UV-enhanced ozone gas sensing response of ZnO-SnO2 heterojunctions at room temperature

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A B S T R A C T
The sensitivity of ZnO-SnO2 heterojunctions to ozone gas was investigated in this work. The two-phase materials of which were prepared via a hydrothermal route, resulting in nanocomposites in which the formation of heterojunctions was confirmed by microscopy analyses. While the sensing effectiveness of these materials is currently verified for application above 150 °C, these temperatures are here drastically reduced to room temperature by considering sensing activity under continuous UV irradiation, even for ozone concentrations as low as 20 ppb. This approach resulted in a fast sensing response, a short recovery time and a good selectivity compared to other gases, demonstrating a great potential of such heterojunctions for applications in environmental monitoring devices.

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1. Introduction

Nanostructured oxide semiconductors have been generating tremendous interests in the last years due to their great importance for addressing some basic issues in fundamental physics as well as their potential applications as advanced materials [1–3]. In particular, ZnO and SnO2 are n-type wide band gap semiconductors (Eg = 3.37 and 3.6 eV, at 300 K, respectively) [4,5]. These compounds have drawn the interest of many researchers due to their wide range of applications, mainly as devices for gas detection or chemiresistors [6–8].

We should here note that, as sensing materials, ZnO and SnO2 have generally found application for use at temperatures > 150 °C [6,9,10]. This hinders the monitoring of gas composition in an environment containing explosive species since high temperature could trigger an explosion [12]. One possible solution that can be considered is the use of UV-light irradiation, as showing to be an efficient and inexpensive way for room temperature stimulation and improvement of the chemiresistors sensing activity [6–8,11,12].

In the present work, the approach mentioned just above was applied for room-temperature sensing of ozone by using ZnO-SnO2 heterojunctions as active elements. This study was conducted with the expectation that, as dealing with heterojunctions to which corresponds a superior performance (related to an efficient charge separation [13]), nanomaterials based on ZnO and SnO2 are potential candidates for practical applications as ozone gas sensors.

2. Experimental

2.1. Samples’ preparation and characterization

ZnO–SnO2 heterojunctions with the composition (100-x)ZnO:(x)SnO2, where x = 0, 30, 50, 70, and 100 wt.% were prepared via the hydrothermal method, starting from the synthesis of the individual phases, as described in the following. On the one hand, ZnO nanoparticles were obtained by the dissolution of zinc(II) nitrate (0.05 M, Zn(NO3)2·6H2O, Aldrich) and potassium hydroxide (1 M, KOH, Aldrich) in deionized water at room temperature under continuous stirring. After 30 min, a precipitated white powder was obtained, respectively. Afterwards, the powder

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using dried water 2.2. was SnO2 nanoparticles was precipitated in ethyl alcohol (anhydrous). Afterwards, it was slowly added to this deionized water solution for obtaining a molar ratio of Sn**2+ H2O = 1:500. At the end, the chloride anions were removed by dialysis, and the precipitate was dried on an electric oven during 12 h at 80°C.

In sequence, the hydrothermal treatment method was used to prepare the heterojunctions. The suspensions containing pre-formed nanocrystals of ZnO and SnO2 in different proportions were treated in an autoclave to 200°C at a heating rate of 2°C min⁻¹, and annealed then for 4 h. The suspensions were prepared from dried nanoparticles precisely mixed in the correct weight ratio. The compositions (100-x)ZnO:(x)SnO2 investigated were x, x = 0, 30, 50, 70, and 100 wt.%. The samples were identified according to their composition. The precipitated powders were washed with deionized water and isopropylalcohol. The powders were then dried at 80°C for 12 h.

The samples were characterized by X-ray diffraction (XRD) in a 2θ = 20 to 60° range with a 0.02° step, at a 2° min⁻¹ scanning speed, using CuKα radiation (Rigaku, RotaFlexRU200B), HRTEM analyses of the (as-prepared) materials were performed using, respectively, a FEI microscope Tecnai G2TF20 operating at 200 kV, while their surface area were measured using the Brunauer-Emmett-Teller (BET) method (ASAP2020, Micromeritics Instruments Corps).

