

Article

Flame-Spray-Made Undoped Zinc Oxide Films for Gas Sensing Applications

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Abstract: Using zinc naphthenate dissolved in xylene as a precursor undoped ZnO nanopowders were synthesized by the flame spray pyrolysis technique. The average diameter and length of ZnO spherical and hexagonal particles were in the range of 5 to 20 nm, while ZnO nanorods were found to be 5–20 nm wide and 20–40 nm long, under 5/5 (precursor/oxygen) flame conditions. The gas sensitivity of the undoped ZnO nanopowders towards 50 ppm of NO₂, C₂H₅OH and SO₂ were found to be 33, 7 and 3, respectively. The sensors showed a great selectivity towards NO₂ at high working temperature (at 300 °C), while small resistance variations were observed for C₂H₅OH and SO₂, respectively.

Keywords: undoped ZnO; flame spray pyrolysis; NO₂; C₂H₅OH; SO₂; gas sensor

1. Introduction

Zinc oxide has attracted increased attention during the last few years due to the possibility of its relatively simple transformation into various nanoscale structures. Nanostructures like rods and particles

have become the most promising research materials because of their wide range of applications. Different techniques, namely sol-gel [1], spray pyrolysis [2], hydrothermal method [3,4], electrospinning [5], thermal evaporation [6,7], *etc.* [8–13] are prevalent for the synthesis of zinc oxide nanoparticles and nanorods. In the present work, nanorods and nanoparticles have been prepared by flame spray pyrolysis (FSP), a promising technique for the synthesis of high purity nano-sized materials with controlled size and crystallinity in a single step. This was systematically investigated by using an external-mixing gas-assisted atomizer supported by six premixed methane-oxygen flamelets [14].

Semiconducting metal oxide sensors have been extensively studied due to their simple preparation and high sensitivity under ambient conditions [15–20]. Zinc oxide (ZnO), an n-type metal oxide semiconductor sensing material with a wide band gap ($E_g = 3.37$ eV at 300 K), has attracted much attention due to its high chemical stability, low cost, and good flexibility in fabrication. It was found that ZnO exhibits pronounced gas sensing properties towards many toxic/non-toxic gases such as NO₂, SO₂, ethanol, *etc.* [21–31]. A summary on the sensing properties toward NO₂, ethanol (C₂H₅OH) and SO₂ gases of the undoped ZnO prepared by several synthetic methods is shown in Table 1.

Table 1. A summary on the gas sensing properties of differently-prepared undoped ZnO for NO₂, ethanol (C₂H₅OH) and SO₂ gases.

Authors [ref.]	Method	Nanoparticles	Gas concentration	Sensitivity
Ghimbeu <i>et al.</i> [21]	Electrostatic spray deposition (ESD) technique	Undoped ZnO	1 ppm of NO ₂ , at 300 °C	~1.84
Cho <i>et al.</i> [22]	Hydrothermal	Undoped ZnO	1 ppm of NO ₂ , at 300 °C	~1.8
Sadek <i>et al.</i> [23]	Conventional solid-state method	Undoped ZnO	10 ppm of NO ₂ , at 350 °C	~1.81
Lupan <i>et al.</i> [26]	A solution method	Undoped ZnO	100 ppm of SO ₂	<0.5
Singh <i>et al.</i> [28]	A simple chemical route	Undoped ZnO	250 ppm of ethanol, at 400, 600 and 800 °C	~6.5, 5.6 and 4,
Hieu <i>et al.</i> [31]	Thermal evaporation	Undoped ZnO	500 ppm of ethanol, at 300 °C	5.3
Present work	Flame spray pyrolysis (FSP)	Undoped ZnO	1, 5 and 10 ppm of NO ₂ , at 300 °C	~2.7, 6.2 and 11.8
			100 ppm of SO ₂ , at 300 °C	~2.8
			200, 300 and 500 ppm of ethanol, at 300 °C	~18.2, 22.4 and 27.5

Great interest in improving the gas sensitivity as well as selectivity and in decreasing the working temperature has been witnessed. Nitrogen dioxide (NO₂) is considered a common air pollutant produced during combustion in automotive engines, industrial factories, and power plants. Therefore, the development of stable NO₂ gas sensors that can detect extremely low concentrations of NO₂ with high sensitivity is highly desirable [32]. In this study, undoped ZnO nanopowders have been prepared by the flame spray pyrolysis process and their gas sensing responses towards different gases have been comparatively examined. In particular, three types of sensors were tested under oxidizing and reducing gases, like nitrogen dioxide, ethanol and sulfur dioxide.

