Response of a Zn$_2$TiO$_4$ Gas Sensor to Propanol at Room Temperature

Ibrahim Gaidan $^{1,2,*}$, Dermot Brabazon $^2$ and Inam Ul Ahad $^2$

$^1$ Faculty of Engineering, Electrical & Electronics Eng. Department, Sirte University, Sirte, Libya
$^2$ Advanced Processing Technology Research Centre, Dublin City University, Dublin 9, Ireland; dermot.brabazon@dcu.ie (D.B.); inamul.ahad@dcu.ie (I.U.A.)

* Correspondence: igaidan555@gmail.com; Tel.: +21-891-816-0062

Received: 29 June 2017; Accepted: 9 August 2017; Published: 31 August 2017

Abstract: In this study, three different compositions of ZnO and TiO$_2$ powders were cold compressed and then heated at 1250 °C for five hours. The samples were ground to powder form. The powders were mixed with 5 wt % of polyvinyl butyral (PVB) as binder and 1.5 wt % carbon black and ethylene-glyco-Imono-butyl-ether as a solvent to form screen-printed pastes. The prepared pastes were screen printed on the top of alumina substrates containing arrays of three copper electrodes. The three fabricated sensors were tested to detect propanol at room temperature at two different concentration ranges. The first concentration range was from 500 to 3000 ppm while the second concentration range was from 2500 to 5000 ppm, with testing taking place in steps of 500 ppm. The response of the sensors was found to increase monotonically in response to the increment in the propanol concentration. The surface morphology and chemical composition of the prepared samples were characterized by Scanning Electron Microscopy (SEM) and X-Ray Diffraction (XRD). The sensors displayed good sensitivity to propanol vapors at room temperature. Operation under room-temperature conditions make these sensors novel, as other metal oxide sensors operate only at high temperature.

Keywords: gas sensors; XRD; ZnO and TiO$_2$

1. Introduction

The detection and quantification of alcohols with high sensitivity and selectivity is required in various industrial sectors, such as the pharmaceutical, chemical, clinical laboratories, agro-food and alcohol-based fuel industries. A number of conventional spectroscopic techniques are currently used in industries for accurate alcohol detection. However, these techniques often require complex sample preparation steps, and therefore need highly skilled and trained operators, and are not suitable for rapid onsite measurements. Due to complexity of the instruments and the high costs, the requirement for highly sensitive and selective alcohol sensors with real-time monitoring capabilities has increased. Alcohol sensors can be categorized on the basis of the type of transducer used to convert the alcohol content information into an electrical signal. Chemical- and enzyme-based biosensors are two major classes of alcohol sensors. Biosensors are highly selective in nature, due to the specific reaction between the enzyme and the tested alcohol; they are not suitable for long-term use, and have limited shelf-life. Chemical sensors demonstrate high sensitivity, but are prone to poor selectivity. Semiconducting metal oxide composite materials have been used as the sensing element for fabrication of thin film chemical alcohol sensors. Thin film metal oxide sensors are inexpensive, easy to fabricate, demonstrate long term stability, and provide real-time monitoring. However, metal oxide sensors require high operating temperatures as the sensing material needs to be heated up to several hundred degrees to transform from insulator to semiconductor. For example, the sensitivity of SnO$_2$- and
In$_2$O$_3$-based sensors with platinum interdigitated electrodes on alumina substrates for detecting ethanol was investigated over a range of 10–5000 ppm [1]. A TiO$_2$ thin film was used to detect alcohol by Sberveglieri et al. [2]. This sensor was fabricated on alumina substrate with Pt interdigitated electrodes using a sol-gel technique. The sensor was used to detect methanol, ethanol and propanol at 2100, 2000 and 2600 ppm at operating temperatures of 300, 400 and 500 °C, respectively. In another study, SrFeO$_3$ oxide P-type semiconductor gas sensor was investigated. A solid-state reaction method was used to deposit the sensing material. The sensor worked at operating temperatures of 275 to 375 °C and a concentration range of 0–2000 ppm [3]. This sensor demonstrated good sensitivity and selectivity to the vapors of Ethanol (C$_2$H$_5$OH). The effect of adding CdO to ZnFe$_2$O$_4$-based semiconductors for improved sensitivity in air and for ethanol was reported [4]. A Zn$_2$TiO$_4$ ethanol gas sensor was investigated. The sensor was used at concentration ranges of 50 and 200 ppm at 300–500 °C [5]. TiO$_2$ thin film-based gas sensors were demonstrated for detection of methanol, ethanol and benzene at room temperature [6]. Titanium and tungsten oxide-based gas sensors were used to detect NO$_2$ and CO [7]. Nb-doped titanium dioxide thin films with a thickness of 300 nm, deposited on Al$_2$O$_3$ substrate, were used to detect nitrogen dioxide (NO$_2$) [8]. The sensitivity of the sensor to NO$_2$ was recorded to be 1.0/ppm at 350 °C. Improved sensitivity of ZnO nano-wires on hydrogen sulfide (H$_2$S) was also demonstrated, emphasizing the effect of nano-size effect on producing high response in presence of even trace-level of a gas [9]. The sensor was used to detect different gases, and showed good sensitivity and selectivity to H$_2$S at low concentrations (5 ppb). The sensor was tested at an operating temperature of 300 °C. A micro hotplate was used to control the temperature. TiO$_2$ thin film for detecting NO$_2$ was investigated [10]. A ZnO sensor was used to detect O$_3$ (0.1 ppm) [11]. The sensor exhibited the highest sensitivity to O$_3$ at 250 °C. A gas sensor based on Zn$_2$TiO$_4$ as a sensing material for ethanol was studied [5]. The sensor was tested at operating temperatures of 300–500 °C, and exhibited the highest sensitivity at 500 °C. TiO$_2$ and ZnO, or mixture of both, have been used by many researchers to detect different gases. For example, TiO$_2$/ZnO has been used to detect ethanol [12,13], ZnO to detect NO$_2$ [14], and TiO$_2$ to detect chloroform [15].

