

Preparation of CO Gas Sensor from ZnO Material Synthesized via Thermo-Oxidation Process

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Abstract

Carbon monoxide (CO) is poisonous to human because of its nature which is capable to bind to the haemoglobin in blood stronger than oxygen, so that causing toxication and even death. Therefore a sensor to early detect the presence of CO gas is necessary. ZnO is one of semiconductor materials which widely applied as a sensor material. However, ZnO is rarely reported as a CO gas sensor material. In this study, ZnO as a sensor material has been synthesized by thermo-oxidation of Zn powder at oxidation temperature variations of 800, 850 and 900 °C. The synthesized ZnO was crushed and compacted to form pellet for sensor chip. The ZnO pellets were then sintered at 500 °C. The material structures were examined using Scanning Electron Microscope (SEM), X-Ray Diffractometer (XRD), and Brunauer-Emmet-Teller (BET) analysis. The sensitivity test towards CO gas was conducted with the variations in sensing operating temperatures of 30, 50, 100 °C and variation of CO gas input concentration of 10 ppm, 50 ppm, 100 ppm, 250 ppm, and 500 ppm. The sensitivity test results showed that the sensitivity towards CO gas decreased as the oxidation temperature increased. In addition the sensitivity increased along with the increasing of the sensing operating temperature and CO gas input concentration. Hence, the highest sensitivity value was obtained from ZnO material synthesized at 800 °C due to the highest active surface area of 69.4 m²g⁻¹ with CO concentration of 500 ppm and sensor operating temperature of 100 °C.

Keywords: ZnO, thermo-oxidation, CO gas, sensitivity

1. Introduction

Carbon monoxide (CO) is a poisonous gas having characteristics of colorless and odorless. It occupies the earth atmosphere in long period and is unable to dissolve in water. This gas is produced from incomplete combustion of carbon-based materials such as wood, coal, oil fuel and other organic substances (Kao and Nanagas, 2004). It is also a side product of living-organism metabolisms. The important biological characteristic of CO is its ability to bind to hemoglobin, the red blood cell pigment, which carried oxygen throughout the body. These properties result in the formation of carboxy-hemoglobin (HbCO) which is 200 times more stable than oxy-hemoglobin (HbO₂). The relatively slow decomposition of HbCO can impede the work of the pigment molecules in the function of cells in carrying oxygen throughout the body. These conditions could cause poisoning even death. Due to the nature of CO gas that cannot be perceived by human senses and the hazard of CO gas to the human body, therefore, a sensor to early detect the presence of CO gas in the air is very necessary.

Research on metal oxide materials gradually spreads because the applications of metal oxide materials are quite a lot including as toxic gas sensors, optical and modulation optoelectrochromic, photocatalyst, hydrophilic surface design, and catalyst. The metal oxides frequently used for sensor materials are TiO₂, SnO₂, ZnO, and WO₃ (Wang, et al., 2003). As one of the most prominent materials for gas sensors, ZnO has shown good response towards pollutant gas such as H₂S, NO_x, and benzene (Calestani et al., 2010) and other gases such as H₂, CO, ethanol and acetone (Moon et al., 2009).

ZnO has been successfully synthesized by various techniques such as hydrothermal (Peng and Huo, 2009), vapor-liquid-solid (Tsueh et al., 2007), sol-gel (Tseng, et al., 2012), spray pyrolysis (Widiyastuti et al., 2012) and physical vapor deposition (PVD) (Jimenes-Cadena et al., 2010). Those methods are quite complicated and

expensive. One method that is simple and inexpensive is direct thermo-oxidation of Zn powder into ZnO (Khanlary et al., 2012).

