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SnO_2 Sensing Performance Toward Volatile Organic Compounds †

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Abstract: Metal oxide semiconductor gas sensors are widely used for their simplicity, low cost, high sensitivity, fast response and recovery time. Among these, tin oxide (SnO_2) was considered a good candidate to develop high-performance resistive sensors for the detection of volatile organic compounds (VOCs), such as diacetyl. Indeed, diacetyl is a VOC that confers a butter-like aroma in many foods and beverages, and it is naturally produced in small quantities during the fermentation and the storage processes in many products. The effects of different carrier gases and analyte concentrations of both aqueous and alcoholic diacetyl solutions on a SnO_2 sensor produced by a hydrothermal process were investigated.

Keywords: tin oxide; MOS; VOC; diacetyl; resistive sensor.

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1. Introduction

Volatile organic compounds (VOCs) impact on the profile of flavors, affecting our senses of smell and taste. Indeed, they contribute to identify appealing and affordable foods and drinks and can unambiguously characterize the quality of products [1]. As an example, diacetyl is among the VOCs that confers a butter-like aroma in many foods and beverages [2]. It is naturally produced in small quantities during the fermentation and the storage processes in many products such as beer, wine, brandy, balsamic vinegar, roasted coffee, honey, butter, yogurt, and several cheeses [2]. However, if diacetyl threshold value is overcome, its presence may indicate an issue in the production or storage processes. Therefore, the monitoring of diacetyl concentrations contributes to the quality of the final product. Moreover, the influence of the atmosphere composition, such as anaerobic and aerobic, usually determined by foods production processes, were reported to play a key role in diacetyl detection and monitoring [3].

Metal oxide semiconductor (MOS) gas sensors are widely used as chemoresistive sensors for their numerous advantages and the capability to detect several analytes [4,5]. Among MOS, tin oxide (SnO_2), was considered as a good candidate to develop a high-performance sensor for the detection of VOCs [6].

In this work, SnO_2 was obtained through a hydrothermal process and characterized by means of complementary investigation techniques. The detection of diacetyl vapors was performed in different working conditions, in order to evaluate the effect of both aerobic and anaerobic scenario on the sensor behavior, as well as its selectivity when other substances, such as ethanol, were contemporary present (i.e. beer, wine, etc.). From these preliminary results, SnO_2 showed promising sensing properties toward diacetyl.

2. Materials and Methods

2.1. Sample Preparation and Characterization

Tin oxide sample was prepared by using a facile hydrothermal procedure [7]. Briefly, 1.135 g of $SnCl_2$(II) were added to 150 ml of ethanol (96% purity). The mixture was ultrasonically stirred for 20 minutes until $SnCl_2$ was fully dissolved. Then, it was transferred into a PTFE-lined stainless-steel autoclave, heated at 200°C for 6 h 40′, and finally cooled down to room temperature. The yellow precipitate was collected by centrifugation, washed with ethanol until free from chlorides, and dried in oven at 80°C overnight.

The powder sample was characterized by X-ray powder diffraction (XRD) analysis in the 2θ range from 10 to 80° (Cu $K\alpha 1$ = 1.54056 Å), whereas sample morphology was investigated by Scanning Electron Microscopy (SEM).

2.2. Sensor Preparation and Testing

SnO_2 powder was mixed with a proper quantity of ethanol to form a paste that was deposited onto an alumina planar substrate (3×6 mm) supplied with interdigitated Pt electrodes on the front side and a heating element on the back side [4]. Before sensing tests, the sensor was conditioned in air for 2 h at 400 °C. Measurements were performed positioning the sensor in a testing cell and flowing a total gas stream of 100 sccm by using different type of carrier gases and different diacetyl-based analyte solutions. Humidity was kept under control and oscillated between 5% and 10%. All gas fluxes were measured by computer-controlled mass flow meters. The sensor resistances data were collected in the four-point mode by an Agilent 34970A multimeter while a dual-channel power supplier instrument (Agilent E3632A) allowed controlling the sensor temperature.

Sensor response was defined as $S = R/R_0$ if $R>R_0$ and $S=R_0/R$ if $R<R_0$, where R_0 was the resistance of the sensor just exposed to the carrier flow whereas R was the sensor resistance in the presence of the analyte gas. The sensor was exposed to the analyte gas (response) and to the carrier one (recovery) at the operating temperature of 200°C. The response time of the sensor was defined as the time taken by the sensor to reach 90% of its saturation limit after the exposure to the analyte gas, while the recovery time was defined as the time taken by the sensor to reach the 10% of its original resistance value once the target gas was switched off and the sensor exposed to the carrier gas only. Four different carriers were used: air, nitrogen (N_2), carbon dioxide (CO_2) and a 25:75 ratio mixture of CO_2 and air respectively (CO_2+Air). Diacetyl at different concentrations both in aqueous and alcoholic (5% ethanol) solution were tested. Diacetyl vapor was obtained by bubbling the carrier gas in the solution maintained at 20°C. The experimental conditions are summarized in the Table 1.