Some mixture formulas, such as xCO$_2$O$_4$, xFe$_2$O$_4$ and xTiO$_4$ (x = Ni, Cu, Zn, Zn$_2$, Sn, Cd, Mg, etc.), have become more common to use in gas sensing applications. xCO$_2$O$_4$ (x = Ni, Cu, or Zn) was used to detect CH$_3$COOH at 300 °C [16]. ZnCo$_2$O$_4$ and Zn$_2$SnO$_4$/SnO$_2$ gas sensors were investigated to detect CO, C$_3$H$_8$ and NO$_2$ at 600 °C [17]. A ZnCo$_2$O$_4$ sensor exhibited a good sensitivity to LPG at both high and low temperatures. The sensor was tested at (room temperature −400 ºC). The highest sensitivity to 40 ppm LPG was recorded at 250 ºC [18]. A NiCo$_2$O$_4$ sensor was studied for detecting O$_3$ [19]; the sensor demonstrated the highest sensitivity at 200 ºC. Table 1 presents a brief list of selective research studies on different metal oxide composite sensing materials developed to test selected gases.

It can be concluded from the research studies that a high operating temperature is required for transforming the metal oxides from insulator to semiconductor state. Hotplates are normally used to increase the temperature of the sensing material for sensing the desired gas. This results in high power consumption, oxidation of sensing materials, and limited use of the sensing materials for miniaturized sensing platforms and wearable sensors. Additionally, gold or platinum electrodes are commonly used, which makes these sensors expensive.

These limitations of metal oxide-based sensors have encouraged researchers to use polymer gas sensors, which work at room temperature with low power consumption. For example, to detect methanol, ethanol and benzene at room temperature, a TiO$_2$ dispersed in poly vinylidenefluoride (PVDF) gas sensor was used [6]. The film was deposited on glass substrate with gold electrodes. The sensor not only demonstrated a great sensitivity to methanol, ethanol and benzene gases at low concentrations, but longer response (2 min) and recovery (6 min) times were also recorded. Although the shelf-life of conductive polymer-based metal oxide gas sensors is limited compared to the above-mentioned sensors, they still have a longer lifetime than enzyme-based biosensors [20]. In previous studies by our group, NiFe$_2$O$_4$ and ZnFe$_2$O$_4$ gas sensors were developed and tested for sensing methanol, ethanol, and propanol at room temperature [21–23].
Table 1. List of selected sensing materials for sensing different gases.