2.2. Gas-sensing experiments

The 10 mg of ZnO-SnO2 heterojunction were dispersed in 1 mL isopropyl alcohol by an ultrasonic cleaner for 30 min and the suspension was then spin-coated onto an Al2O3 substrate containing 100 nm thick Pt electrodes separated by a distance of 50 nm, illustrated in Fig. 1. The samples were annealed in air at 500°C for 2 h.

Gas sensing measurements were performed at room temperature (26°C) under a UV-light irradiation provided by a UV light-emitting diode (LED, Nichia, λ = 325 nm; 200 μW). The distance between the UV-LED and the sensing material was kept at 10 mm. Initially, the samples were irradiated for 60 min with the UV-LED to stabilize the electrical resistance. A 1 V dc voltage was applied to the sample while the electrical resistance was monitored by using a Keithley (model 6514) electrometer. Dry air was used as both the reference and the carrier gas, maintaining a constant total flow of 500 SCCM via mass flow controllers. Ozone gas was generated by oxidizing oxygen using a pen-ray UV lamp (UVP company, model 97-0067-01), resulting in an O3 output level from 20 to 300 ppb. The ozone levels were calibrated by using a gas toxic detector (ATI, model F12). For comparison in terms of selectivity, this work considered performing NO2, NH3, and CO gas sensing measurements, under UV illumination at room temperature, for concentrations varying from 1 to 4 ppm.

The gas sensor response (S) was defined as S = Rgas/Rair for O3 and NO2 (oxidizing ambient) and S = Rair/Rgas for NH3 and CO (reducing ambient), where Rgas and Rair are the electric resistances of the sensor device exposed to the target gas and air, respectively.

3. Results and discussion

Fig. 2 shows the XRD patterns of the (1-x)ZnO:(x)SnO2, x = 0, 30, 50, 70, and 100 wt.%, materials prepared in this work. As can be seen, all reflections correspond to crystalline ZnO and SnO2 phases, in accordance with Joint Committee on Powder Diffraction Standards (JCPDS) files 36-1451 and 41-1445, respectively. We are talking about the hexagonal wurtzite structure for ZnO with the P63 mc space group, while the broad SnO2 peaks refer to tetragonal phase with the P4/mmm space group.

Fig. 3 shows, as a good representative example, the TEM and HRTEM images obtained from the Zn50Sn50 sample. In general, like in Fig. 3a, the TEM images from these composite revealed microstructures consisting of SnO2 nanoparticles, with approximately 5.5 nm diameter, coalesced over ZnO needle-like structures. Analysis of the HRTEM image of region A, Fig. 3b, reveals the crystalline nature of the ZnO needle, exhibiting an interplanar distance of approximately 0.28 nm which corresponds to the (100) crystallographic plane of the hexagonal ZnO phase [12]. The interplanar distance in the SnO2 nanoparticles is approximately 0.33 nm, corresponding to the (110) crystallographic plane of the rutile SnO2 phase [14].

Observation by TEM and HRTEM that the SnO2 nanoparticles are intimately attached on the ZnO needle-like structures is indicative that the junction between ZnO and SnO2 was successfully produced, this ZnO-SnO2 heterojunction revealing to be of contact type [15]. When comparing among the samples, it was observed that the surface area of the ZnO-SnO2 heterojunctions significantly increased with SnO2 addition, ranging between 4 m² g⁻¹ (holding here for ZnO) to 153 m² g⁻¹ (applying for SnO2). The surface area values of the (100-x)ZnO:(x)SnO2 heterojunctions prepared in this work are presented in Table 1.

In the following, the capability of these materials to sense ozone gas together with the effect of UV illumination was investigated. To start with, Fig. 4 shows, as a reference, the sensor response of pristine SnO2 when exposed for example to 60 ppb of this gas, in presence and not of continuous UV illumination. As reported and discussed elsewhere for n-type semiconductors [2,6], the sensing
response of such materials is expectedly known to manifest as a sudden increase in electrical resistance. Comparison of the curves presented in Fig. 4 clearly shows that UV illumination has no consequence on the material’s sensor response. Nevertheless, once the gas flux is interrupted, the UV irradiation contributes to a marked drop in electrical resistance, ascribed to a reduction in desorption-energy barrier. This means that the energy provided by the UV light contributes to an efficient release of the $O_2$ anions attached to the SnO$_2$ nanoparticles’ surface, the important consequence of which is a gain in complete reversibility compared to the measurement conducted in the dark mode (with no UV illumination).