2. Experimental

2.1. Particle synthesis and characterization

Zinc naphthenate (Aldrich, 8 wt% Zn) was used as a precursor. The precursor was dissolved in xylene (Carlo Erba, 98.5%) to obtain a 0.5 mol/L precursor solution. In a typical run, the precursor was fed into a FSP reactor by a syringe pump with a rate of 5 mL/min while 5 L/min O₂ was being dispersed (5/5 flame). The gas flow rates of methane and O₂ supporting flamelets were 1.19 and 2.46 L/min, respectively. The pressure drop at the capillary tip was kept constant at 1.5 bars by adjusting the orifice gap area at the nozzle.

The flame height was observed to be approximately 10–12 cm. The sample showed a yellowish-orange flame. The liquid precursor mixture was rapidly dispersed by a gas stream and ignited by a premixed methane/oxygen flame. After evaporation and combustion of precursor droplets, particles are formed by nucleation, condensation, coagulation and coalescence. Finally, the nanoparticles were collected on glass microfiber filters with the aid of a vacuum pump. The undoped ZnO nanopowders were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Specific surface area (SSA_{BET}) of the nanoparticles was also investigated by nitrogen adsorption (BET analysis).

2.2. Sensing film preparation and characterization of the gas sensing properties

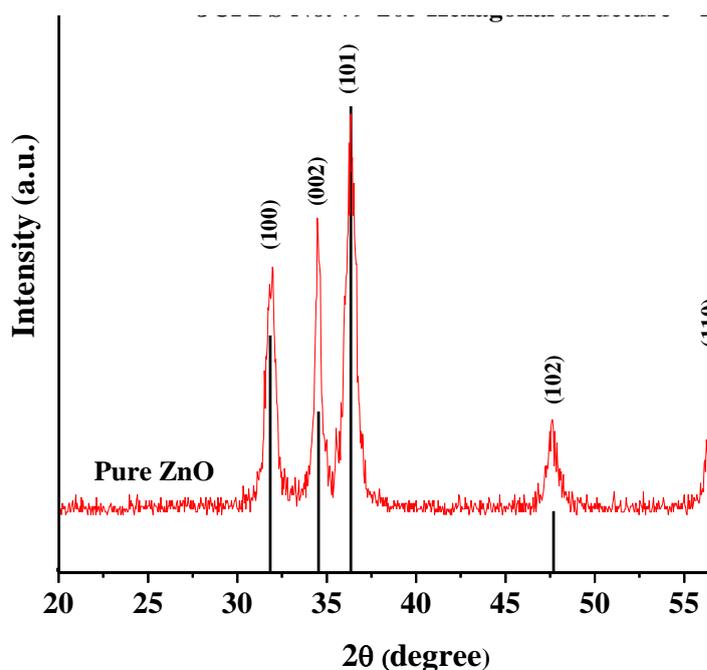
The undoped ZnO sensing film was prepared by mixing the nanoparticles into an organic paste composed of ethyl cellulose and terpineol, which acted as a vehicle binder and solvent, respectively. The resulting paste was spin-coated on Al₂O₃ substrates with predeposited interdigitated Au electrodes. The films were then annealed at 400 °C for 2 h (with heating rate of 2 °C/min) for binder removal. The morphology and the cross section of sensing films were analyzed by SEM.

The gas-sensing characteristics of the undoped ZnO nanoparticles towards NO₂, C₂H₅OH and SO₂ were characterized. The flow through technique was used to test the gas-sensing properties of thin films. A constant flux of synthetic air of 2 L/min was mixed with desired concentrations of pollutants. All measurements were conducted in a temperature-stabilized sealed chamber at 20 °C under controlled humidity. The external NiCr heater was heated by a regulated dc power supply to different operating temperatures. The operating temperature was varied from 200 °C to 350 °C. The resistances of various sensors were continuously monitored with a computer-controlled system by voltage-amperometric technique with 5 V dc bias and current measurement through a picoammeter. The sensor was exposed to a gas sample for ~5 minutes for each gas concentration testing and then the air flux was restored for 15 minutes. The concentration of NO₂, C₂H₅OH and SO₂ were varied from 1 to 50 ppm, 50 to 100 ppm and 10 to 500 ppm, respectively.