Zn is one of some metals having low melting temperature of 420 °C and low boiling temperature of 907 °C (Gaskell, D.R., 1973). The free energy formation of ZnO at 25 °C is -79.19 kcal mole⁻¹ (Perry et al., 1997) hence thermodynamically the oxidation process of Zn into ZnO occurs spontaneously at room temperature. However, kinetically the process is relatively slow. The Gibbs' free energy of Zn oxidation into ZnO based on this below reaction:



$$\Delta G^\circ = -115,420 - 10.35T \log T + 82.38T \text{ (cal)} \quad (2)$$

in temperatures ranging from 897 °C to 1727 °C in which the Zn is in the gaseous state (Gaskell, D.R., 1973). In those temperature ranges, the oxidation process also occurs spontaneously since the Gibbs' free energy is always negative. The oxidation process of Zn into ZnO is an endothermic process. For endothermic process, increasing the temperature will cause the equilibrium to shift to the right, meaning that the reaction will proceed almost completely in relatively short time.

Therefore, in this research, ZnO was synthesized from Zn powder which was directly heated under atmospheric air to become ZnO at temperatures nearly close to the boiling temperature of Zn to let the oxidation process to complete fast. The ZnO powder was then compacted into pellet and applied as a sensor chip for CO gas. The correlations between ZnO structure and sensitivity towards CO gas were analyzed and reported.

2. Method

Synthesis of zinc oxide (ZnO) was conducted by heating 2 grams of Zn powder (Merck, size <45 µm) in a muffle furnace under atmospheric air at various temperatures of 800, 850, and 900 °C for 40 minutes. The resulted ZnO was crushed and sieved to form powder with sizes less than 80 µm. The powder was then pelletized using hydraulic compaction machine with a pressure of 200 bar. The pellet had dimensions of 14 mm in diameter and 3 mm in thickness. To enhance the bonding of ZnO, the pellets were sintered at 500 °C for 1 hour. The opposite edges of the ZnO pellet were sputtered by Pd/Au alloy metal target for 30 minutes to form electrodes and electrical connections.

X-ray powder diffraction patterns were obtained using a Philips XRD Analytical for ZnO samples before and after sensitivity test. The tests were performed using X-ray Cu Kα source with wavelength of 1.54056 Å and angle range of 10-90°. Scanning Electron Microscope (SEM FEI S-50) was used to observe the morphology of ZnO samples after thermo-oxidation, after sieving process, after sintering process and after sensitivity tests. BET (Quantrachrome AsiQwin) was conducted to determine the active surface of the ZnO powder using nitrogen gas.

The sensitivity test towards CO gas was performed inside a stainless-steel chamber equipped with a thermo-controller, electrical connections to potentiostat instrument (Versastat 4.0 by Par Ametek) and channels to a vacuum pump and gas sources. The sample was placed in the middle of a ceramic disk heater inside the chamber. The chamber was initially pumped to vacuum and the sample was set at room temperature (30 °C). The air was flown inside the chamber with a volume of 20 liters (the volume of chamber). The air resistance was measured using potentiostat instrument under the potential difference of 1.5 V. The resistance of air was denoted as R_o (Ω). The CO gas was then flown inside a chamber using a mass flow controller (MFC Sierra C50) so that the CO concentration was set at 10 ppm. The resistance under the presence of CO gas was measured and denoted as R_g (Ω). These steps were repetitively performed with different CO gas concentrations of 100 ppm, 250 ppm, and 500 ppm. After completion, the operating temperatures were successively changed to 50 °C and 100 °C, each with various CO gas concentrations as mentioned above. The sensitivity values were calculated with the equation below (Wang et al., 2003):

$$S = |R_g - R_o| / R_o \quad (3)$$

Where S is the sensitivity of the sensor, R_g is the resistance after CO gas flowing and expressed in ohms (Ω), and R_o is the resistance of air before CO gas flowing and expressed in ohms (Ω).

