Sensing Properties of Indium, Tin and Zinc Oxides for Hexanal Detection

A. Malara, L. Bonaccorsi, A. Donato, P. Frontera, A. Piscopo, M. Poiana, S. G. Leonardi and G. Neri

Abstract The properties of ZnO, In_2O_3, and SnO_2 have been investigated as possible sensing layer in resistive sensors for monitoring hexanal in food applications. Sensors performances were tested at different temperatures (100–350 °C) and analyte concentrations (50–100 ppm). Results showed the ability of the analyzed metal oxides sensors, each one characterized by its own features and operating conditions, to detect hexanal. Moreover, the different oxides response has been also related to their Gibbs free energy of formation. According to preliminary results both indium and zinc oxides show promising sensing characteristics compared to tin oxide.

Keywords Hexanal · Metal oxides · Resistive sensors

1 Introduction

Hexanal is one of the major volatile compound released during food storage due to lipids oxidation and is considered an important indicator of food quality in packaging [1–3]. In addition, hexanal has been proposed as an odor reference standard for sensory analysis of drinking water [4]. Despite its importance as a quality marker in the food industry, hexanal has not been extensively studied yet. Tin oxide-based resistive sensors have been previously proposed for hexanal detection [5]. According to the best authors' knowledge, indium and zinc oxides have instead not been tested so far. Therefore, we started a study with the aim to investigate the sensing properties of In_2O_3 and ZnO as possible sensing layer in resistive sensors for monitoring hexanal in food applications and compare their performances with the most investigated SnO_2-based sensor.

A. Malara (✉) · L. Bonaccorsi · A. Donato · P. Frontera
Dipartimento DICEAM, Università Mediterranea, Loc. Feo di Vito, 89060 Reggio Calabria, Italy
e-mail: angela.malara@unirc.it

A. Piscopo · M. Poiana
Dipartimento di Agraria, Università Mediterranea, Loc. Feo di Vito, 89060 Reggio Calabria, Italy

S. G. Leonardi · G. Neri
Dipartimento di Ingegneria, Università di Messina, C.da Di Dio, 98166 Messina, Italy

B. Andò et al. (eds.), *Sensors*, Lecture Notes in Electrical Engineering 539,
https://doi.org/10.1007/978-3-030-04324-7_6

2 Experimental

2.1 Samples Preparation and Characterization

Metal oxide powders have been prepared by precipitation from aqueous solution of nitrate precursors (0.68 M) hydrolyzed with an aqueous potassium carbonate solution (1 M). The precipitates were then filtered, washed with deionized water, dried at 110 °C for 12 h and then calcinated at 500 °C for 2 h in air.

Powder samples were characterized by XRD analysis (Bruker, D2 Phaser) in the 2θ range 10°–80° (Cu $K_{\alpha 1} = 1.54056$ Å) and their morphology studied by Scanning Electron Microscopy SEM (Phenom ProX). The Brunauer–Emmett–Teller (B.E.T.) surface areas of the prepared powders were determined from nitrogen adsorption–desorption isotherms at 77 K (ChemiSorb 2750 Micromeritics).

2.2 Sensor Preparation and Testing

The procedure to prepare a metal oxide sensor was as follows: a paste was obtained by mixing the oxide powder with a proper quantity of ethanol and deposited on an alumina planar substrate (3 mm × 6 mm) supplied with interdigitated Pt electrodes and a heating element on the back side. Before sensing tests, the sensor was conditioned in air for 2 h at 400 °C in order to stabilize the deposited film.

Measurements were performed positioning the sensor in a stainless steel testing cell and flowing a mixture of dry air and hexanal vapor at different concentrations for a total gas stream of 100 sccm. The hexanal vapor was obtained by bubbling dry air in liquid hexanal maintained at a controlled temperature by a refrigerated circulating bath (temperature range $-5/-15 \pm 0.01$ °C). All air fluxes were measured by Brooks mass flow controller systems. The sensors resistance data were collected in the four-point mode by an Agilent 34970A multimeter while a dual-channel power supplier instrument (Agilent E3632A) allowed to control the sensor temperature.

Sensor response S to hexanal was defined by the sensor resistance ratio:

$$S = \frac{R_{(air)}}{R_{(air+hexanal)}}$$

Measurements were performed varying sensors temperature in the range of 100–350 °C and for three hexanal concentrations: 50, 150 and 300 ppm.

