Particle Size Effect On Gas Sensing Properties Of ZnO Pellets

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Abstract— **In this work, zinc oxide (ZnO) nanopowders were prepared by a homogeneous precipitation method. Eight samples were prepared under different conditions using Taguchi method. Structural and morphological properties were analyzed by X-ray diffraction (XRD) and scanning electron microscopy (SEM), respectively. Pellets were manufactured at different pressing conditions and pellets were measured in propane gas (C_3H_8) at different concentration and measuring temperatures. Best sensitivity was obtained with the pellet ZnO-1 of a particle size of 38.7 nm with an order of magnitude of 4.**

Keywords—Taguchi Method; ZnO pellets; gas sensing; ZnO nanopowders

I. Introduction

In recent years, the monitoring of toxic gases has become an important point of discussion as these gases exist in domestic and industrial environments, causing irreversible damage to both health and the environment (1). For this reason, the scientific community has opted for the development of a reliable, easy handling and low cost gas sensor (2). Semiconducting metal oxide sensors are one of the best options, as these a cheap and simple method for monitoring gases (3). In the literature a variety of metal oxides are reported in the design of chemical gas sensors, such as: WO_3 (4), NiO (5), TiO_2 (6), ZrO_2 (7), SnO (8), In_2O_3 (9), Nb_2O_5 (10), CuO (11), and ZnO (12), amongt others. ZnO and SnO_2 are the most studied materials, due to its simple synthesis in standard laboratories.

With a wide bandgap of Eg = 3.37 eV, a large exciton binding energy, 60meV, at room temperature; an n-type metal oxide semiconductor sensing material and it has good chemical stability, ZnO is one of the most attractive and extensively functional semiconductor materials (13-15). Various methods have been reported for producing the ZnO film form, such as pulsed-laser deposition (15), electrochemical reaction (16), and spray pyrolysis (17); but a few authors have reported techniques to obtain the Zinc oxide into a powder form, such as the sol-gel method (18) and homogeneous precipitation (19). Using the homogeneous precipitation has demonstrated to obtain a high quality material.

ZnO is a multifunctional material by its interesting optical, physical and electrical properties, so this material has been widely used in the optoelectronic, and its main applications are solar cells (20), gas sensors (21), photocatalysis (22), varistors (23), etc. Therefore, ZnO is considered to be a good chemical gas sensor, which gas molecules are adsorbed on the surface, transforming this chemical information into an electrical signal (24-25).

Sensing properties have a close relationship with the structure of materials, and then an optimal nanostructure is a key factor for gas sensors materials, producing an increase in the active surface area of the material. A nanometric level, zinc oxide has been reported with different geometries such as, nanospheres (26), nanoneedles (27), nanowires (28), nanorods (29), etc.; preserving its physical properties of nanocrystals. Some sensitivity results, which have been reported in the literature with different nanostructures, are shown in Table I.

TABLE I. BRIEF REVIEW OF THE RELATIONSHIP BETWEEN NANOSTRUCTURES AND SENSITIVITY OF ZNO

No.	*Structure / Size [nm]*	*Atmosphere*	*Sensitivity / Operating Temperature [°C]*	*Reference*
1	Nanorods / 100	O_2, H_2 and CO_2	0.90, 0.94, and 0.98 (%) / 100-120	(25)
2	Polymorph / 20	C_2H_5OH, gasoline, C_4H_{10}, and H_2	4.8, 11.5, 8.2, and 6.4 / 300	(31)
3	Nanorods / 5.6	NO_2	0.9 (%) / 290	(32)
4	Irregular/ 60-70	CO	6.5 / 250-300	(33)
5	Nanosphere/ 6	C_2H_5OH	68.3 / 391	(34)
6	Nanoflower / L = 700 and D= 800	C_2H_5OH and NO_2	4.2 and 3.1 / 350	(35)
7*	Nanowire / D= 100	H_2, NH_3, i-Butane, and CH_4	0.34 %/ Room Temperature	(36)

In all examples, the sensitivity was defined as the ratio ($S = R_a / R_g$) of the resistance of the sensor in dry air (R_a) to that in target gases (R_g) at each temperature, except the number 7, the sensitivity for this reference was defined as ($[S = G_g - G_a]/ G_g$) where G_g and G_a are the conductance of ZnO nanowires.

