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Resistive CO gas sensors based on In_2O_3 and $InSnO_x$ nanopowders synthesized via starch-aided sol–gel process for automotive applications

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Abstract

Pure and Sn-doped In_2O_3 nanopowders have been synthesized by a starch-aided sol–gel process. A detailed characterization by means of TEM and HRTEM, TG–MS, XRD and ^{119}Sn solid-state NMR analysis has been carried out. It has shown that the grains of the samples as-synthesized and dried at 120 °C are in the nanometer range. Moreover, on the Sn-doped In_2O_3 sample, the homogeneous distribution of the dopant with no segregation phase effects has been demonstrated. The thermal treatment at 550 °C induced an increase of grain size up to about 30 nm and of crystallinity.

The behaviour of the resistive gas sensors based on the synthesized nanopowders in the monitoring of carbon monoxide for automotive applications has been evaluated. Electrical and sensing tests have been performed on the sensor devices in a thick film configuration depositing pure and Sn-doped In_2O_3 nanopowders by screen-printing over a ceramic substrate. The results have been discussed in relation to the chemical and microstructural properties of the synthesized nanopowders. The good sensing behaviour of these samples has been associated with their special features such as very small grains and high oxygen vacancies due to the peculiar reductive character of starch pyrolysis.

Keywords: Indium oxides; Sol–gel route; CO gas sensors

1. Introduction

Sol–gel routes allow obtaining metal oxides starting from molecular species (generally inorganic salts or metal organic compounds) via inorganic polymerization reactions involving hydrolysis followed by olation (i.e., polycondensation with preferential elimination of water) and oxolation (i.e., polycondensation with preferential elimination of alcohol) reactions. Besides the advantages of starting from atomic scale reagents, sol–gel and the chemical approaches in general are simple, versatile and inexpensive compared to physical methods [1].

Among all the possible oxides, indium-based metal oxides have been result very effective as material for gas-sensor making [2–9]. This peculiar property can be further improved by reducing the indium oxide grain size to nanoscale [10]. This effect is primarily linked to the fact that, as a consequence of grain size reduction, the surface available for the gas target-sensing layer interaction is maximized. Moreover, when the particle size is very small the gas interacting zone extends over the whole grain, i.e., the particle is fully depleted [8]. The superior sensing performances of pure In_2O_3 and SnO_2 nanopowders, with respect to corresponding bulk materials, have been exhaustively reported [2–6,10–14].

The use of size stabilizers, such as capping agents or templates is commonly associated to the classic sol–gel process [15]. Among them, we recently reported the synthesis of various metal oxides in the presence of starch sol using ordinary salts as precursors [16–18]. Starch is an organic macromolecule essentially composed of amylose, an unbranched single chain polymer of 500–2000 units linked through α-1,4 glucosidic bonds; it behaves in water solutions as a hydrophilic non-ionic stabilizer of metal oxide and hydroxide nanoparticles prepared by the hydrolytic route. It was proved that the polysaccharide presence offers many advantages, such as high availability at low cost,

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clean easy biodegradation to soluble glucosidic units and original particle shape maintenance during heat treatment, owing to the possible coordination of glucosidic moieties with particle surface. Moreover, the organic hydrophilic envelope of the particles facilitates the formation of colloidal suspensions with convenient binders, which are usually used to obtain thick films through various methods, such as screen-printing.

Here, therefore we focused our attention on the sensing applications of the pure and Sn-doped In_2O_3 nanopowders prepared with the above-mentioned methodology.

The sensing behaviour regarding the materials under study was investigated in the monitoring of carbon monoxide (CO). Carbon monoxide is an odorless, colorless and toxic gas due to the formation of carboxyhemoglobin in the blood, which inhibits oxygen intake. At lower levels of exposure, CO causes mild effects including headaches, dizziness, disorientation and fatigue. At higher concentrations, it causes impaired vision and coordination, confusion leading to death.

For these reasons, CO monitoring at ppm levels is of outmost importance in domestic, environmental and industrial ambient. For example, CO produced from the incomplete combustion of fossil fuels from car engines causes high concentrations of CO in urban area and particularly in closed ambience such as in the cabin vehicles, garages, tunnels and underwear parking [19]. Then, as drivers are subjected to high carbon monoxide concentration when moving in these areas, CO is monitored in these ambience with the scope to control the ventilation system [20–22]. Nowadays, vehicles with devices for automatically selecting the air inlet mode adjusted according to the information provided by HC, CO and NO_x sensors have been increasing, to accomplish more severe legislation about car passenger health [20]. Moreover, CO monitoring allows the ventilation systems to operate in the pulse mode, varying automatically the ventilation rate of individual fans to ensure that the CO concentration in the ambience of vehicles and indoor car parking is maintained within safe levels, further saving energy.

