by metal oxide nanocrystals is the high surface-to-volume ratio. The high percentage of surface atoms introduce many size-dependent phenomena which can, for example, modify the interaction of the metal oxide nanocrystals with the surrounding gaseous atmosphere, a mechanism well exploited in catalysis and gas sensing. So, nanostructured metal oxides have receiving considerable attention in the last years for sensing applications [1].

SnO_2, a wide band gap semiconductor (~3.6 eV at room temperature) with relatively low electrical resistivity (~10^{-4} Ω cm) and good chemical stability [2,3] is utilized in nanostructured form for highly reflective coatings, UV and IR filters, heating layers for protective wide screens, transparent electrodes in solar cells, flat panel displays, and gas sensors [4,5]. Many methods had been developed to synthesize SnO_2 nanoparticles such as high energy ball milling method [6], homogeneous precipitation [7], sonochemical [8], hydrothermal [9], solvothermal [10], microemulsion [11], sol–gel route [12], spray pyrolysis [13], polymerized complex citrate route [14] and non-aqueous approaches [15]. However, generally a thermal treatment at high temperature is performed in order to obtain a crystalline material [2,16–19], while only few articles have described the preparation of crystalline tin oxide nanostructures without high temperature treatments [20–22].

In the present work, we report the preparation of tin oxide nanostructures by a simple and low cost wet chemical route assisted by microwave irradiation without necessity of any time-consuming post-synthesis annealing treatment. Indeed, as dipoles in the solution absorb microwaves, the irradiation is converted into heat with high energy efficiency. Enormous accelerations in reaction time can be achieved, so a reaction that takes several hours under conventional conditions can be completed over the course of minutes. Here, we reported that the SnO_2 nanostructures were prepared within few (5–15) min.

SnO_2-resistive type ethanol sensors are commonly applied in the biomedical and chemical industries to assess wine quality, food degradation, to identify drunk drivers, and to monitor fermentation and other processes in chemical industries, etc. [23–25]. Generally,

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these sensors operate at high temperatures (>150 °C) in order to promote the sensing mechanism and obtain higher response and reduced response/recovery time. Low temperature operating sensors are however desirable to decrease power consumption [26].

SnO_2 nanoparticles synthesized in the present study were therefore investigated in order to assess their sensing properties towards ethanol monitoring at low operating temperature (<100 °C). Interestingly, an anomalous behavior in the sensing of ethanol has been observed. Indeed, although the n-type behavior typical of SnO_2 has been ascertained with other reducing gases such as CO on these sensors, ethanol behaves differently showing an inversion of response. Such an unusual behavior has been attributed to a specific interaction between the surface of SnO_2 and ethanol molecule through its hydroxyl group.

2. Experimental

2.1. Synthesis

A tin hydroxide solution was first prepared by dissolving tin chloride with double distilled water at 0.1 M concentration. The ammonia solution was added to above precursor solution under constant stirring until the pH of the solution is 8. The resulting precipitate was washed with double distilled water until no chlorine ions were detected in the silver nitrate test.

The obtained precipitate was divided into two parts. While a part of solution was left to evaporate slowly and then dried at 120 °C in a conventional oven (SnO_2-0-120), the remaining solution was further divided into three parts and these solutions were separately placed in a microwave oven (2.45 GHz, 800 W) and irradiated for 5 min; the resulting precipitated were dried at 120 °C in a conventional oven and named (SnO_2-5-120), 10 min (SnO_2-10-120) and 15 min (SnO_2-15-120) respectively. Further, a portion of sample SnO_2-15, named (SnO_2-15-400), and has been annealed at 400 °C for 2 h in air.

2.2. Characterization

The crystalline structure of the samples were analyzed by X-ray diffraction (XRD) using a Bruker AXS D8 Advance instrument and using the Cu $K\alpha_1$ wavelength of 1.5406 Å. The average crystalline size of the crystallites was evaluated using the Scherrer's formula $d = k\lambda/\beta\cos\theta$ where d is the mean crystalline size, k is a grain shape dependent constant (0.9), λ is the wavelength of the incident beam, θ is a Bragg's reflection angle, and β is the full width half maximum. The surface morphology of the nanostructures were observed by scanning electron microscopy (SEM), using a JEOL 5600LV microscope at an accelerating voltage of 10 kV. Transmission electron microscopy (TEM) was recorded on a TechnaiG20-stwin using an accelerating voltage of 200 kV. The Fourier transform infrared spectra (FT-IR) of the samples were recorded using a 5DX FTIR spectrometer. The chemical compositions have been investigated by means of X-ray photoelectron spectroscopy (XPS) acquiring the spectra by means of a *K*-Alpha system from thermo scientific equipped with a monochromatic Al $K\alpha$ source (1486.6 eV) and operating with an analyzer in CAE mode with a pass energy of 200 and 50 eV for survey and high resolution spectra, respectively. A spot size diameter on the samples of about 400 μm has been adopted. Surface charging effects have been avoided using an electron flood gun.