Since in the homogeneous precipitation method there are many parameters that are important to prepare powders of nanometric size, the Taguchi statistical method was used. Taguchi method is a combination of mathematics and statistics used for robust processes (30).

This study aims (1) to investigate the parameters involved in obtaining ZnO nanopowders by the homogeneous precipitation method, applying Taguchi method, and (2) to analyze the effect of particle size on the sensitivity of gas sensor fabricated in the form of pellets in a propane, C_3H_8, atmosphere.

II. Methodology

A. Preparation of ZnO nanopowders

ZnO nanopowders were synthesized by homogeneous precipitation method. The precursors started with zinc acetate dihydrate [$Zn(CH_3COO)_2 \cdot 2H_2O$] and zinc nitrate [$Zn(NO_3)_2 \cdot 6H_2O$] as Zn precursors. Ethanol (C_2H_5OH), and Methanol (CH_3OH), as solvent (Ethanol (C_2H_5OH) and Methanol (CH_3OH) were used as solvents). Sodium hydroxide (NaOH), and ammonium carbonate [$(NH_4)_2CO_3$] were used as agent precipitating. All the chemicals were analytical grade. The homogeneous precipitation method is generally as follows: first, two aqueous solutions were prepared separately; one contains zinc ions dissolved in 60 ml of deionized water, and the other excess OH^- dissolved in 100 ml of methanol or ethanol, according to the matrix (Table III). These solutions were mixed keeping a temperature of 70 °C and constant stirring by 2 h. The precipitate was centrifuged and washed with methanol for three times. The obtained paste was dried in a conventional furnace at 100 °C for 1 h, to be later calcined at 400°C for 2 h.

Taguchi design method was utilized to explore the variables involved in the synthesis of ZnO powders and find the smallest particle size. Table II shows the parameters and levels used in this experiment. Using Taguchi design, the number of experiments is reduced to 8 in comparison to 64 that if the traditional experimental method was used. The orthogonal array L8 is showed in Table III.

TABLE II. PARAMETERS AND LEVELS USED IN THIS STUDY.

ID	Factor	Level	
		1	2
A	Precursor type	$Zn(CH_3COO)_2 \cdot 2H_2O$	$Zn(NO_3)_2 \cdot 6H_2O$
B	Agent precipitating type	NaOH	$(NH_4)_2CO_3$
C	ZnO molar concentration	0.1	0.35
D	Excess OH^- (%)	60	70
E	Solvent Type	CH_3OH	C_2H_5OH
F	Stirring rate (rpm)	100	1200

TABLE III. ORTHOGONAL ARRAY FOR CONDUCTING EXPERIMENTS CORRESPONDING TO L8 TAGUCHI'S EXPERIMENTAL.

Sample	A	B	C	D	E	F
ZnO-1	1	1	1	1	1	1
ZnO-2	1	1	1	2	2	2
ZnO-3	1	2	2	1	1	2
ZnO-4	1	2	2	2	2	1
ZnO-5	2	1	2	1	2	2
ZnO-6	2	1	2	2	1	1
ZnO-7	2	2	1	1	2	1
ZnO-8	2	2	1	2	1	2

B. Characterization of the samples

The crystal structure and orientation of ZnO powders were studied with X-ray diffraction (XRD) using the Cu-kα radiation (λ = 0.15406 nm) in a diffractometer system (PANalytical, model X'PERT-PRO). The spectra were taken in the 2Θ mode, in the 30 to 80° range, with a 0.02°/min scan increment. The morphological properties were determined by scanning electron microscopy (SEM), AURIGA microscope.

C. ZnO pellets fabrication

The sensor pellets were manufactured mechanically, using a hydraulic pressing machine (Mexican ITAL). In order to get a mechanically stable pellet, 0.60 g of powder were used in each sample at 10 Ton for 30 min using a Ø12 mm die. Two ohmic contacts were outlined onto the pellets by using high purity silver paint (from SPI).

Finally, sensitivity tests were carried out in a sealed quartz chamber containing propane gas at different concentrations: 1, 5, 50, 100, 200, 300, 400, and 500 ppm, also the operation temperatures were variable: 100, 200 and 300 ° C.

