CHAPTER 3

RESULTS AND DISCUSSION

3.1 Particles properties

3.1.1 X-ray diffraction analysis

It can be seen that all samples were highly crystalline, and all peaks can be confirmed to be the hexagonal structure of ZnO which match with JCPDS file No. 79-205. Figure 3.1 (a) shows the XRD patterns of the pure ZnO, 0.2-2.0 at% Ptdoped ZnO nanopowders. Moreover, the Pt peaks were found in very small intensity for 1.0-2.0 at% Pt-doped ZnO nanoparticles, the samples patten can be confirmed to be the face center cubic (FCC) structure of Pt (JCPDS No.4-802). Figure 3.1 (b) shows the XRD patterns of the pure ZnO, 0.2–2.0 at% Pt-doped ZnO nanoparticles (P0-P2.0), Au/Al₂O₃ substrate (Sub), and Pt-doped ZnO sensing films after annealing (S1, S2, S3 and S4). It can be seen that All samples were highly crystalline, and all peaks can be confirmed to be the hexagonal structure of ZnO (Inorganic Crystal Structure Database [ICSD] Coll. Code: 067454 [126,127]). The diffraction peaks of Al₂O₃ (ICSD Coll. Code: No. 085137 [126,128]) (filled triangle) and Au (ICSD Coll. CAS No. 7440-57-5 [126,129]) (filled rectangular) from the substrates are also visible from Sub, S1-S4 samples. It should be noted that differences in intensity between sensing films (Sub, S1-S4) and their corresponding nanoparticles (P0, P0.2, P1.0, P2.0) are due to the change in texturization of the crystal plane orientation while preparing sensing films. (Data for S1-S4 are XRD pattern from sensing film coated on Au/Al₂O₃ substrates while data for P0–P2.0 are XRD pattern from pure powder).



Figure 3.1(a) XRD patterns of flame-spray-made (5/5) 0.0–2.0 at% Pt-doped

ZnO nanopowders.



Figure 3.1(b) XRD patterns of flame-spray-made (5/5) 0.2–2.0 at% Pt-doped ZnO as-prepared (P0–P2.0), Au/Al₂O₃ substrate (Sub), and samples P0, P0.2, P1.0, and P2.0 were spin-coated on Au/Al₂O₃ substrate after annealing and sensing test (S1, S2, S3, and S4) ((\bullet) ZnO; (\blacktriangle) Al₂O₃; (\blacksquare) Au).

3.1.2 BET analysis

The average BET equivalent particle diameter (d_{BET}) as shown in Figure 3.2 were calculated using the average of the density of pure ZnO and Pt-doped ZnO taken into account for their weight content of different doping. It can be seen that SSA_{BET} monotonically increases while d_{BET} decreases with increasing Pt concentration from 0 to 2.0 at%. The results can be explained as follows. When Pt particles were formed and deposited on ZnO supports in the flame, Pt created a new nucleation center, which in turns changed the nucleation type from homogeneous to heterogeneous. The d_{BET} of Pt- doped ZnO nanoparticles would be the average size of the combined Pt and ZnO nanoparticles. With the increasing Pt doping, the number of Pt particles increased and hence the average particles would decrease because the size of Pt nanoparticles was expected to be much smaller than that of ZnO nanoparticles.



Figure 3.2 The specific surface area (SSA_{BET}), BET diameter (d_{BET}) of the pure ZnO and 0.2–2.0 at% Pt-doped ZnO nanoparticles. Error bars (ISD.) indicate the variation over five samples for each Pt concentration.

3.1.3 Scanning electron microscopy (SEM)

The morphology of highly crystalline flame-made (5/5) are shown in figs. 3.3 (a) the pure ZnO (P0), (b) 0.2 at% Pt-doped ZnO (P0.2), (c) 0.5 at% Pt-doped ZnO (P0.5), (d) 1.0 at% Pt-doped ZnO (P1.0), (e) 1.5 at% Pt-doped ZnO (P1.5) and (f) 2.0 at% Pt-doped ZnO (P2.0) nanoparticles for SEM analysis. SEM micrographs in Figure 3.3 (a) show the nanospheres with an average diameter of 10–20 nm, and several nanospheres connected with each other. From this observation, it was found that the rough morphology and the rough particle sizes were not changed with increasing Pt doping levels. Nevertheless, the accurate sizes and morphology of the nanoparticles can be estimated from the TEM analysis. While the SEM images provide 3D morphology and estimated particle sizes, TEM images reveal internal structure and a more accurate measurement of particle size and morphology.



Figure 3.3 SEM micrographs of highly crystalline flame-made (5/5) (a) the pure ZnO (P0) and doped with (b) 0.2 at% Pt (P0.2), (c) 0.5 at% Pt (P0.5), (d) 1.0 at% Pt (P1.0), (e) 1.5 at% Pt (P1.5) and (f) 2.0 at% Pt (P2.0) nanoparticles for SEM analysis.