Fig. 5(a)–(e) shows the room-temperature gas sensor responses of the ZnO-SnO$_2$ heterojunctions when exposed to 60 ppb of ozone, under continuous UV irradiation. The exposition was of 30 s during each sensing measurement. As seen, all these samples exhibit a good sensitivity to ozone gas, even for such a really short exposition time, as well as a good reproducibility over cycles (three cycles were tested in each case). For a good comparison between samples, we chose to keep an identical Y-axis from Fig. 5(a)–(e). Fig. 5(f) compares the gas sensor responses of these heterojunctions depending on composition; the observed order of gas sensing performance is 50Zn50Sn > 70Zn30Sn > 30Zn70Sn > SnO$_2$ > ZnO. When compared to SnO$_2$ and ZnO, which are the typical semiconducting materials separately applied for the detection of ozone gas, it is straightforward concluding that the sensing response from the 50Zn50Sn sample is approximately 5 times higher. In addition, the latter presents a fast response time of approximately 13 s and a short recovery time of approximately 90 s. The mechanism behind this interesting ZnO-SnO$_2$ compositional-dependent sensitivity, showing a maximum for 50Zn50Sn, is discussed later in this report.

Based on the above results, the 50Zn50Sn sample was chosen for further room-temperature sensing measurements under UV illumination, while exposed to different O$_2$ concentrations, the results of which are shown in Fig. 6. As can be seen, this sample presents a good sensing response even for the lowest O$_2$ level tested here (20 ppb), total reversibility, and a good repeatability. It is important to remember that ozone levels above 120 ppb are known to be hazardous to human health [8,16]; therefore, the ZnO-SnO$_2$ heterojunctions present a great potential of application in the detection of relatively low levels of ozone gas even at room temperature by using UV illumination. Just for reference, Table 2 summarizes several results reported in the literature for good sensing activity (ozone level and operating temperature) of different semiconducting metal oxides that have been investigated as ozone gas sensor. Notice that values as high as 1000–1500 are reported for S in this

<table>
<thead>
<tr>
<th>Sample</th>
<th>Composition</th>
<th>SSA (m$^2$ g$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnO</td>
<td>100% ZnO</td>
<td>4</td>
</tr>
<tr>
<td>70Zn30Sn</td>
<td>70% ZnO–30% SnO$_2$</td>
<td>40</td>
</tr>
<tr>
<td>50Zn50Sn</td>
<td>50% ZnO–50% SnO$_2$</td>
<td>65</td>
</tr>
<tr>
<td>30Zn70Sn</td>
<td>30% ZnO–70% SnO$_2$</td>
<td>105</td>
</tr>
<tr>
<td>SnO$_2$</td>
<td>100% SnO$_2$</td>
<td>153</td>
</tr>
</tbody>
</table>

**Table 2**

Summary of results of sensor performance reported for ozone gas sensors based on several semiconducting metal oxides, giving the operating temperature and response, $S (= R_{gas}/R_{air})$, depending on the ppb level considered in each study.