The electrical resistance measurements were obtained using a Keithley 2001 multimeter. The gas concentration into the quartz chamber was controlled by varying the partial pressure of propane and it was detected using a TM20 Leybold detector. The sensitivity, S, was calculated according to equation 1.

$$S = [R_a - R_g] / R_g \qquad (1)$$

Where, R_a, is the the electrical resistance measured in a normal atmosphere, and R_g, is the the electrical resistance measured in a propane atmosphere.

III. Results and Discussion

A. XRD diffraction analysis

To evaluate the structural properties of the nanoparticles obtained, X ray diffraction technique was used. Fig. 1 shows the XRD diffraction patterns of 8 samples calcined at 400°C, which all peaks indicate a hexagonal wurtzite structure ZnO, according to the card (JCPDS 36-1451) (21). In all the cases a preferential growth is observed in the (101) plane located at 34.3°.

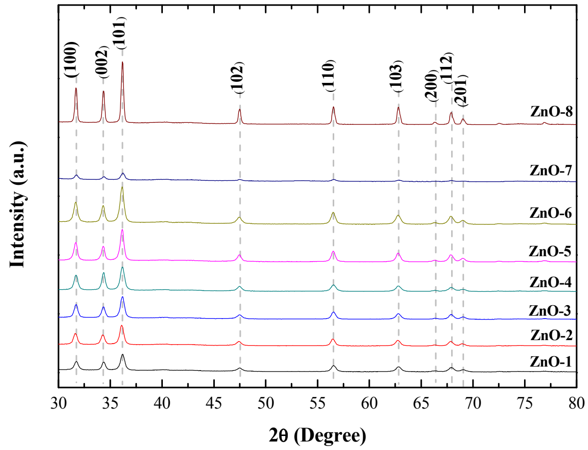

Fig. 1. XRD pattern of ZnO nanopowders calcinated at 400°C for 2 h.

The crystallite size of the ZnO nanoparticles were estimated from the Scherrer equation (Eq. 2) using the highest peak (101), resulting a size around 32-55 nm.

$$D_{hkl} = c\lambda / \beta\cos\theta \quad (2)$$

Where, c is a constant (~0.89), λ is the X-Ray wavelength (0.154 nm), θ is the Bragg´s diffraction angle in degrees, and β is the line width at half peak intensity in radians (36).

B. SEM analysis

The average particle size of each sample was determined statistically from SEM images, see Fig. 2.

In addition, the SEM images revealed a spherical morphology for all (of the obtained) ZnO powders. Also, some agglomerates were observed, a particle size and uniform distribution in Fig. 2 (a), (b), (e), (f), (g) and (h). In Fig. 2 (d) the self-assembly of a porous sphere is observed because at the junction of each spherical particle there is a notorious hole thereby creating pores.