| Sensing Materials | Sensitive Gases          | Year/Reference |
|-------------------|--------------------------|----------------|
| ZnO               | H₂S                      | 2017 [9]       |
| ZnO–SnO₂          | O₂                       | 2016 [24]      |
| TiO₂              | NO₂                      | 2015 [10]      |
| Zn₂TiO₄           | C₂H₅OH                   | 2015 [5]       |
| ZnO               | NO₂                      | 2013 [14]      |
| Zn/Zn₂SnO₄ + SnO₂ | CO/C₂H₆                 | 2013 [17]      |
| TiO₂              | Chloroform               | 2014 [15]      |
| TiO₂ and ZnO      | C₂H₅OH                   | 2012 [13]      |
| TiO₂–ZnO          | NO₂                      | 2010 [12]      |
| ZnO               | C₂H₅OH                   | 2010 [25]      |
| SnO₂ and Pt/SnO₂  | CO                       | 2006 [26]      |
| ZnO               | C₂H₅OH and Acetone       | 2006 [27]      |
| SnO₂              | H₂S and CO               | 2006 [28]      |
| SnO₂              | O₃, CO and NO₂           | 2006 [29]      |
| SnO₂              | O₃ and NO₂               | 2006 [30]      |
| SnO₂/Al/Ni        | LPG gas                  | 2006 [31]      |
| SnO₂ or Ga₂O₃     | CO and CO₂               | 2005 [32]      |
| SnO₂              | H₂, C₂H₅OH and CH₄       | 2005 [33]      |
| SnO₂              | CO and CO₂               | 2005 [34]      |
| WO₃               | Hydrocarbon gases        | 2005 [35]      |
| TiO₂              | CO                       | 2004 [36]      |
| Fe₂O₃–SnO₂        | NO₂ and C₂H₅OH           | 2004 [37]      |
| Pt–SnO₂           | C₂H₅OH                   | 2004 [38]      |
| SnO₂              | C₄H₁₀                     | 2004 [39]      |
| SnO₂–ZnO and SnO₂–ZnO–CuO | H₂S LPG, NO₂, CO₂, CO and CH₄ | 2004 [40] |
| SnO₂–Co₃O₄        | CO and H₂                | 2004 [41]      |
| CdSnO₃            | Cl₂                      | 2004 [42]      |
| BaSnO₃            | H₂S, CH₃SH               | 2004 [43]      |
| ZnO–TiO₂          | Alcohol, Acetone, Benzene, Toluene and xylene | 2004 [44] |
| MFe₂O₄            | H₂S, CH₃SH               | 2003 [45]      |
| NiO-doped WO₃     | NO₂                      | 2003 [46]      |
| WO₃               | H₂S                      | 2001 [47]      |

In the current study, new composite materials were developed by mixing different weight percentages of TiO₂ and ZnO to fabricate a novel gas sensor with high sensitivity towards alcohols. The conductive polymer polyvinyl butyral (PVB) was mixed with the metal oxide composites, along with carbon black, to increase the porosity and make them operational at room temperature. The morphological and chemical characterizations of the prepared samples were examined, and the developed sensors were tested for sensing propanol vapors using a specially designed gas test chamber. The response of the developed sensors was recorded for propanol vapors at two concentration ranges (500 to 3000 ppm and 2500 to 5000 ppm) at room temperature.

2. Experimental Work

Titanium dioxide (TiO₂), zinc oxide (ZnO) and carbon black was supplied by Alfa Aesar. Figure 1 shows the experimental working steps. Three powder samples with different molecular weight percentage of TiO₂ and ZnO were prepared according to Table 2. Samples were prepared using 75, 50 and 25 Mwt % of TiO₂, mixed with 25, 50 and 75 Mwt % of ZnO. The powders were mixed with wet-ball milled in alcohol for 24 h, dried in an oven at 120 °C, and then compressed at 2 ton to form pallets. The pallets were heated in a furnace at 1250 °C at a rate of 5 °C/min, followed by a cooling rate of 3 °C/min in air. The solid pallets were then broken up and ground down to powder form using mortar and pestle. The powders were filtered with a 10 micron sieve. The powders were mixed again with a wet-ball mill in alcohol (isopropanol) and then dried again in an oven to produce fine powders.
Two grams of prepared powder from each sample was mixed with 5 wt % of polyvinyl butyral (PVB) and 1.5 wt % carbon black. PVB was used as a binder and carbon black was used to increase the conductivity of the films. Ethylen-glycol-monobutyl-ether was used as a solvent for PVB to make pastes for screen printing. To fabricate sensors, alumina substrates were used to deposit copper electrodes using a novel approach as described previously [48]. The prepared pastes were then screen printed on the top of thin copper electrodes on alumina substrate using a DEK RS 1202 automatic screen printer. Figure 2 presents the configuration of the developed sensors. SEM images were obtained for the mixed powders and screen-printed thin films. XRD measurements (from 10° to 70°, 2θ) were also performed on the screen-printed sensing materials to examine the final compositions.