The EDS spectrum images of all elements shows in figs. 3.4 (a) 1.0 at% Pt and (b) 2.0 at% Pt-doped ZnO nanoparticles. It can be seen that Zn, O and Pt elements are quite evenly distributed over the area. In addition, the density of Pt sites is approximately a few percents of those of Zn and O sites. This is consistent with expected elemental composition. The average Pt concentrations of 1.0 at% and 2.0 at% Pt-doped ZnO nanoparticles are estimated by EDS quantitative analysis software (Oxford Instrument) to be 1.06% and 1.18%, respectively. The differences between the measured concentrations and the intended concentrations are possibly due to the losses during FSP processing steps such as precursor injection and dispersion. Nevertheless, the EDS spectrum and the map confirm the existence of Pt and indicate that Pt is uniformly dispersed in the mixture of nanoparticles. Figure 3.5 shows EDS-dot mapping images of all elements in (a) the pure ZnO, (b) 1.0 at% Pt-doped ZnO and (c) 2.0 at% Pt-doped ZnO nanoparticles.



Figure 3.4 The EDS spectra images of all elements in the (a) 1.0 at% and (b)

2.0 at% Pt-doped ZnO nanoparticles.



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Figure 3.5 (a) EDS-dot mapping images of all elements in the pure ZnO nanoparticles.



Figure 3.5 (b) EDS-dot mapping images of all elements in the 1.0 at% Ptdoped ZnO nanoparticles.



Figure 3.5 (c) EDS-dot mapping images of all elements in the 2.0 at% Pt-

doped ZnO nanoparticles.

3.1.4 Transmission Electron Microscopy (TEM, HRTEM)

Figures 3.6 (a-f) show TEM images of 0–2.0 at% Pt-doped ZnO nanoparticles, respectively. It can be seen that very small Pt nanoparticles seen as darker spots are deposited on larger ZnO nanoparticles. The ZnO particles have spherical, hexagonal and rod-like morphologies. The sizes of spherical and hexagonal ZnO particles are found to be ranging from 5 to 20 nm while ZnO nanorods are 5–20 nm in width and 20–40 nm in length. HRTEM images show all Pt nanoparticles dispersed on the surface of ZnO particles having spherical morphology. The average diameter of Pt nanoparticles deposited on ZnO is estimated to be 1 nm for both 1.0 and 2.0 at% Pt-doped ZnO. In addition, it can be noticed that Pt nanoparticles are not agglomerated at all and this interesting feature would make them effective for gas-sensing.



Figure 3.6 HRTEM images of (a) the pure ZnO (P0) and Pt-doped with (b) 0.2 at% Pt (P0.2), (c) 0.5 at% Pt (P0.5), (d) 1.0 at% Pt (P1.0), (e) 1.5 at% Pt (P1.5) and (f) 2.0 at% Pt (P2.0) nanoparticles. ZnO particle sizes and morphology were spherical, hexagonal and rod-like. The darker spots on TEM images are Pt deposited on ZnO nanoparticles.



Figure 3.6 (Cont.) HRTEM images of (a) pure ZnO (P0) and doped with (b) 0.2 at% Pt (P0.2), (c) 0.5 at% Pt (P0.5), (d) 1.0 at% Pt (P1.0), (e) 1.5 at% Pt (P1.5) and (f) 2.0 at% Pt (P2.0) nanoparticles. ZnO particle sizes and morphology were spherical, hexagonal and rod-like. The darker spots on TEM images are Pt deposited on ZnO nanoparticles.

3.1.5 SEM sensing layer

The cross-section, film thickness, and surface morphology of the sensing film layer (S1, S2, S3 and S4) after annealing and sensing test at 400°C were observed using SEM analysis as shown in Figure 3.7. The film thickness of sensing film was approximately 10 μ m (side view) as shown in the Figure 3.7 (a), (b), (c) and (d), which benefited tremendously to gas sensing properties. Regularities 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 annealing process, a denser film layer was formed.

Figure 3.8 shows EDS line scan images of all elements in (a) the pure ZnO and (b) 2.0 at% Pt- doped ZnO sensors. It can be seen that Zn, O and Pt elements are quite evenly distributed over the area. In addition, the density of Pt sites is approximately a few percents of those of Zn and O sites. This is consistent with expected elemental composition. The EDS line confirms the existence of Pt and indicates that Pt is uniformly dispersed on the surface of nanoparticles.



Figure 3.7 SEM micrographs of flame-made ZnO thick films as a sensor (a) S1, (b) S2, (c) S3 and (d) S4 on an Al₂O₃ substrate interdigitated with Au electrodes after annealing and sensing test at 400°C in dry air. The film thickness was approximately $10 \,\mu$ m.



Figure 3.8 (a) The EDS line scan mode-SEM analysis of sensor based on pureZnO nanoparticles (S1). The histograms showed the elemental compositions of samples. The lines scans correspond to Al, Au, Zn, and O elements.



Figure 3.8 (b) The EDS line scan mode-SEM analysis of sensor based on 2.0 at% Pt-doped ZnO nanoparticles (S4). The histograms showed the elemental compositions of samples. The lines scans correspond to Al, Au, Zn, O and Pt elements.