Table 1. Experimental conditions.

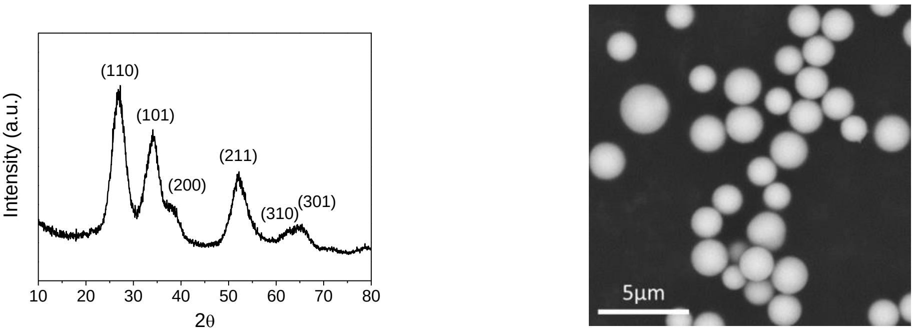
Carrier	Analyte		
	Diacetyl (mg/l)	**Ethanol (%)**	**EtOH+Diacetyl (%; mg/l)**
Air	0.4	5	5; 0.4
N_2	0.4	5	5; 0.4
CO_2	0.05 | 0.2 | 0.4 | 1.6 | 0.4	5	5; (0.4 | 0.8 | 1.6 | 3.2)
CO_2+Air (25:75)	0.4	5	0; 0.4

3. Results and Discussion

3.1. SnO_2 Microstructural and Morphological Characterization

SnO_2 crystal phases and purity were identified by the XRD pattern showed in Figure 1a. The main characteristic peaks were detected at 26.8°, 34.1°, 37.7°, 52.1°, 62.6° and 65.1°, corresponding to the (110), (101), (200), (211), (310) and (301) crystal planes. Peaks related to mixed phases were absent in the XRD pattern proving a high purity sample. However, peaks appeared broad and with weak intensities, indicating a low crystallinity and small average crystallites size. In turn, the low crystallinity was likely due to the existence of defects on the material surface, that greatly affected the reactive sites and electronic structure of the gas-sensing material, hence influencing the gas sensing properties [8].

The morphology of the SnO_2 powder, investigated by SEM analysis (Figure 1b), showed that the sample was composed of small sphere-like particles with size distribution ranging from 1.3 to 2.7 μm.



(**a**) (**b**)

Figure 1. Microstructural and morphological characterization of as- prepared SnO_2: (**a**) XRD diffractogram and (**b**) SEM image.