A gas testing chamber, designed and developed previously, was used to test the response of the three screen-printed sensors with different molecular weights of metal oxides. This specially designed gas testing chamber enable measurement of different gases with predefined concentrations using screen-printed sensors.

3. Results and Discussion

3.1. SEM and XRD Results

Figure 3A,C,E shows the SEM images for the powders of sample 1, 75/25; sample 2, 50/50; and sample 3, 25/75 TiO\(_2\)/ZnO Mwt % and Figure 3B,D,F shows the corresponding screen-printed thin films. The SEM images of powders from all three samples demonstrated similar morphology. The powder grain size was typically between 2 and 5 microns. The SEM images of the screen-printed
films (Figure 3B,D,E) demonstrated uniform deposition of the sensing material. The samples displayed a granular structure and good porosity. For Sample 1, with the highest TiO$_2$ contents, a large granular and porous structure was observed. For Sample 2, the screen-printed film showed a similar structure to sample one. The grain size was smaller than that of the Sample 1 sensor; however, the porosity was similar. In the third sample, a fine granulated structure was observed with an average grain size of 1 micron to 5 microns.

Figure 3. SEM images of TiO$_2$/ZnO mixed powder (A,C,E) and screen-printed sensing material (B,D,F) for Sample 1–3 respectively.

Figure 4 shows the XRD patterns of screen-printed samples from 10° to 70°, 2θ. The results were analyzed using JCPDs files No.: 18-1487 and 01-1292 for Zn$_2$TiO$_4$ and TiO$_2$, respectively. XRD data of the samples showed that, after heating and screen printing, the ratio of Zn$_2$TiO$_4$ to TiO$_2$ depended mainly on the ratio of TiO$_2$ to ZnO used in the preparation of the powder mixtures before heating. XRD data for Sample 2 and Sample 3, with 50/50 and 25/75 Mwt % of TiO$_2$/ZnO, showed that the highest intensity was observed for the peak associated with Zn$_2$TiO$_4$. However, in the case of Sample 1 (with 75/25 Mwt % TiO$_2$/ZnO), the highest intensity in the final composition was observed for TiO$_2$. The differences observed in the final compositions were due to solid-state reactions between both oxides during heating, and the ratio of oxides in the mixtures. Therefore, many characteristic peaks of TiO$_2$ were observed in the final composition of Sample 1. The XRD results of Zn$_2$TiO$_4$ were in good agreement with the previous studies [5,49–51].
where $\Delta R$ is change in resistance, $R_{\text{gas}}$ is sensor resistance when exposed to gas, and $R_{\text{air}}$ is base resistance of the sensor in air.

$$\Delta R = \left( \frac{R_{\text{gas}} - R_{\text{air}}}{R_{\text{air}}} \right) \times 100$$

3.2. Response of the Sensors to Propanol

Figure 5 shows the response of the sensors to propanol vapors at room temperature in increasing steps of 500 ppm at a concentration range of 500–3000 ppm. Figure 6A,B illustrates the response of the sensors to propanol vapors at room temperature at a concentration range of 2500–5000 ppm. The response for the sensors was calculated using the following relationship:

$\Delta R = \left( \frac{R_{\text{gas}} - R_{\text{air}}}{R_{\text{air}}} \right) \times 100$ (1)

where $\Delta R$ is change in resistance, $R_{\text{gas}}$ is sensor resistance when exposed to gas, and $R_{\text{air}}$ is base resistance of the sensor in air.

Figure 5. The response of the Zn$_2$TiO$_4$ sensors to propanol at concentration range 500–3000 ppm increasing with a step size of 500 ppm at room temperature.
Figure 6. The response of the Zn$_2$TiO$_4$ sensors to propanol at a concentration range of 2500–5000 ppm at room temperature. (A) The response of the sensors with time (Sec.) and (B) The response of the sensors with gas concentration (ppm).

From these results, it can be concluded that:

- The response of the sensors increased as the gas concentration increased;
- However, no significant difference was observed in the response of the three sensors at low concentrations; sensor 2 (50/50 TiO$_2$/ZnO) had the highest sensitivity for propanol, followed by sensor 3 and then sensor 1 at higher concentrations (above 4000 ppm);
- This difference in sensor response could be associated with the final composition of the sensing materials. The XRD results proved that the peaks of Zn$_2$TiO$_4$ were higher for Samples 2 and 3 (the highest density) than for Sample 1. The TiO$_2$ was at the highest density in Sample 1. In addition to this, the surface morphology of the three samples was also different in terms of the number, size and shape of the pores on the surface of the films (see Figure 3);
- The signal noise was high in the lower concentration range (500–2500 ppm) compared with the response of the same sensors for the higher concentration range (2500–5000 ppm). This high
noise could be attributed to the effect of a slight change in the working temperature or the effect of some other gases that were already in the air of the gas testing chamber.