3. Results and Discussion

XRD results for ZnO powder before sensitivity test are shown in Figure 1. These results match well with the JCPDF number 790206 of ZnO with hexagonal structure. The XRD patterns showed the three dominant crystal plane orientations (101) at $2\theta = 36.25^\circ$, (100) at 31.77° , and (002) at 34.42° . As synthesis temperature increased, the XRD peaks became sharper and the intensities also became higher. Hence the samples had better crystalline quality as the synthesis temperature increased (Khanlary, et al., 2012).

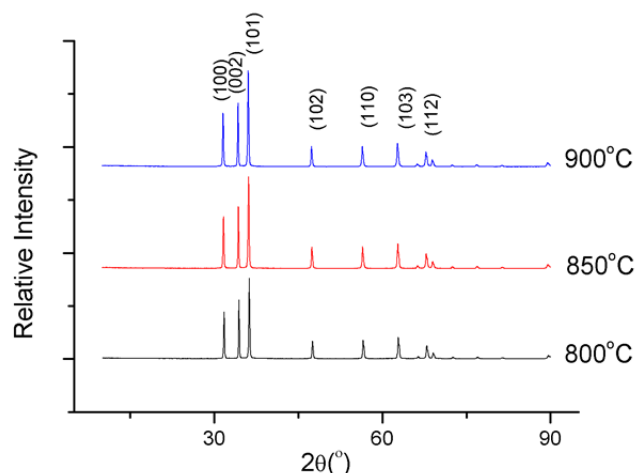


Figure 1. Comparison of the diffraction patterns of ZnO pellets synthesized at 800 °C, 850 °C , and 900 °C before sensitivity test towards CO gas

Table 1. Comparison of the crystalline size with synthesis variation temperature before and after sensitivity test towards CO gas

Synthesis Temperature (°C)	D (Å)	
	before sensitivity test	after sensitivity test
800	683.25	585.84
850	585.45	585.63
900	585.34	585.65

XRD characterizations were also conducted to ZnO pellets after sensitivity test towards CO gas as shown in Figure 2. The XRD patterns were similar to those in Figure 1. Hence CO gas and operating temperature variations during sensitivity tests did not contribute to the structure changes of ZnO sensor material. The crystalline sizes of the ZnO pellets before and after sensitivity tests are listed in Table 1 based on Scherrer's formula (Cullity and Stock, 2001, pp 170). The crystalline sizes before and after sensitivity test were almost similar, except the sample synthesized at 800 °C, the crystalline size became smaller after the sensitivity test, which perhaps caused by the operating temperatures and mechanical treatments during sensitivity measurement, as we have encountered in our previous experiment (Susanti, et al., 2014(b)).

Figure 3 shows SEM images of ZnO synthesized at various temperatures 800 °C, 850 °C and 900 °C prior being crushed into powder. From the SEM images, the sample synthesized at 800 °C has more pores than the others. A material with larger porosity will certainly have a greater surface area. As shown in Table 2, the sample synthesized at 800 °C has the largest active surface area based on BET measurements. While those synthesized at 850 °C and 900 °C have almost similar active surface area. As synthesis temperature increased, material will have larger particle size, hence less pores (Dutta and Bose, 2012).

Table 2. Surface area of ZnO powder from BET measurement

	Synthesis temperature (°C)		
	800	850	900
BET surface area (m ² g ⁻¹)	69.4	0.38	0.42

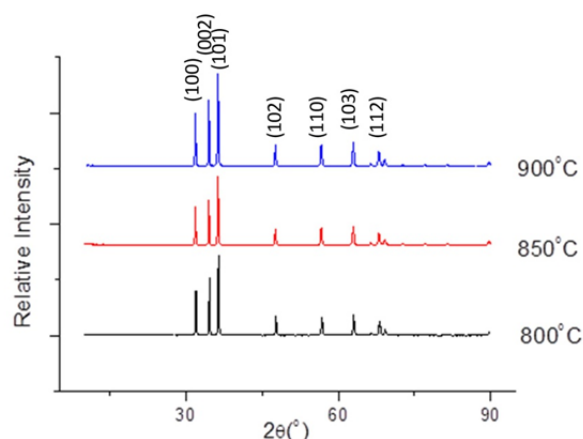


Figure 2. Comparison of the diffraction patterns of ZnO pellets synthesized at 800 °C, 850 °C and 900 °C after exposure to CO gas