For these automotive air quality monitors, the CO detection limit should be about 10 ppm. Moreover, for such applications it is important that the sensor responds very fast. The air inlet valve should be closed before low-quality air is allowed into the car. A response time in the order of a few seconds is therefore required.

2. Experimental

2.1. Materials

All starting chemicals were commercially available products, used without further purification. $InCl_3$ and $SnCl_4$ (Aldrich, Steinheim, Germany), starch from rice and H_2O_2 30% were BioChemika-Fluka products. α-Amylase from barley malt, type VIII-A with 2000 U, was purchased from Sigma.

2.2. Nanopowder synthesis

Two samples were prepared (pure and Sn-doped In_2O_3) with the starch-aided sol–gel method as follows. The precursors, pure $SnCl_4$ and water-diluted $InCl_3$, were added by doping funnels to a starch water suspension (50 g/L) at 100 °C in a three-necked flask under vigorous mechanical stirring, the pH being kept around 7.0 by simultaneous addition of 0.5 M NaOH in order to maintain ions in solution and not to affect the subsequent yeast digestion. At room temperature, the starch component was further degraded by α-amylase (20 mg/L) with reduction of gel viscosity. Starch was completely de-polymerized in a few hours, with the formation of a colloidal suspension. Quantitative recovery of solid oxides was obtained by centrifugation (10 min at 4000 rpm). The resulting products were recovered after washing with doubly distilled H_2O to remove soluble by-products, and treatment with H_2O_2 (30%, w/w in water) at 50 °C for 24 h. Pure In_2O_3 (sample A) and $1.5In_2O_3$–$1.0SnO_2$ (sample B) were dried at 120 °C for 12 h and stored under dry conditions. A portion of these samples was then heated in air up to 550 °C at a rate of 5 °C min^{-1} to eliminate the residual organic part completely.

2.3. Characterization

XRD spectra were collected on a Rigaku Dmax III diffractometer in the Bragg-Brentano configuration, using Cu Kα radiation and a diffracted-beam graphite focusing monochromator, operating at 40 kV and 30 mA. Samples were analyzed after packing the powders in a glass holder and measuring intensity data by step-scanning in the 2θ range between 10° and 80°, with a counting time of 5 s and a sampling interval of 0.05°. Phase identification and mean crystallite sizes were defined with the MAUD program version 1.999 [23].

Solid-state NMR experiments were carried out on a Bruker Avance 400 WB spectrometer, operating at 149.1 MHz for ^{119}Sn, under the following experimental conditions: 2.3 μs for 90° pulse, 30 s for recycle delay to produce fully relaxed spectra, and 5 kHz of rotating speed. Samples were packed in 4-mm diameter zirconia rotors. The crystalline SnO_2 peak, set at −604.3 ppm with respect to the primary tin shift of $Sn(CH_3)_4$ reference, was used as the secondary reference for ^{119}Sn.

Thermogravimetric (TG) and differential thermal analyses (DTA) were performed with a LabSys Setaram thermobalance on the samples dried at 120 °C. Thermal analyses were carried out in the range 20–1000 °C, with a heating rate of 10 °C min^{-1}, working under a 100 cm^3 min^{-1} He flow. Powdered samples (20–40 mg) were analyzed in 100 nm^3 alumina crucibles, with α-Al_2O_3 as a reference. Mass spectra analysis was carried out on a VG-QMD-1000 quadrupole mass spectrometer Carlo Erba Instruments. Electron impact mass spectra (70 eV) were continuously recorded with frequency of 1 scan s^{-1} in the 3–500 amu range.

Specific surface area values of 550 °C-treated samples were determined by N_2 adsorption at 77 K on an ASAP2010 Micromeritics analyzer. Equilibrium points were considered inside the 0.05–0.33 p/p_0 range; data were processed by BET and BJH equations [24,25].

For transmission electron microscopy (TEM) studies, one or more drops of the solution of the nanoparticles dispersed in ethanol were deposited on amorphous carbon film copper grids. TEM and HRTEM analyses were carried out on a JEOL