In a previous study, Zn$_2$TiO$_4$ particles were prepared using the ball-milling technique, and deposited as a thick film to detect alcohol gases (ethanol) at 50 and 200 ppm over an operating temperature range of 300–500 °C [5]. The highest sensitivity of the sensor was observed at 500 °C. The sensor was developed without using any polymer binder, and can only be used for high temperature applications. ZnFe$_2$O$_4$ and NiFe$_2$O$_4$ thick films were also used in previous studies by our group to detect methanol, ethanol and propanol at room temperature [21–23,52]. In the current study, Zn$_2$TiO$_4$ exhibited good sensitivity to propanol at room temperature. The response of the sensor depends on the final composition of the sensing material. In this study, no significant effect was observed in the final composition of the response, particularly at lower concentrations, as can be seen in Figures 5 and 6.

It is well known that the interaction of a gas on the sensing material surface depends on the type of the sensing material (p- or n-type) and type of testing gas (oxidation or reduction gases). These two factors provide the basis for the increment or decrement in the resistivity of films.

The reaction of the gas on the surface of metal oxides has been reported in many studies [5,11,13,15,24]. However, the mechanism of the reaction of the gases on the surface of the films is still not well understood. In particular, for the sensors developed and tested in the current study, the interaction mechanism and conductivity response would be influenced by the complicated chemistry of the sensing material, which consists of composite metal oxides, polymer, and carbon black. Further detailed studies will be performed to investigate the adsorption of gas molecules on to the sensing material surface.

The Zn$_2$TiO$_4$ sensors developed in this study were novel in terms of composition. Conductive polymer was used as binder to combine the oxides and adhere it to the substrate. This study indicates that the use of the conductive polymer increased the pores in the surface of the films, which increased the sensitivity of the sensors at room temperature without heating the sensing material. Therefore, these sensors can be used for real-time monitoring of propanol with lower power consumption requirements; thus, they can be used in miniaturized sensing platforms and wearable sensing systems. Additionally, the use of copper electrodes makes the sensor more cost effective and able to interface with electronic circuits in simple configurations.

4. Conclusions

In the current work, the composition of ZnO/TiO$_2$ was varied significantly from those reported in the literature and, as a result, properties were observed that were different from those previously reported. Thick film gas sensors, based on a Zn$_2$TiO$_4$ semiconductor with different ZnO and TiO$_2$ contents were developed and tested for sensing propanol vapors. The electrochemical results from these sensors showed:

- They had good sensitivity to propanol vapor at room temperature;
- The response of the sensors monotonically increased as the gas concentration increased;
- XRD measurements of the screen-printed sensing materials illustrated that the final compositions (Zn$_2$TiO$_4$ to TiO$_2$) depended on the ratio of TiO$_2$ to ZnO used in preparing the mixtures before being heated;
- SEM images of the films showed granular microstructure ranging from 2–5 microns;
- Using copper as an electrode material makes sensors cost effective compared to sensors with Pt and Au electrodes;
- The developed sensors consume very low power compared with those sensors reported in the literature in [5,12], as heating of the sensing material is not required;
- The simple structure of the sensor with copper electrodes makes it easy to interface with electrical systems;
• The developed sensors can be used in various applications at room temperature, including as gas safety monitors;
• Further detailed studies are required to better understand the interaction mechanism between the sensing material and the tested gas.

Acknowledgments: This publication has emanated from research conducted with the financial support of the European Union’s Horizon 2020 Research and Innovation Programme under grant agreement No. 691473.

Author Contributions: All authors contributed in conceiving and designing the experiments. Ibrahim Gaidan performed the experiments. All authors analyzed the data and contributed in writing the paper.

Conflicts of Interest: The authors declare no conflict of interest.