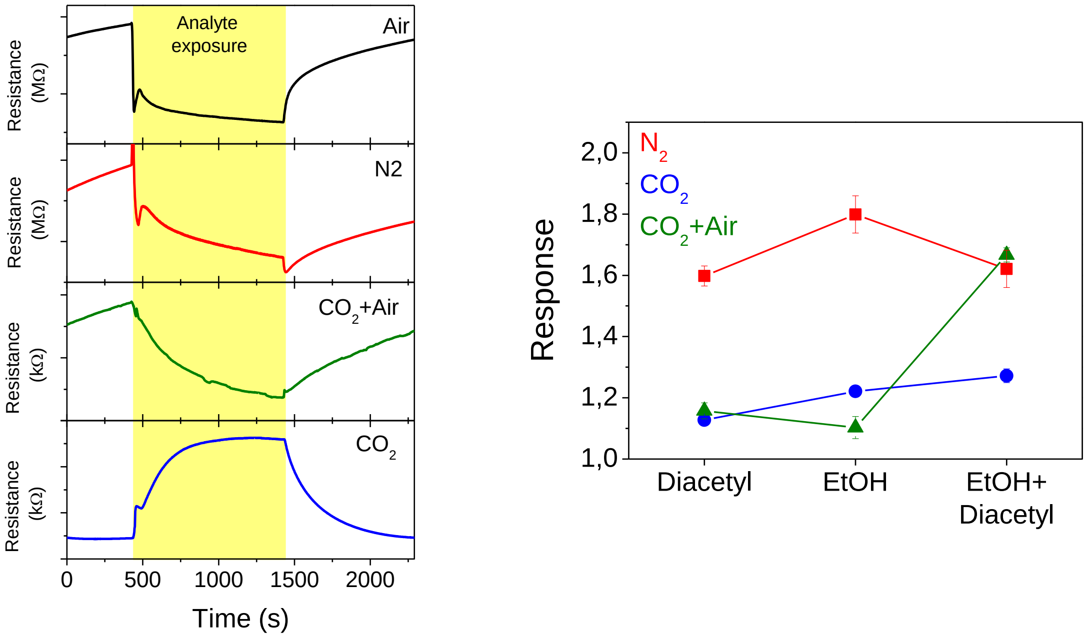
3.2. *Gas Sensor Measurements*

Tin oxide is a MOS showing the n-type behavior: the electrical resistance of the deposited layer decrease in the presence of a reducing gas such as CO [9], H_2S [10], NH_3 [11], CH_4 [12] or SO_2 [13] due to the oxidation of the target gas on the MOS surface.

Measurements, carried out in the aqueous diacetyl solution (0.4mg/l) under air, N_2 and CO_2+Air atmospheres (Figure 2a), confirmed the n-type behavior with $R<R_0$, while the measurement carried out in only CO_2 showed an inverse behavior, with $R>R_0$. Indeed, in CO_2 atmosphere SnO_2 worked as a p-type sensor. In detail, the sensor tested under N_2 condition showed a response similar to that observed under air, in terms of shape and magnitude, even if the sensor in N_2 did not show a complete recovery. The response time in both air and N_2 atmosphere was short, while the recovery time in N_2 was longer than in air. Measurements performed in CO_2+Air atmosphere exhibited long response and recovery times and moreover during the analyte exposure the sensor resistance continued to increase. In CO_2 atmosphere the resistance R was greater than R_0 displaying a p-type behavior. The sensor was able to detect diacetyl vapor and showed a complete recovery. The sensor response in air and N_2 atmospheres (1.43 and 1.60, respectively) was higher than that observed in CO_2+Air and CO_2 (1.16 and 1.13, respectively).

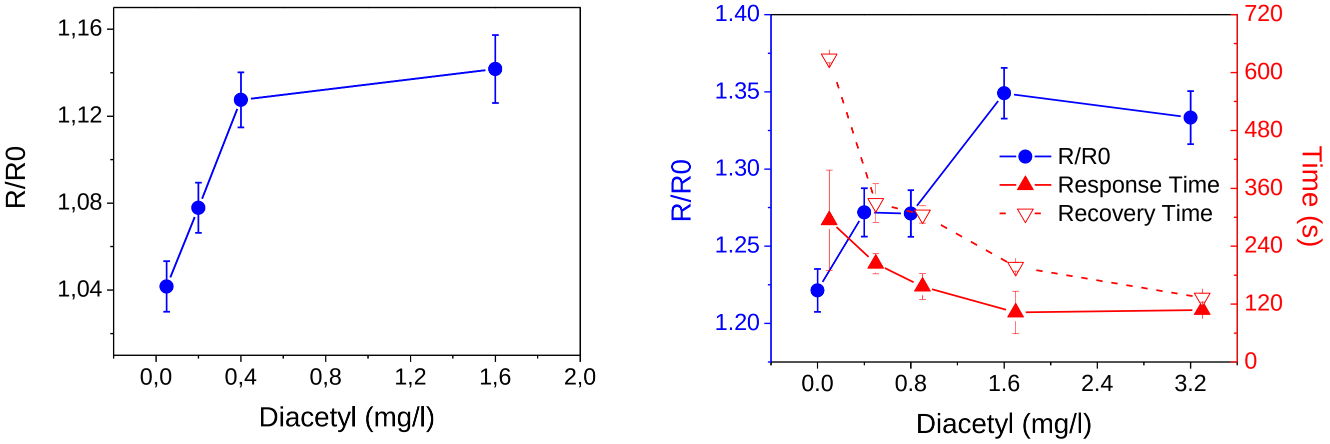
The response values evaluated by testing the 5% ethanol solution with and without 0.4mg/l of diacetyl in different atmospheres are summarized in Figure 2b. In the alcoholic solution the sensor showed an increment in the response in both N_2 and CO_2 atmospheres, while a reduction of the response was detected in CO_2+Air. When diacetyl was added to the 5% ethanol solution, the response in N_2 ambient was 1.61, comparable with the value measured with the aqueous diacetyl solution. In CO_2 and CO_2+Air atmospheres, an increment in the response up to 1.67 and 1.27, respectively, was detected. The high response value found in CO_2+Air was likely due to the formation of oxygen groups on the SnO_2 surface provided by the presence of air in the carrier flow. Recovery times in N_2 and CO_2+Air ambient resulted higher than in CO_2.