2.3. Electrical and sensing test

Sensors were made by depositing by drop coating films (1–10 μm thick) of the nano-powders dispersed in water on alumina substrates ($6 \times 3\ mm^2$) with Pt interdigitated electrodes and a Pt heater located on the backside. The sensors were introduced in a stainless-steel test chamber for the sensing tests. The experimental bench for the electrical characterization of the sensors, allows to carry out measurements in controlled atmosphere. Preliminary tests were carried out in order to evaluate the electrical resistance of the sensor by increasing the temperature from 25 to 100 °C, with step of 8 °C/min, under 100 cm^3/min dry air flow. Electrical sensing tests were carried out in the temperature range from room temperature (25 °C) to 100 °C, with steps of 25 °C, under a dry air total stream of 100 sccm, collecting the sensors resistance data in the four point mode. Gases coming from certified bottles can be further diluted in air at a given concentration by mass flow controllers. A multimeter data acquisition unit Agilent 34970A was used for this purpose, while a dual-channel power supplier instrument Agilent E3632A was employed to bias the built-in heater of the sensor to perform measurements at super-ambient temperatures. The gas response, *S*, is defined as:

$$S = \left[\frac{\Delta R}{R_{air}}\right] \times 100 \quad (1)$$

where $\Delta R = R_{gas} - R_{air}$, with R_{gas} representing the electrical resistance of the sensor at different ethanol concentrations in dry air and R_{air} the baseline resistance in dry air.

3. Results and discussion

3.1. Materials characterization

Microwave treatment is known to be a rapid approach to the synthesis of SnO_2 nanostructures, with a good capability to control the particle shape and particle size [27–31]. In many cases, a surfactant/template agent is also added. For example, Xi et al., obtained SnO_2 nanoparticles via a microwave method in conjunction with the presence of a surfactant and template [32]. Instead, in our synthesis approach, no surfactant or template agents have been utilized.

Fig. 1a shows the XRD pattern of the dried precipitate and microwave irradiated samples for 5 and 15 min, respectively. The XRD pattern of SnO_2-0-120 indicates that, in the absence of microwave irradiation, a tin (oxy) hydroxide phase having the composition $Sn_6O_4(OH)_4$ (JCPDS no. 84-2157) has been formed. Sekar and coworkers also reported the formation of the $Sn_6O_4(OH)_4$ phase under similar synthesis conditions [33]. However, they were unable to obtain the crystalline SnO_2 phase after microwave irradiation and an annealing at high temperature (500 °C) of the intermediate SnO formed was necessary to complete the conversion to crystalline SnO_2.

On the contrary, our microwave irradiated samples shows the formation of SnO_2 nanostructures. Indeed, the XRD patterns of all irradiated samples matches well with JCPDS card no. 41-1445 of SnO_2 in the cassiterite-type tetragonal crystal structure [16,34]. This confirms that the microwave radiation causes the conversion of tin hydroxyl group into SnO_2 nanostructures without necessity of post-synthesis heating. Furthermore, the increase of peak intensity suggests also that the microwave treatment improved the crystalline structure. Fig. 1b shows an enlargement of the [2 1 1] diffraction peak. Increasing the irradiation time from 5 to 15 min only a slight decrease of the line broadening at half the maximum intensity (FWHM) has been observed. By using Scherrer's formula the average crystalline size of the tin oxide crystals were calculated to be 21 and 24 nm for the samples SnO_2-5-120 and SnO_2-15-120, respectively.

FT-IR spectra of irradiated samples are shown in Fig. 2. Data collected are in agreement with XRD results. The narrow peaks at 623 cm^{-1} confirm the formation of crystalline SnO_2 phase [17,18,35]. The spectra exhibit also a common broad band