References
1. Takada, T. Temperature drop of semiconductor gas sensor when exposed to reducing gases—Simultaneous measurement of changes in sensor temperature and in resistance. Sens. Actuators B Chem. 2000, 66, 1–3. [CrossRef]
2. Sberveglieri, G.; Comini, E.; Faglia, G.; Atashbar, M.Z.; Wlodarski, W. Titanium dioxide thin films prepared for alcohol microsensor application. Sens. Actuators B Chem. 2000, 66, 139–141. [CrossRef]
3. Wang, Y.; Chen, J.; Wu, X. Preparation and gas-sensing properties of perovskite-type SrFeO$_3$ oxide. Mater. Lett. 2001, 49, 361–364. [CrossRef]
4. Chu, X.; Liu, X.; Meng, G. Effects of CdO dopant on the gas sensitivity properties of ZnFe$_2$O$_4$ semiconductors. Sens. Actuators B Chem. 2000, 65, 1–3.
5. Santhaveesuk, T.; Gardchareon, A.; Wongratanaphisan, D.; Choopun, S. Ethanol sensing properties of Zn$_2$TiO$_4$ particles. Ceram. Int. 2015, 41, S809–S813. [CrossRef]
6. Mabrook, M.; Hawkins, P. A rapidly-responding sensor for benzene, methanol and ethanol vapours based on films of titanium dioxide dispersed in a polymer operating at room temperature. Sens. Actuators B Chem. 2001, 75, 197–202. [CrossRef]
7. Carotta, M.C.; Ferroni, M.; Gnani, D.; Guidi, V.; Merli, M.; Martinelli, G.; Casale, M.C.; Notaro, M. Nanostructured pure and Nb-doped TiO$_2$ as thick film gas sensors for environmental monitoring. Sens. Actuators B Chem. 1999, 58, 310–317. [CrossRef]
8. Yamada, Y.; Seno, Y.; Masuoka, Y.; Nakamura, T.; Yamashita, K. NO$_2$ sensing characteristics of Nb doped TiO$_2$ thin films and their electronic properties. Sens. Actuators B Chem. 2000, 66, 164–166. [CrossRef]
9. Chen, Y.; Xu, P.; Xu, T.; Zheng, D.; Li, X. ZnO-nanowire size effect induced ultra-high sensing response to ppb-level H$_2$S. Sens. Actuators B Chem. 2017, 240, 264–272. [CrossRef]
10. Xie, T.S.; Steffens, N.; Wen, K.; Liu, B.; Deb Nath, G.; Davydov, R.; Gomez, A.; Motayne, A. UV-assisted room-temperature chemiresistive NO$_2$ sensor based on TiO$_2$ thin film. J. Alloys Compd. 2015, 653, 255–259. [CrossRef] [PubMed]
11. Catto, A.C.; da Silva, L.F.; Ribeiro, C.; Bernardini, S.; Aguir, K.; Longo, E.; Mastelaro, V.R. An easy method of preparing ozone gas sensors based on ZnO nanorods. RSC Adv. 2015, 5, 19528–19533. [CrossRef]
12. Santhaveesuk, T.; Wongratanaphisan, D.; Choopun, S. Enhancement of Ethanol Sensing Properties by Alloying. IEEE Sens. J. 2010, 10, 39–43. [CrossRef]
13. Chen, H.; Liu, Y.; Xie, C.; Wu, J.; Zeng, D.; Liao, Y. A comparative study on UV light activated porous TiO$_2$ and ZnO film sensors for gas sensing at room temperature. Ceram. Int. 2012, 38, 503–509. [CrossRef]
14. Mun, Y.; Park, S.; An, S.; Lee, C.; Kim, H.W. NO$_2$ gas sensing properties of Au-functionalized porous ZnO nanosheets enhanced by UV irradiation. Ceram. Int. 2013, 39, 8615–8622. [CrossRef]
15. Perillo, P.M.; Rodrigue, D.F. A room temperature chloroform sensor using TiO$_2$ nanotubes. Sens. Actuators B Chem. 2014, 193, 263–266. [CrossRef]
16. Zhang, G.-Y.; Guo, B.; Chen, J. MC$_2$O$_4$ (M = Ni, Cu, Zn) nanotubes: Template synthesis and application in gas sensors. Sens. Actuators B Chem. 2006, 114, 402–409. [CrossRef]
17. Sun, F.; Li, X.; Liu, L.; Wang, J. Novel Zn–M–O (M = Sn, Co) sensing electrodes for selective mixed potential CO/C$_3$H$_8$ sensors. Sens. Actuators B Chem. 2013, 184, 220–227. [CrossRef]
18. Gawande, K.B.; Gawande, S.B.; Thakare, S.R.; Mate, V.R.; Kadam, S.R.; Kale, B.B.; Kulkarni, M.V. Effect of zinc: Cobalt composition in ZnCo$_2$O$_4$ spinels for highly selective liquefied petroleum gas sensing at low and high temperatures. *RSC Adv.* 2015, 5, 40429–40436. [CrossRef]