<table>
<thead>
<tr>
<th>Sensing material</th>
<th>Ozone level (ppb)</th>
<th>Operating temp (°C)</th>
<th>Response, $S$</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnO</td>
<td>33</td>
<td>250</td>
<td>5.6</td>
<td>[17]</td>
</tr>
<tr>
<td>WO$_3$</td>
<td>30</td>
<td>250</td>
<td>16.0</td>
<td>[9]</td>
</tr>
<tr>
<td>In$_2$O$_3$</td>
<td>100</td>
<td>300</td>
<td>1500.0</td>
<td>[18]</td>
</tr>
<tr>
<td>SnO$_2$</td>
<td>1000</td>
<td>250</td>
<td>10000.0</td>
<td>[8]</td>
</tr>
<tr>
<td>CuO</td>
<td>50</td>
<td>250</td>
<td>1.6</td>
<td>[19]</td>
</tr>
<tr>
<td>V$_2$O$_5$–SnO$_2$</td>
<td>50</td>
<td>250</td>
<td>1.1</td>
<td>[20]</td>
</tr>
<tr>
<td>SnO$_2$–Cu$_2$O$_2$</td>
<td>100</td>
<td>250</td>
<td>3.0</td>
<td>[21]</td>
</tr>
<tr>
<td>α-Ag$_2$WO$_4$</td>
<td>80</td>
<td>300</td>
<td>1.5</td>
<td>[16]</td>
</tr>
<tr>
<td>Zn$<em>{30}$Sn$</em>{70}$O$_2$</td>
<td>20</td>
<td>26$^\circ$</td>
<td>8.0</td>
<td>Present work</td>
</tr>
</tbody>
</table>

* Under continuous UV illumination.
Table, which arose from considering higher ppb levels and operating temperatures. Reporting a good sensing ability of the 50Zn50Sn heterojunction at room temperature is the novelty from the present work.

The ozone sensing mechanism of ZnO–SnO₂ samples under UV light can be explained as follows. First, when the heterojunctions are exposed to the air, oxygen molecules will be adsorbed onto these surfaces,

\[ \text{O}_2\text{ (gas)} \rightarrow \text{O}_2\text{ (ads)} \quad (1) \]

the \( \text{O}_2\text{ (ads)} \) molecules of which will capture the free electrons from the conduction band, forming ionized oxygen anions \[6,7\]. At room temperature, the ionic \( \text{O}_2^- \) species are dominant \[2\],

\[ \text{O}_2\text{ (ads)} + e^- \rightarrow \text{O}_2^- \text{ (ads)} \quad (2) \]
contributing to the formation of a high-resistance depletion layer at the sample surface, responsible for an increase in the overall sample’s electrical resistance. When the heterojunctions are now exposed to UV irradiation, electron–hole pairs are photogenerated ($h^+ + e^- \rightarrow h^+ + e^-$) [6,7], followed by migration of the holes ($h^+$) to the sample surface, while the $O_2^-$ species will be photodesorbed,

$$h^+(hv) + O_2^{(ads)} \rightarrow O_2^{(des)}(hv)$$

As a consequence, the depletion layer is diminished and the remaining unpaired electrons contribute to an increase in the electrical conductivity [6,7]. Upon exposure to $O_3$ gas, $O_3$ molecules will be adsorbed onto the heterojunctions-containing sample surface, according to the following reaction:

$$O_3(g) + e^-(hv) \rightarrow 1/2 O_2^{(des)}(hv) + O_2^{(ads)}(hv)$$

This reaction widens the depletion-layer at the sample surface, hindering the flux of charge carriers and, consequently, the electrical resistance is increased when the sensing material is exposed to $O_3$ gas [6].

In light of the results presented here, it is reasonable to propose that the improvement in $O_3$ gas sensor response under UV irradiation, as observed in the ZnO–SnO$_2$ heterojunctions, should be linked to a reduction in charge carriers recombination promoted at the two-phase interface. This hypothesis is based on the fact that, when such heterojunctions are illuminated with the UV-light, electron-hole pairs are photogenerated, and the electrons move to the SnO$_2$ phase while the holes move to the ZnO phase [11,22]. Accordingly, this charge carrier migration is allowed to develop only across the ZnO–SnO$_2$ interfaces, hindering charge carrier recombination and enhancing the gas sensing performance of the heterojunctions [2,11]. This approach is in agreement with observation of a maximum of sensitivity to ozone gas for 50Zn50Sn, the nanocomposite expected to present the maximum of heterojunctions density.

Gas selectivity is one of the most important parameters of sensors in practical applications [23]. Based on this observation, we also proceeded with a comparison of the sensor response from the 50Zn50Sn heterojunction to other gases. Fig. 7 displays the sensor response (S) observed when this material is exposed to oxidizing (NO$_2$) as well as reducing (NH$_3$, CO) gases, for measurements similarly conducted at room temperature under continuous UV irradiation. After various tests from which a low response to these gases was detected, we finally chose to perform the measurements for gas concentrations from 1 to 4.0 ppm, i.e., significantly higher than the highest 0.3 ppm value considered in this work for ozone. In Fig. 7(d), the sensing responses of the material for 0.3 ppm $O_3$, $NO_2$, $NH_3$, and $CO$ are depicted.