3. Results and Discussion

3.1. Particle properties

Figure 1 shows the XRD patterns of the undoped ZnO sample. All peaks can be confirmed to correspond to the hexagonal structure of ZnO (JCPDS No. 79-205).

Figure 1. The XRD patterns of flame-spray-made (5/5) undoped ZnO nanopowders.

An average BET equivalent particle diameter (d_{BET}) was calculated using the average density of ZnO as shown in Table 2. The accurate particle size and morphology of undoped ZnO dispersion were confirmed by SEM and TEM images.

Table 2. The specific surface area (SSA_{BET}) and d_{BET} of undoped ZnO nanoparticles.

Sample	Specific surface area (SSA_{BET}), (m^2/g)	d_{BET} (nm)
Undoped ZnO	78.8	13.6

Figure 2 shows the morphology of highly crystalline flame-made (5/5) undoped ZnO nanoparticles from SEM analysis. The SEM micrograph clearly showed nanostructural homogeneities and remarkably different morphologies of the undoped ZnO nanoparticles synthesized by the FSP technique. The SEM result showed the presence of agglomerated nanospheres with an average diameter of 10–20 nm. Therefore, from this observation only the rough morphology was found. Nevertheless, the accurate sizes and morphology of the nanoparticles can be estimated from the TEM analysis. While the SEM images provide 3-D morphology and estimated particle sizes, TEM images can reveal internal structure and a more accurate measurement of particle size and morphology.

Figure 3 shows the TEM-bright-field images of undoped ZnO nanoparticles. The ZnO morphologies were revealed to be spherical, hexagonal and rod-like. The presence of ZnO spherical nanoparticles along with a few nanorods was observed as shown in Figure 3(a). The crystallite sizes of spherical particles were found to be in the range of 5–20 nm whereas the nanorods were found to be ranging from 5–20 nm in width and 20–40 nm in length. Hexagonal ZnO nanoparticles with the size of 5–20 nm were also observed, as shown in Figure 3 (b).

Figure 2. The SEM micrograph of highly crystalline flame-made (5/5) undoped ZnO nanoparticles.

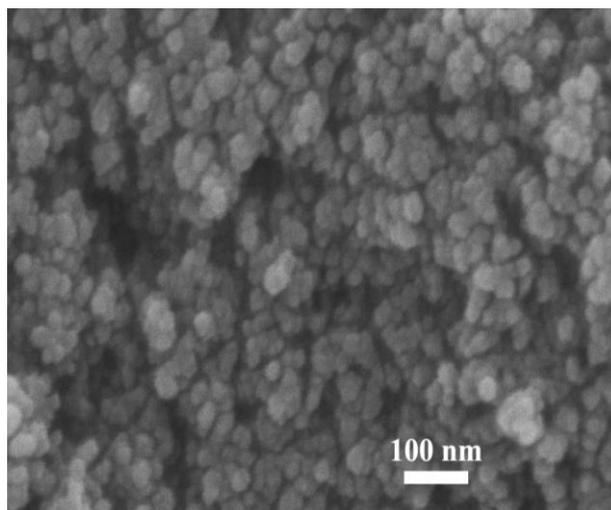
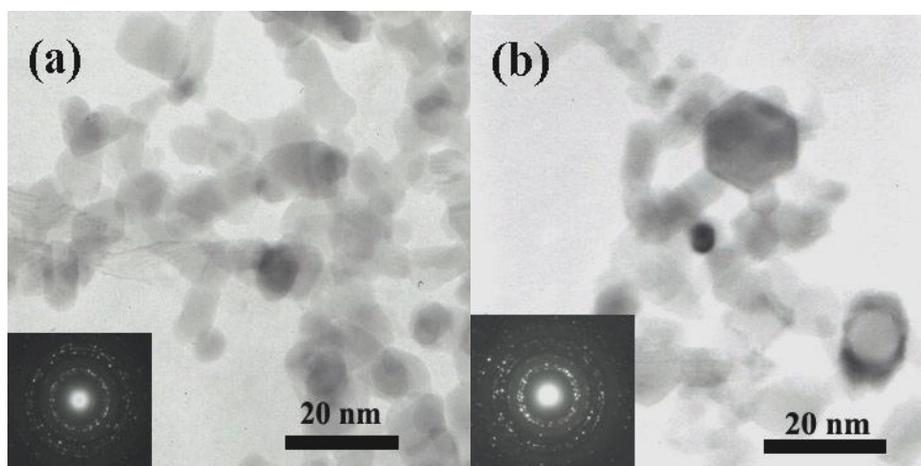


Figure 3. The TEM images of undoped ZnO morphologies showing the spherical, hexagonal and rod-like shapes.