19. Joshi, N.; da Silva, L.F.; Jadhav, H.; M’Peko, J.C.; Torres, B.B.M.; Aguir, K.; Mastelaroa, V.R.; Oliveira, O.N., Jr. One-step approach for preparing ozone gas sensors based on hierarchical NiCo$_2$O$_4$ structures. *RSC Adv.* 2016, 6, 92655–92662. [CrossRef]

20. Schaller, E.; Bosset, J.O.; Escher, F. ‘Electronic noses’ and their application to food. *LWT-Food Sci. Technol.* 1998, 31, 305–316. [CrossRef]

21. Arshak, K.; Gaidan, I.; Moore, E.G.; Cunniffe, C. The effect of the addition of carbon black and the increase in film thickness on the sensing layers of ZnO/ZnFe$_2$O$_4$ in polymer thick film gas sensors. *Superlattices Microstruct.* 2007, 42, 348–356. [CrossRef]

22. Arshak, K.; Gaidan, I. NiO/Fe$_2$O$_3$ polymer thick films as room temperature gas sensors. *Thin Solid Films* 2006, 495, 286–291. [CrossRef]

23. Arshak, K.; Gaidan, I. Effects of NiO/TiO$_2$ addition in ZnFe$_2$O$_4$-based gas sensors in the form of polymer thick films. *Thin Solid Films* 2006, 495, 292–298. [CrossRef]

24. Da Silva, L.F.; M’Peko, J.C.; Catto, A.C.; Bernardini, S.; Mastelaro, V.R.; Aguir, K.; Ribeiro, C.; Longo, E. UV-enhanced ozone gas sensing response of ZnO-SnO$_2$ heterojunctions at room temperature. *Sens. Actuators B Chem.* 2017, 240, 573–579. [CrossRef]

25. Hongstith, N.; Chaopun, S. Enhancement of ethanol sensing properties by impregnating platinum on surface of ZnO tetrapods. *IEEE Sensors J.* 2010, 10, 34–38. [CrossRef]

26. Roessler, A.L.; Pratsinis, A.; Sahm, S.E.; Gurlo, T.; Barsan, A.; Weimar, N. Direct formation of highly porous semi-conducting gas sensors by selective filter for atmospheric pollutants detection. *Mater. Sci. Eng.* 2006, 390, 283–295.

27. Xu, H.; Liu, X.; Cui, D.; Li, M.; Jiang, M. A novel method for improving the performance of ZnO gas sensors. *Sens. Actuators B Chem.* 2006, 114, 283–295.

28. Kersen, U.; Holappa, L. H$_2$S-sensing properties of SnO$_2$ produced by ball milling and different chemical reactions. *Anal. Chim. Acta* 2006, 562, 110–114. [CrossRef]

29. Viricelle, J.; Fauly, J.P.; Mazet, A.; Brunet, L.; Bouvet, J.; Varenne, M.; Pijolat, C. Selectivity improvement of semi-conducting gas sensors by selective filter for atmospheric pollutants detection. *Mater. Sci. Eng.* 2006, 290–296. [CrossRef]

30. Kamionka, M.; Breuil, P.; Pijolat, C. Atmospheric pollution measurement with a multi-materials sensing device. *Mater. Sci. Eng.* 2006, 26, 186–195. [CrossRef]

31. Jain, K.; Pant, R.P.; Lakshmikumar, S.T. Effect of Ni doping on thick film SnO$_2$ gas sensor. *Sens. Actuators B Chem.* 2006, 113, 823–829. [CrossRef]

32. Lampe, U.; Simon, E.; Pohle, R.; Fleischer, M.; Meixner, H.; Frerichs, H.P.; Kiss, G. GasFET for the detection of reducing gases. *Sens. Actuators B Chem.* 2005, 111, 106–110. [CrossRef]

33. Pijolat, C.; Viricelle, J.P.; Tourignier, G.; Montmeat, P. Application of membranes and filtering films for gas sensors improvements. *Thin Solid Films* 2005, 490, 7–16. [CrossRef]

34. Saukko, S.; Lassi, U.; Lantto, V.; Kroneld, M.; Novikov, S.; Kuivalainen, P.; Mizsei, J. Experimental studies of O$_2$-SnO$_2$ surface interaction using powder, thick films and monocrystalline thin films. *Thin Solid Films* 2005, 490, 48–53. [CrossRef]