![Image](Image_90x616_to_331x784.png)

**Fig. 6.** Room-temperature gas sensing response of 50Zn50Sn sample as a function of ozone gas concentration.

![Image](Image_90x616_to_331x784.png)

**Fig. 7.** Room-temperature gas sensing response of 50Zn50Sn sample exposed towards (a) $NO_2$, (b) $NH_3$, and (c) $CO$. (d) Comparison of the sensor responses of 50Zn50Sn sample to different gases.
1.0 ppm NO₂, 1.0 ppm NH₃, and 1.0 ppm CO are compared. Notice that the 502 nitrogen sample exhibits a higher response for O₃ gas, irrespective of talking here about a really lower gas concentration level in comparison: the value is S = 3.80 compared to S = 2.0 for NO₂, S = 1.8 for NH₃, and S = 1.4 for CO. Based on these findings, we can state that the 502 nitrogen heterojunction can be considered as a promising material for developing ozone gas sensors for operation at room temperature under UV illumination.

4. Conclusions
In summary, ZnO-SnO₂ heterojunctions were obtained in this work via the hydrothermal method, and tested as gas sensors for operation even at room temperature, under UV light irradiation. Compared to the individual phases, the enhancement in the gas-sensing performance of the heterojunctions is essentially attributed to the high adsorption in good separation of photogenerated charge carriers (electrons and holes) at the two-phase interfaces, the final consequence of which is a significant reduction in charge recombination. This is coherent with observation that the highest response was obtained for the heterojunction with the 50% ZnO:50% SnO₂ composition. By comparing response with other gases like NO₂, NH₃ and CO, selectivity of such materials for ozone gas sensing was also verified. These findings show that ZnO-SnO₂ heterojunctions have a remarkable potential for practical applications as ozone gas sensor in environmental monitoring devices.

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References

Biographies
Luís Fernando da Silva is currently post-doctor at Institute of Chemistry at the São Paulo State University (UNESP), Brazil with a fellowship from São Paulo Research Foundation (FAPESP). He received his PhD in Materials and Engineering from São Carlos School of Engineering, University of São Paulo (Brazil) with a Postdoctoral fellowship from the Laboratory for Multifunctional Materials, Department of Materials, at ETH Zürich, Switzerland. He research interests mostly deals with synthesis of oxide compounds via chemical methods and the characterization of these compounds by X-ray absorption spectroscopy (XAS), photoluminescence, transmission and scanning electron microscopy and the electrical gas sensing properties of these oxide compounds.
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Ariadne Cristina Catto is a PhD student in Materials Science and Engineering at the São Carlos School of Engineering, University of São Paulo, Brazil with a fellowship from São Paulo Research Foundation (FAPESP). The aim of her thesis is the synthesis of Bi-doped ZnO-2COO-thick and thin films obtained by hydrothermal method applied as resistive gas sensors.
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Khalifa Aguir is a professor at Aix Marseille University (France). He was awarded his doctoral d’Etat als Sciences degree from Paul Sabatier University, Toulouse (France) in 1987. He is currently the head of Microsensors Group at the Institute of Materials Microelectronic Nanosciences of Provence (IM2NP-CNRS) at Aix-Marseille University, Marseille (France). His principal research interests are now directed toward...

Caue Ribeiro received his PhD in Physical Chemistry from the Federal University of Sao Carlos in 2005. After a period in the private sector, he joined the Brazilian Agricultural Research Corporation (Embrapa) as a full researcher, in the Instrumentation Center in 2007. His primary research interests include the development of synthesis routes to produce heterogeneous catalysts (mainly inorganic nanoparticles) for water decontamination and energy production, investigation about formation and crystallization mechanisms in nanoparticles and interactions of inorganic nanoparticles with plants and soil (fertilizers and defensives).

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