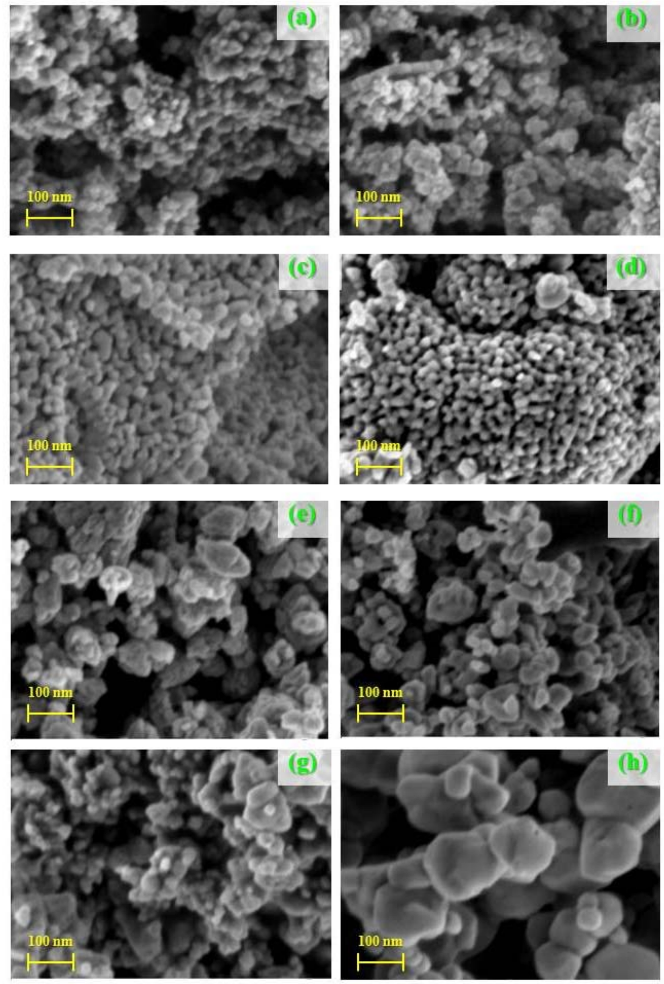

Fig. 2. SEM images of the samples ZnO-1 to ZnO-8 obtained under different conditions, applying Taguchi's design.

C. Taguchi results

Fig. 3 shows the graphs of response used to interpret the relationship between the two levels of each factor to decrease the particle size of the powders of ZnO. The most influential parameter is the type of precursor as it presents a very steep slope, which indicates that the smaller particle size is obtained using zinc acetate. Furthermore, the stirring rate has a minor effect since the line shows a slope close to 0.

Now, according to the trends presented graphs can be determined that the optimal condition for the smaller particle size is given under the following configuration: A1, B1, C2, D1, E2, and F1, recalling that A-F indicate parameter (see Tables II and III) and the configuration for the larger particle size is given by: A2, B2, C1, D2, E1, and F2, which corresponds to the ZnO-8 shows, and this can be verified in Table IV.

TABLE IV. SUMMARY OF EFFECT OF PARTICLE SIZE OF ZnO POWDERS AND SENSING PROPERTIES OF ZnO PELLETS

Sample	***Crystallite size [nm]***	***Average Particle size [nm]***	***Sensitivity***
ZnO-1	36.3	38.7	1.27×10^{4}
ZnO-2	33.7	35.8	3.73×10^{2}
ZnO-3	33.7	41.6	2.13×10^{3}
ZnO-4	32.5	40.3	1.58×10^{-1}
ZnO-5	36.3	47.8	1.26×10^{-1}
ZnO-6	35.0	88.3	3.17×10^{0}
ZnO-7	32.0	65.0	1.30×10^{-1}
ZnO-8	55.5	128.6	8.73×10^{0}

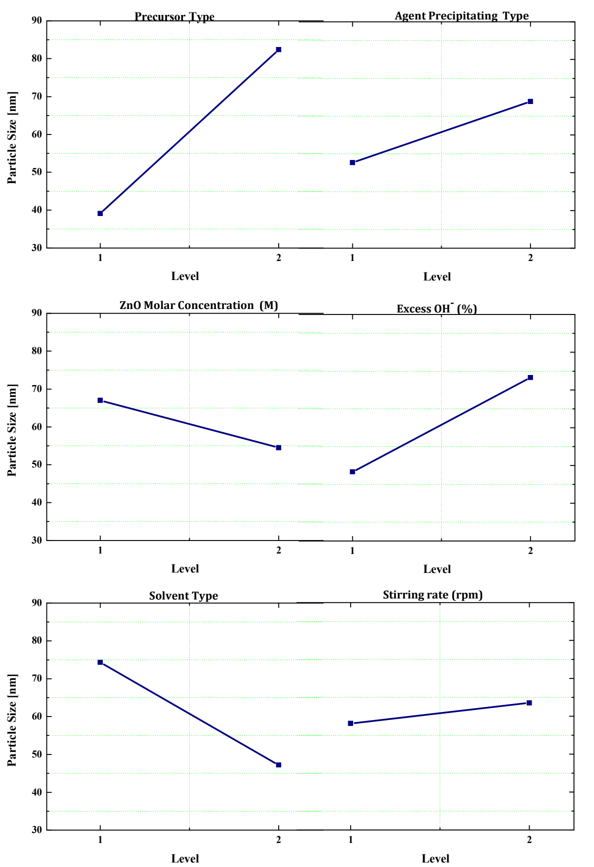

Fig. 3. Graphics of response of the parameters relative for particle size

D. Sensitivity

The sensitivity of the pellets manufactured with ZnO powders measures in a propane atmosphere (C_3H_8) are shown in Fig. 4

Sample ZnO-1 showed the highest sensitivity at a temperature of 300°C, of the order of 10^4, followed by the samples ZnO-2 and ZnO-3 with sensitivity of the order of 10^2 and 10^3, respectively.