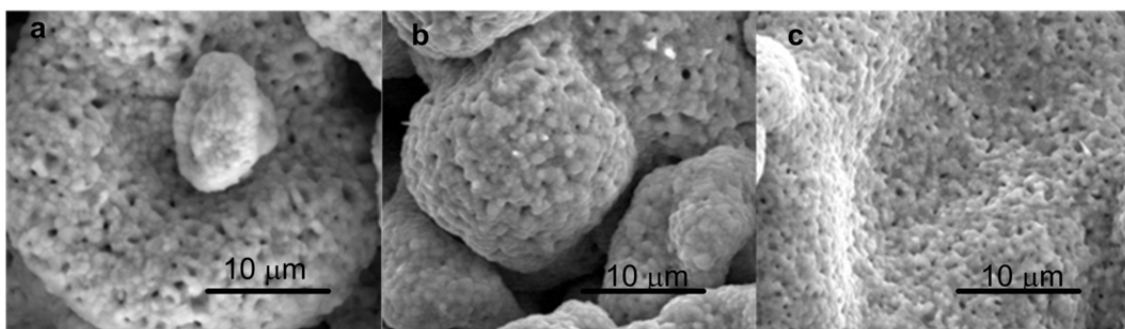


Figure 3. Bright field SEM images for ZnO synthesized at a) 800 °C, b) 850 °C and c) 900 °C before being crushed into powder

Comparing Figure 4 with Figure 5, there is no significant difference between the material morphologies before and after CO gas exposure. These results were in-line with XRD measurements which showed no significant difference in the particle sizes before and after sensitivity measurements. In our previous experiment on WO_3 semiconductor material as CO gas sensor, we also found that the structure and morphology of WO_3 did not change much after CO gas exposure (Susanti, et al., 2014(b)). Hence, ZnO is a good and suitable semiconductor material for CO gas sensor material, since it is stable and inert towards CO gas.

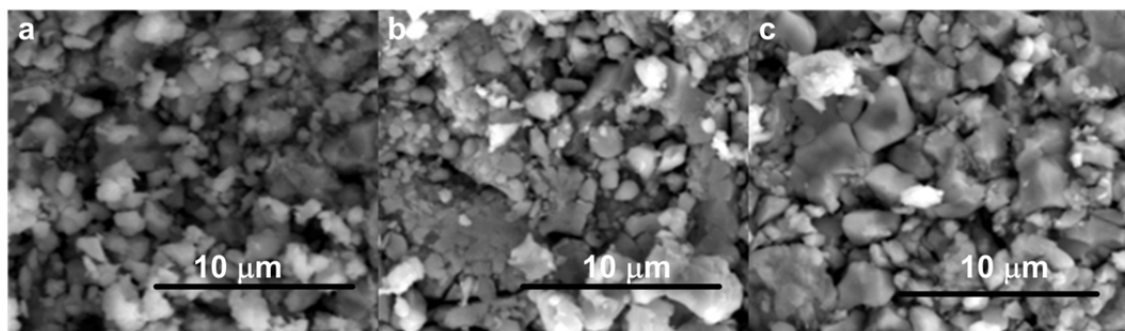


Figure 4. Bright field SEM images of ZnO pellets for sample with various synthesis temperatures a) 800 °C, b) 850 °C and c) 900 °C before CO gas exposure