In order to test the sensor in an anaerobic environment, as previously mentioned, different concentrations of diacetyl both in aqueous and in 5% ethanol solutions were performed in CO_2 atmosphere. Response values are summarized in Figure 3.



(**a**) (**b**)

Figure 2. Measurements acquired in different atmospheres: (**a**) transient sensor response to 0.4 mg/l diacetyl solution in air, N_2, CO_2 and CO_2+Air, (**b**) sensor response in N_2, CO_2 and CO_2+Air for 0.4mg/l diacetyl solution, 5% ethanol solution and 0.4mg/l in 5% ethanol solution. Error bars are calculated on three runs.



(**a**) (**b**)

Figure 3. Sensor response in CO_2 atmosphere: (**a**) sensor response at different concentrations of diacetyl in aqueous solution, (**b**) sensor response and response and recovery time at different concentrations of diacetyl in 5% ethanol solution. Error bars are calculated on three runs.

Sensor response in CO_2 showed an increasing trend with concentration. Response raised from 1.04 to 1.14 upon changing the concentration from 0.05 mg/l to 1.6 mg/l. In the same range of concentrations, the signal registered for diacetyl in the 5% ethanol solution was higher, varying from 1.27 to 1.35. Moreover, an upper threshold value in the detection of diacetyl in alcoholic solution was found when a greater concentration, equal to 3.2 mg/l, was tested. Analysis of response and recovery times showed that the recovery time was higher than the response time for all the evaluated concentrations. In both cases, their values decreased with an exponential law upon increasing the concentration: response time was almost halved, from 204 s to 108 s with a diacetyl variation from 0.4 mg/l to 3.2 mg/l. Analogously, in the same conditions, the recovery time decreased from 330s to 133s.

3.3. Gas Sensing Mechanism

Upon changing the gas atmosphere, the baseline resistance changed from ~30MΩ in air, to ~3MΩ in N_2, to ~300kΩ in CO_2+Air, to ~30kΩ in CO_2.

The behavior of SnO_2 sensor in air was widely studied and reported in literature. In air the surface of SnO_2 grains is covered with negatively charged oxygen adsorbates (O_2^-, O^-, and O^{2-}). The formation of such oxygen adsorbates extracts electrons from the SnO_2 bulk leading to the formation of the space-charged region at the surface of SnO_2 grains and a potential barrier at the grain boundaries [14]. Indeed, the sensor in air had a high resistance value (~30MΩ).

Under N_2 atmosphere the response followed a typical n-type sensing, with a decrease in resistance due to the surface association with diacetyl. The sensor had a lower baseline resistance (~3MΩ), which was expected since the density of oxygen species bounded to the surface was reduced, releasing free carrier electrons back into the conduction band. In addition, the sensor tested under N_2 condition showed a response that was almost identical in shape and magnitude to that observed under air. A similar behavior was observed by testing SnO_2 sensor in argon ambient [15]. The response was fast in the first seconds after the exposure to diacetyl in aqueous solution probably due to the interaction between water molecules and oxide surface, faster than the interaction between diacetyl molecules and surface. Indeed, water decomposed in the proximity of the oxide surface and only later diacetyl interacted with the surface, further reducing the resistance. The recovery was slower than in air cause the poor interaction between N_2 and the surface oxide, with a consequent slow regeneration of oxygen on the surface.

In CO_2 atmosphere the resistance resulted smaller than in air (~30kΩ). Indeed, according to Wang et al. when a working temperature of 240°C, combined with high CO_2 concentration and relative humidity less than 14%, is used, CO_2 behaves as a donor of electrons, similar to a weak reducing gas [16].

In CO_2+Air the effect of CO_2 was mediated with the presence of oxygen molecules in air that reacted with SnO_2 surface; the baseline resistance was lower than in the air case, and higher than in the CO_2 case (300kΩ).

5. Conclusions

A metal oxide semiconductor sensor based on SnO_2 produced by a hydrothermal process was tested to detect volatile organic compounds. The crystal phase and purity of the SnO_2 were identified by XRD, whereas powder morphology was investigated by SEM analysis. Diacetyl sensing was performed in different atmosphere as to replicate different real scenario. The sensor was tested in air, N_2, CO_2 and CO_2+Air showing different baseline resistances due to the different interaction between the carrier gas and the oxide surface. The sensor tested in CO_2 atmosphere showed a p-type behavior, registering an increment of the response with diacetyl concentration both in aqueous and 5% ethanol solutions. The response and recovery times showed a diacetyl concentration dependance too. Further improvements on the detection of diacetyl concentration in aqueous and alcoholic solution could be achieved by a focused evaluation of response and recovery times trends.

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