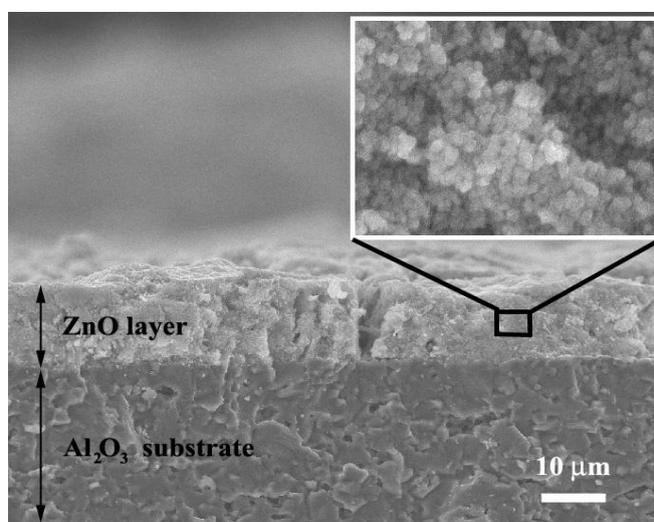
3.2. SEM sensing layer

The cross-section, film thickness, and surface morphology of the undoped ZnO sensing film layer after annealing and sensing test at 300 °C were observed using SEM analysis, as shown in Figure 4. The thickness of sensing film was approximately 10 μm (side view) which benefited tremendously the NO₂, C₂H₅OH and SO₂ gas sensing properties. Irregularities in the film thickness (top view) stem from the spin coating technique. The high density Al₂O₃ substrate interdigitated with Au electrodes was also visible. After the annealing process, a denser film layer was formed.

The sensitivity and response time of the thick films of the undoped ZnO nanoparticles as a function of NO₂, C₂H₅OH and SO₂ concentrations at 300 °C are shown in Figure 5. In Figure 5(a), it can be seen that the sensitivity toward NO₂ is increased considerably at 50 ppm NO₂ concentration. The sensitivity and response time for the undoped ZnO nanoparticles at 50 ppm NO₂ concentration were found to be 33 and 7 s, respectively. The sensitivity, however, are decreased considerably by testing the undoped ZnO sensor with C₂H₅OH and SO₂ at 50 ppm concentration of each gas. The sensitivity of 7

and 3 with the response time of 94 and 17 s are obtained at 50 ppm of C_2H_5OH and 50 ppm of SO_2 , respectively. It is important to note that the undoped ZnO nanoparticles behave as an n-type semiconductor with decreased resistance during NO_2 , C_2H_5OH and SO_2 gas exposure, which is a typical behavior of ZnO material [33]. The gas-sensing sensitivity, S , is defined as the ratio of R_a/R_g where R_a is the resistance in dry air, and R_g is the resistance in test gas. The response time, T_{res} , is defined as the time required until 90% of the response signal is reached. The recovery time, T_{rec} , denotes the time needed until 90% of the original baseline signal is recovered. The sensor behaviors under the operating temperature of 300 °C versus the NO_2 concentrations ranging from 1–50 ppm for the flame-made undoped ZnO nanoparticles were plotted as shown in Figure 5(a). The changes in resistance of the undoped ZnO sensor for C_2H_5OH and SO_2 gases under exposure to 50–1,000 ppm of C_2H_5OH and 10–500 ppm of SO_2 during forward cycle at 300 °C are shown in Figures 5(b,c), respectively.

Figure 4. The SEM micrographs of flame-made undoped ZnO thick films sensor on an Al_2O_3 substrate interdigitated with Au electrodes after annealing and sensing test at 300 °C in dry air. The film thickness was approximately 10 μm .



It is well known that the sensitivity of a semiconductor gas sensor is highly influenced by its operating temperature [34,35]. In order to determine the optimum operating temperatures, the response of the undoped ZnO gas sensor to 50 ppm concentration of nitrogen dioxide, ethanol and sulfur dioxide in air was tested as a function of operating temperature, as shown in Figure 6. It is clear that the responses of three gases tested varied with operating temperature. The sensitivity to NO_2 first increased with temperature, up to 300 °C, and then gradually decreased. The maximum sensitivity towards NO_2 was 33, at 300 °C. For ethanol and SO_2 , the sensitivity continuously increased when operating temperatures varied from 200 to 300 °C, and then decreased. The maximum sensitivities obtained were 7 and 3, at 300 °C. Therefore, optimal operating temperatures of 300 °C were chosen for NO_2 , ethanol and SO_2 respectively, to further examine the characteristics of the gas sensor. Results suggest that the undoped ZnO sensor can act as a multifunctional selective gas sensor, detecting NO_2 , ethanol and SO_2 gases. In other words, the above mentioned sensor can be used as an excellent NO_2 sensor at an operating temperature of 300 °C.