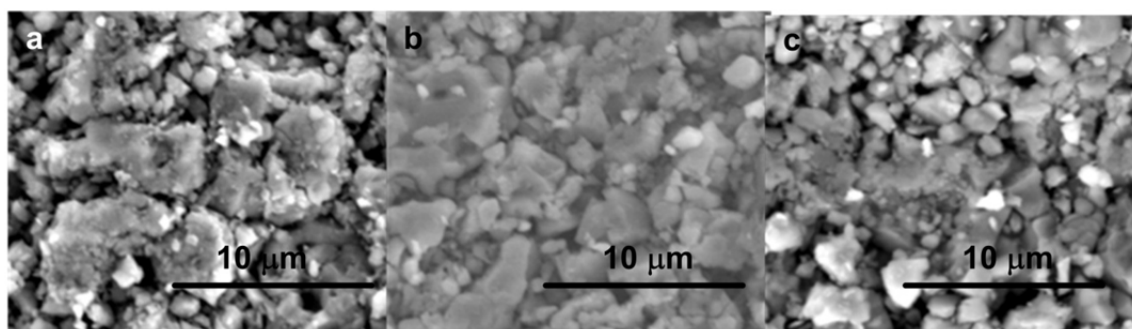


Figure 5. Bright field SEM images of ZnO pellets for sample with various synthesis temperatures a) 800 °C, b) 850 °C and c) 900 °C after CO gas exposure

Figures 4 and 5 show the bright field SEM images of ZnO pellets, before and after sensitivity measurements towards CO gas respectively. ZnO material in the three samples had irregular shapes. Some of them formed clusters in bigger sizes as the influence of compaction and sintering process. The sample synthesized at 800 °C has particle sizes ranging from 0.83-1.77 μm , while those synthesized at 850 °C and 900 °C have particle sizes ranging from 1.16 – 5.81 μm and 1.48-6.22 μm , respectively. The synthesis temperature certainly has great effect on the material structure.

The results of sensitivity test of the ZnO-based CO gas sensor are displayed in Figure 6. From Figure 6, the sample synthesized at 800 °C always has the highest sensitivity, followed by the sample synthesized at 850 °C and 900 °C. Tamaki, et.al reported that the grain size strongly influenced the sensitivity of WO_3 towards nitrogen oxides. The sensitivity of the sensor increased as the grain size decreased. Hidayat, et.al also reported that the adsorption performance of tungsten oxide towards methylene blue is dependent on particle size. The interaction between surface atoms of tungsten oxide and methylene blue molecules was increased with reduction in tungsten oxide particle size. In this experiment, ZnO synthesized at 800 °C had the highest active surface area and the smallest particle sizes. Therefore it showed the most sensitivity towards CO gas. Larger active surface area will accommodate more CO gas and increase the sensitivity.

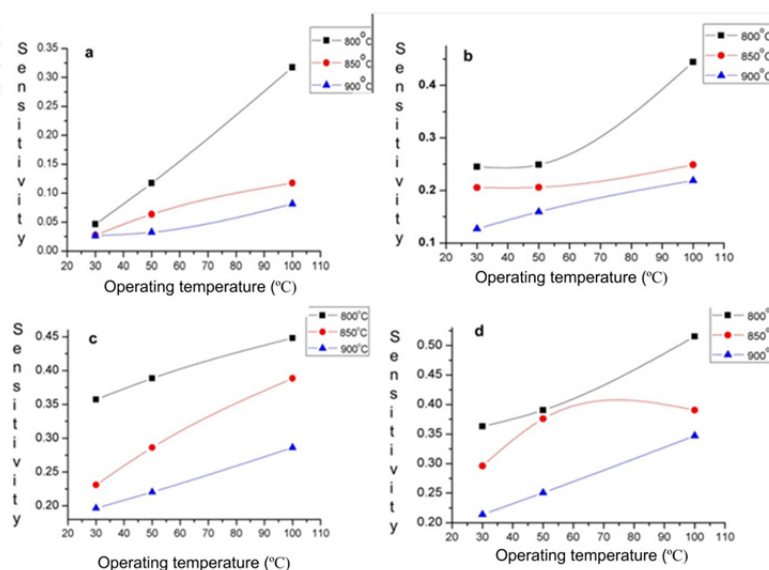
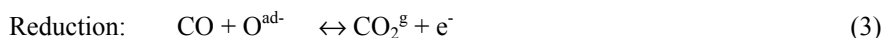