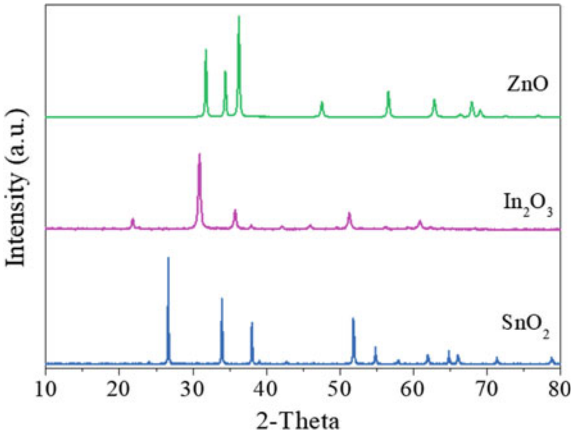

Fig. 1 XRD diffractograms of the synthesized ZnO, In_2O_3 and SnO_2 powders after calcination

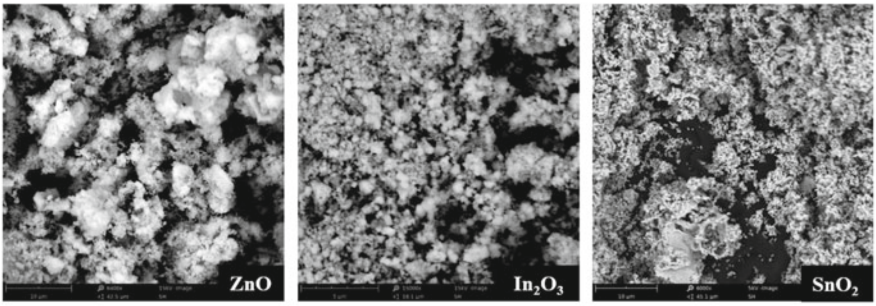

Fig. 2 SEM images of the synthesized powders after calcination

3 Results and Discussion

3.1 Metal Oxides Characterization

The metal oxides crystallinity was measured by XRD after calcination (T = 500 °C). All synthesized powders resulted with no impurities or amorphous phases, as shown in diffractograms of Fig. 1.

The morphological analysis carried out by scanning electron microscopy demonstrated the formation of very small crystalline particles in all cases, as consequence of the synthesis method used (Fig. 2). The B.E.T. surface area, however, showed some differences among samples. Indium oxide, indeed, was the powder with the highest specific surface area equal to 20.3 m^2/g, followed by zinc oxide with a specific surface area of 9.6 m^2/g and tin oxide with the lowest value of 8.4 m^2/g.

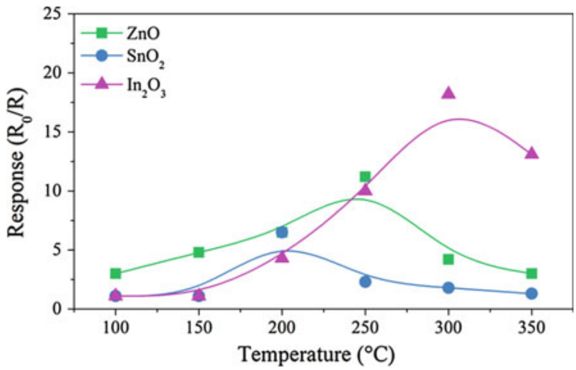

Fig. 3 Sensor responses versus temperatures at 50 ppm hexanal

3.2 *Hexanal Detection Measurements*

In this work, a preliminary study on the sensing properties of three metal oxides largely used in resistive sensors, ZnO, In_2O_3 and SnO_2, have been carried out to evaluate the best response to the hexanal molecule under controlled conditions. Zinc oxide, in particular, has not been tested for hexanal detection so far while SnO_2 is the most studied [5].

In Fig. 3 the responses of the tested sensors are compared at different temperatures for a hexanal concentration of 50 ppm in air.

The results demonstrate that both In_2O_3 and ZnO can detect hexanal in air with higher response than tin oxide. Some differences, however, exist indeed indium oxide has given the highest response at 300 °C, while ZnO can detect hexanal also at lower temperature, as low as 100 °C, with appreciable response.