35. Kotsikau, D.; Ivanovskaya, M.; Orlik, D.; Falasconi, M. Gas-sensitive properties of thin and thick film sensors based on Fe$_2$O$_3$-SnO$_2$ nanocomposites. *Sens. Actuators B Chem.* 2004, 101, 199–206. [CrossRef]

36. Ivanov, P.; Llobet, E.; Vilanova, X.; Brezmes, J.; Hubalek, J.; Correig, X. Development of high sensitivity ethanol gas sensors based on Pt-doped SnO$_2$ surfaces. *Sens. Actuators B Chem.* 2004, 99, 201–206. [CrossRef]

37. Su, P.-G.; Chen, I.C. Laminating two-layer thick films structure tin oxide-based butane gas sensor operating at low temperature. *Sens. Actuators B Chem.* 2004, 99, 304–309. [CrossRef]
40. Wagh, M.S.; Patil, L.A.; Seth, T.; Amalnerkar, D.P. Surface cupricated SnO$_2$-ZnO thick films as a H$_2$S gas sensor. Mater. Chem. Phys. 2004, 84, 228–233. [CrossRef]
41. Choi, U.-S.; Sakai, G.; Shimanoe, K.; Yamazoe, N. Sensing properties of SnO$_2$-Co$_3$O$_4$ composites to CO and H$_2$. Sens. Actuators B Chem. 2004, 98, 166–173. [CrossRef]
42. Chu, X.; Cheng, Z. High sensitivity chlorine gas sensors using CdSnO$_3$ thick film prepared by co-precipitation method. Sens. Actuators B Chem. 2004, 98, 215–217.
43. Chu, X. Dilute CH$_3$SH-sensing characteristics of BaSnO$_3$ thick film sensor. Mater. Sci. Eng. B 2004, 106, 305–307. [CrossRef]
44. Zhu, B.L.; Xie, C.S.; Wang, W.Y.; Huang, K.J.; Hu, J.H. Improvement in gas sensitivity of ZnO thick film to volatile organic compounds (VOCs) by adding TiO$_2$. Mater. Lett. 2004, 58, 624–629. [CrossRef]
45. Chu, X.; Zheng, C. Sulfide-sensing characteristics of MFe$_2$O$_4$ (M = Zn, Cd, Mg and Cu) thick film prepared by co-precipitation method. Sens. Actuators B Chem. 2003, 96, 504–508.
46. Noh, W.; Shin, Y.; Kim, J.; Lee, W.; Hong, K.; Akbar, S.A.; Park, J. Effects of NiO addition in WO$_3$-based gas sensors prepared by thick film process. Solid State Ionics 2002, 152–153, 827–832. [CrossRef]
47. Solis, J.L.; Saukko, S.; Kish, L.; Granqvist, C.G.; Lantto, V. Semiconductor gas sensors based on nanostructured tungsten oxide. Thin Solid Films 2001, 391, 255–260. [CrossRef]
48. Arshak, K.; Cunniffe, C.; Moore, E.; Cavanagh, L.; Harris, J. A novel approach to electronic nose-head design, using a copper thin film electrode patterning technique. In Proceedings of the 28th International Spring Seminar on Electronics Technology, Wiener Neustadt, Austria, 19–22 May 2005; pp. 185–190.
49. Girish, K.M.; Naik, R.; Prashantha, S.C.; Nagabhushana, H.; Nagaswarupa, H.P.; Raju, K.A.; Nagabhushana, B.M. Zn$_2$TiO$_4$: Eu$^{3+}$ anophosphor: Self explosive route and its near UV excited photoluminescence properties for WLEDs. Spectrochim. Acta Part A Mol. Biomol. Spectrosc. 2015, 138, 857–865. [CrossRef] [PubMed]
50. Siriwong, C.; Tamaekong, N.; Panichpphant, S. Characterization of single phase Pt-doped Zn$_2$TiO$_4$ nanoparticles synthesized by flame spray pyrolysis. Mater. Lett. 2012, 68, 97–100. [CrossRef]
51. Siriwong, C.; Panichpphant, S. Flame-made single phase Zn$_2$TiO$_4$ nanoparticles. Mater. Lett. 2011, 65, 2007–2009. [CrossRef]
52. Arshak, K.; Gaidan, I. Development of an array of polymer/MnO$_2$/Fe$_2$O$_3$ mixtures for use in gas sensing applications. Sens. Actuators B Chem. 2006, 118, 386–392. [CrossRef]