Figure 6. The sensitivity test of ZnO-based CO gas sensor synthesized at various temperatures 800 oC, 850 oC and 900 oC at different operating temperatures 30 oC, 50 oC and 100 oC and CO gas concentration a) 10 ppm, b) 100 ppm, c) 250 ppm, d) 500 ppm

Figure 6 also depicted the sensitivity dependencies to operating temperature and CO gas concentration. For all of the samples, the sensitivity increased as operating temperature and CO gas concentration increased. The sensor worked based on the chemisorption principle of CO gas onto ZnO surface. The oxygen molecule from the air

would be adsorbed onto ZnO surface area and would bind to electrons extracted from the conduction band of ZnO. When CO gas was present, the adsorbed oxygen and CO gas would react to form CO₂ gas and release the electrons back to the conduction band of ZnO as shown in equation (2) and (3). The electron flows influence the electrical resistance changes of ZnO sensor (Hung, et al., 2010). As CO gas concentration increased, more electrons would be extracted from semiconductor material conduction band and hence the resistance along with the sensitivity would increase.



The reaction between oxygen and CO gas certainly need energy (Liu et al., 2008). Therefore at low operating temperature, the sensitivity of the sensor was also low. However at higher temperature, more oxygen and CO would be adsorbed onto ZnO surface and react to become CO₂ gas, leading to the increase in sensor resistance and sensitivity (Susanti et al., 2014a).

Comparing with our previous results on WO₃ for CO gas sensor (Susanti, et al., 2014(a) and 2014(b)), the highest sensitivity towards CO gas of 0.52 performed by the sample synthesized at 800 °C at 100 °C operating temperature and 500 ppm CO gas concentration was lower although it had higher active surface area than the WO₃ sample performed the highest sensitivity. Therefore, it was not only the high active surface area determining the sensitivity, but also some other aspects such as the particle size, crystallite size, active surface area, oxygen vacancy, crystallinity, material electrical conductivity and interdependency among those aspects (Susanti et al., 2014(a)).

Comparing with the work reported by Hsueh, et.al (2007) on the sensitivity of ZnO deposited on top of patterned Ga/SiO₂/Si towards CO gas, our highest sensitivity was comparable. They reported the highest sensitivity to be 0.57 (57%) at 320 °C operating temperature and 500 ppm CO gas concentration resulted from ZnO sensor material synthesized using 0.25 gram Zn. Liu, et.al (2008) reported even higher sensitivity. They reported the highest sensitivity of ZnO sensor material to be 0.6 (60%) at 250 °C operating temperature and 70 ppm CO gas concentration.

Despite of the lower sensitivity reported in our work, ZnO has been proved to be a good candidate for CO gas sensor material.

4. Conclusions

ZnO as a material for CO gas sensor has been successfully synthesized via thermo-oxidation process of Zinc powder. XRD measurements confirmed the formation of ZnO having hexagonal structure without any other impurities. The ZnO sensor pellet synthesized at 800 °C performed the highest sensitivity towards CO gas for its largest active surface area. It was also showed that the sensitivity towards CO gas increased with operating temperature and CO gas concentration. The highest sensitivity towards CO gas was measured to be 0.52 performed by the sample oxidized at 800 °C at operating temperature of 100 °C and CO gas concentration of 500 ppm. SEM and XRD analysis have also revealed the potency of ZnO material for CO gas sensor, since there was no significant change in the morphology and structure of ZnO material after CO gas exposure. Therefore ZnO is a good candidate for CO gas sensor material since it is stable and inert towards CO gas.

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