The hexanal sensing mechanism is based on the aldehyde oxidation on the metal oxides surface due to the adsorbed oxygen and the consequent electrons release:

$$C_6H_{12}O + O^-_{(ads)} \rightarrow C_5H_{11}COOH + e^-$$

The different oxides response has been related to their Gibbs free energy of formation, ΔG, calculated at the different sensing temperatures according to the equation [6]:

$$\Delta G(T_f) = \frac{T_f}{T_0} G^0(T_0) - T_f(T_f - T_0)\frac{\Delta H^0}{T_f^2}$$

being G^0 and ΔH^0 (enthalpy of formation) at the standard temperature $T_0 = 298.15$ K. In Fig. 4 the Gibbs energy of the three metal oxides is plotted against temperature. For all metal oxides, the Gibbs energy shows the same trend, being negative from room temperature up to T ≈ 350 °C, when the metal oxides become less stable.

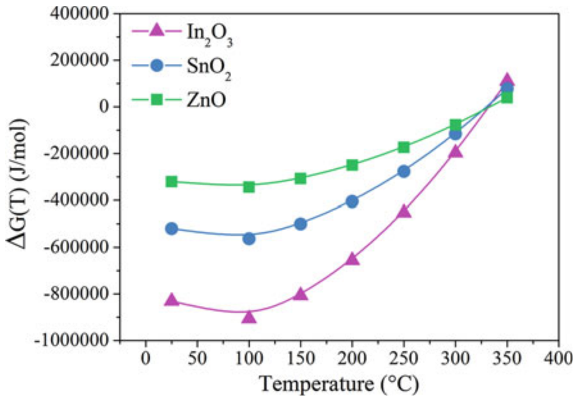

Fig. 4 Metal oxides Gibbs free energy of formation versus temperature

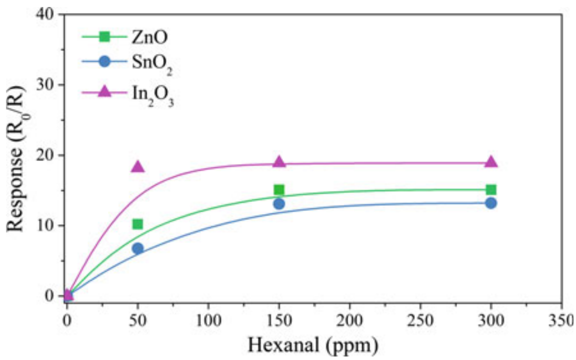

Fig. 5 Sensor responses versus hexanal concentration at the temperature of maximum sensitivity

Indium oxide shows the highest stability while ZnO the lowest (Fig. 4). The difference in among Gibbs energy of the three metal oxides is more evident at low temperatures and decreases approaching 350 °C. Zinc oxide, indeed, can be considered "less stable" compared to In_2O_3 and SnO_2 and was the sensor able to detect hexanal in air at 100 °C (see Fig. 3). On the opposite, indium oxide, which is the more stable oxide, showed the highest sensitivity but at 300 °C.

In Fig. 5, the sensor response versus concentration is shown for all sensors investigated and operating at the temperature of maximum sensitivity. It can be observed that all the analyzed samples exhibit a similar trend in the range of concentration investigated. In particular, sensors are highly sensitive at low hexanal concentration but saturate at higher concentration. Sensing results are also in agreement with specific surface area values. Indeed, the more sensitive sensor, In_2O_3, is characterized by a high specific surface area, whereas SnO_2 and ZnO sensing behavior reflects a low specific surface area value.

4 Conclusions

The comparative study on the sensing properties of In_2O_3, ZnO and SnO_2 in detecting hexanal in air has demonstrated that all the three metal oxides gave a response with peculiar properties. Indium oxide has given the highest response but at the highest temperature (300 °C), tin oxide response was better at low temperature (200 °C) and zinc oxide sowed the best compromise between sensing temperature and response. From these preliminary results, indeed, both indium and zinc oxides show promising sensing characteristics compared to conventional tin oxide and merit further investigations in the attempt to develop high performance resistive sensors for hexanal detection. The results of this comparative study are particularly important in terms of laying the foundations for the future identification of the better metal oxide sensor to use in food packaging, and in particular as an intelligent packaging, that could monitor the quality variation of different food products during their shelf life.

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