Figure 5. The change in resistance of undoped ZnO sensor for NO₂ (a) C₂H₅OH (b) and SO₂ (c) gases under exposure to oxidizing gas of NO₂ and reducing gases of C₂H₅OH and SO₂ during forward cycle at 300 °C, respectively.

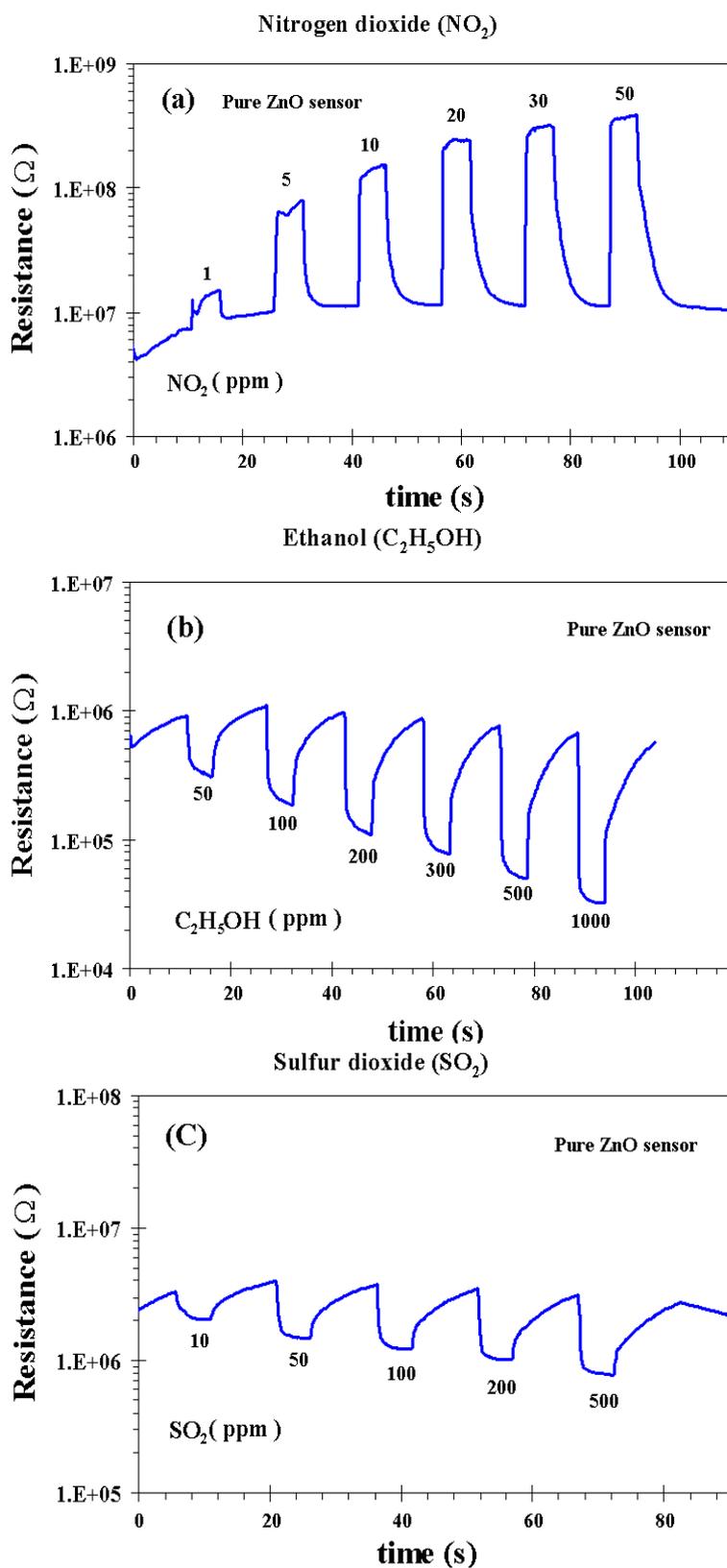
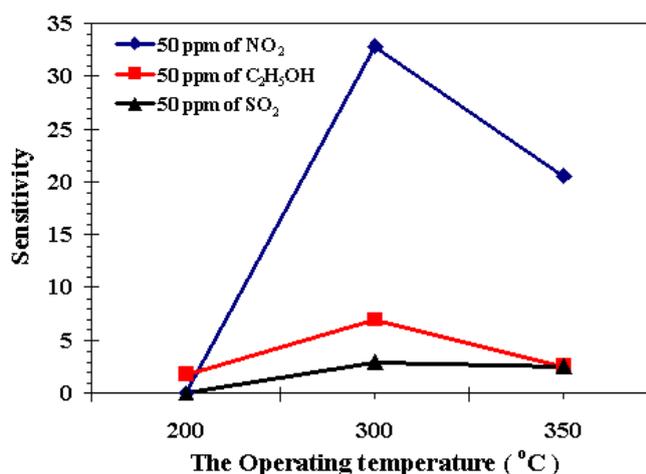
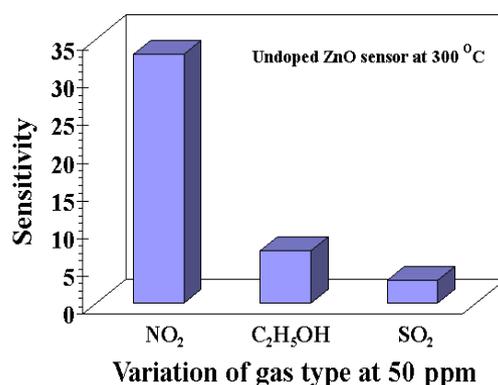