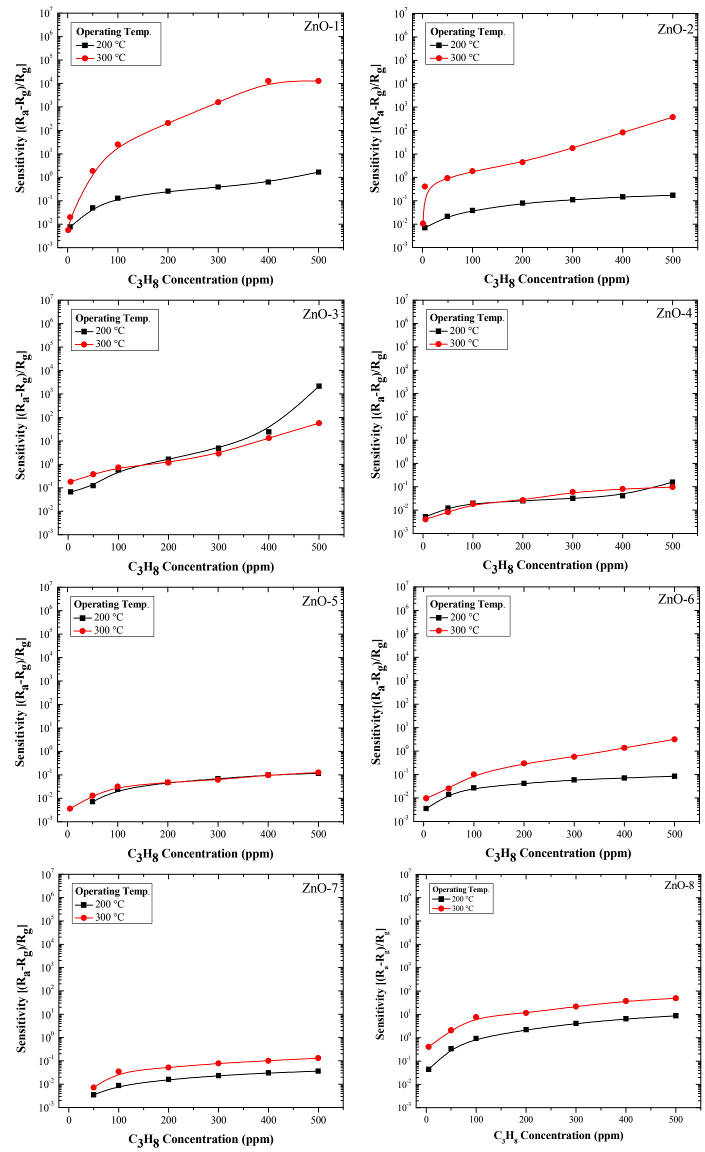

Fig. 4. Plots of Sensitivity versus Concentration, of 8 sensing pellets fabricated of ZnO samples.

The smaller particle size was presented by the ZnO-2 sample, and is one of the three samples exhibiting a good response at propane gas. Note that in most cases the best responses are at 300°C. The ZnO-4, ZnO-5 and ZnO-6 sensors showed a low electrical response in the propane atmosphere.

IV. CONCLUSIONS

In this work the design Taguchi was applied to reduce the particle size in the synthesis of ZnO by homogeneous precipitation method. XRD analysis indicated that hexagonal wurtzite structure was obtained, with a preferential growth on the (101) plane. The results indicated an average crystallite size in a range of 32 to 55 nm and an average particle size of 35.8 to 128.6 nm, obtained by the Scherrer equation and SEM images, respectively.

Through plots of responses could be predicted the smallest and largest particle size according to the level of the variables involved in the process. The pellets manufactured with the sample ZnO-1 showed with an average particle size around of 38.7 nm showed the best sensitivity at 300°C, in a propane atmosphere, 500 ppm.

ACKNOWLEDGMENT *(Heading 5)*

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