Figure 6. The sensitivity *versus* variation of the operating temperature of NO₂, C₂H₅OH and SO₂ (at 50 ppm of concentration) for the undoped ZnO sensor.



The gas sensing selectivity of the undoped ZnO gas sensor has been characterized towards one common oxidizing gas, nitrogen dioxide (NO₂), and two other common reducing gases, ethanol (C₂H₅OH) and sulfur dioxide (SO₂) as shown in Figure 7. In Figure 7, the sensitivities towards NO₂, C₂H₅OH and SO₂ under the operating temperature of 300 °C were found to be 33, 7 and 3, respectively. This indicates an excellent NO₂ selectivity of our undoped ZnO gas sensor.

Figure 7. The sensitivity variation of the undoped ZnO sensor testing with 50 ppm concentration of NO₂, C₂H₅OH and SO₂ under the operating temperature of 300 °C.



The sensitivities of the flame-made ZnO sensor towards different concentrations of NO₂, C₂H₅OH and SO₂ gases obtained from our studies are summarized in Table 3. In comparison with the previously reported sensitivities of other ZnO sensors given in Table 1 [21–24], the flame-made ZnO films showed higher sensitivity towards the same NO₂ concentration in all cases. Sensitivity of flame-made ZnO films towards 100 ppm of SO₂ was 2.8, whereas the result from Lupan *et al.* [26] was less than 0.5. Likewise flame-made ZnO films showed sensitivity towards 200, 300 and 500 ppm of ethanol as 18.2, 22.4 and 27.5 respectively which were higher than the values reported by Singh *et al.* [28] and Hieu *et al.* [31].

Table 3. Sensitivity of flame-made undoped ZnO nanoparticles towards different concentrations of NO₂, C₂H₅OH and SO₂ gases under the operating temperature of 300 °C.

Gas concentration	Sensitivity
1, 5, 10, 20, 30 and 50 ppm of NO ₂	2.7, 6.2, 11.8, 18.5, 26.7 and 33
100 ppm of SO ₂	2.8
200,300, and 500 ppm of ethanol	18.2, 22.4 and 27.5

4. Conclusions

In summary, we have shown that FSP is a promising technique for the synthesis of high purity nano-sized materials with controlled size and crystallinity in a single step, exemplified by the fabrication of an undoped ZnO array sensor that can sense NO₂, C₂H₅OH and SO₂ gases. The undoped ZnO-based NO₂ gas sensor showed the lowest detection limit of 1 ppm with short response and recovery time. Moreover, the sensors showed a high selectivity towards NO₂ at 300 °C when compared with C₂H₅OH and SO₂ gases, respectively. The sensitivity of undoped ZnO film towards 50 ppm of NO₂, C₂H₅OH and SO₂ were 33, 7 and 3 respectively.

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