3.2 Sensor results

3.2.1 Atmospheric pollution gases

3.2.1.1 Gas response of Pt-doped ZnO nanoparticle towards carbon monoxide (CO) gas

The gas response, *S* is defined as the ratio R_d/R_g , where R_a is the resistance in dry air, and R_g is the resistance in test gas. The response and response times of the sensing films of ZnO nanoparticles as a function of CO concentration between 50 and 1000 ppm at 350°C were shown in Figure 3.9. The response was increased considerably by doping 0.2 at% Pt-doped ZnO. The response value of 2.9 and response time of 7 s were obtained at 0.1 vol.% of CO concentration present for 0.2 at% Pt. The response, however, was decreased considerably when doping the 1.0 at% Pt-doped ZnO. It is important to note that the pure ZnO and 0.2 at% Pt-doped ZnO nanoparticles behave as an n-type semiconductor with the resistance decreased during CO gas environment and this is a typical behavior for ZnO material [6]. The semiconducting and gas-sensing behaviors were thus strongly depending on the doping level of Pt on ZnO nanoparticles [7].



Figure 3.9 Variation of response (left) with concentration of CO (0.005–0.1 vol.%) and variation of response times (right) for the pure ZnO, 0.2 and 1.0 at% Pt-doped ZnO sensors.

3.2.1.2 Gas response of the pure ZnO nanoparticle towards nitrogen dioxide (NO₂) and sulfur dioxide (SO₂) gases

The response and response time of the thick films of the pure ZnO nanoparticles as a function of NO₂ (The gas-sensing response, *S* is defined as the ratio R_g/R_a), and SO₂ (The gas-sensing response, *S* is defined as the ratio R_a/R_g) concentrations at 300°C are shown in Figure 3.10. In Figure 3.10(a), the response toward NO₂ increased considerably at 0.005 vol.% of NO₂ concentration. The response and response time for the pure ZnO nanoparticles at 0.005 vol.% of NO₂ concentration were found to be 33 and 7 s, respectively. The response, however,

decreased considerably by testing the pure ZnO sensor with SO₂ at 0.005 vol.% concentration of each gas as shown in Figure 3.10 (b). The response value of 3 with the response time of 17 s was obtained at 0.005 vol.% of SO₂, respectively. It is important to note that the pure ZnO nanoparticles behave as an n-type semiconductor with decreased resistance during NO₂ and SO₂ gas exposure, which is a typical behavior of ZnO material [130]. The gas-sensing response, *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, $T_{\rm res}$, is defined as the time required until 90% of the original baseline signal is recovered. The sensor behaviors under the operating temperature of 300 °C versus the NO₂ concentrations ranging from 0.0001–0.005 vol.% of gas concentration for the flame-made pure ZnO nanoparticles were plotted as shown in Figure 3.10 (a). The changes in resistance of the pure ZnO sensor for SO₂ gas under exposure to 0.005–0.1 vol.% of SO₂ during forward cycle at 300°C are shown in Figure 3.10 (b).



Figure 3.10 The change in resistance of the pure ZnO sensor for (a) NO_2 and (b) SO_2 gases under exposure to oxidizing gas of NO_2 and reducing gases of SO_2 during forward cycle at 300°C, respectively.



Figure 3.10 (Cont.)The change in resistance of the pure ZnO sensor for (a) NO_2 and (b) SO_2 gases under exposure to oxidizing gas of NO_2 and reducing gases of SO_2 during forward cycle at 300°C, respectively.

It is well known that the response of a semiconductor gas sensor is highly influenced by its operating temperature [131–132]. In order to determine the optimum operating temperatures, the response of the pure ZnO gas sensor to 0.005 vol.% concentration of nitrogen dioxide, ethanol and sulfur dioxide in air was tested as a function of operating temperature, as shown in Figure 3.11. It is clear that the responses of three gases tested varied with operating temperature. The response to NO₂ first increased with temperature, up to 300°C, and then gradually decreased. The maximum response towards NO₂ was 33, at 300°C. For SO₂ gas the response continuously increased when operating temperatures varied from 200 to 300°C, and then decreased. The maximum response obtained was 3, at 300°C. Therefore, optimal operating temperatures of 300°C were chosen for NO₂ and SO₂ respectively, to further examine the characteristics of the gas sensor. It can be concluded from the results that the pure ZnO sensor can act as a multifunctional selective gas sensor for detecting NO₂ and SO₂ gases. In other words, the above mentioned sensor can be used as an excellent NO₂ sensor at an operating temperature of 300°C.



Figure 3.11 The response *versus* variation of the operating temperature of NO_2 and SO_2 (at 0.005 vol.% concentration) for the pure ZnO sensor.

The gas sensing selectivity of the pure ZnO gas sensor has been characterized towards one common oxidizing gas, NO₂, and one common reducing, SO₂ gases as shown in Figure 3.12. The responses towards NO₂ and SO₂ under the operating temperature of 300°C were found to be 33 and 3, respectively. This indicates an excellent NO₂ selectivity of our pure ZnO gas sensor.

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Figure 3.12 The response variation of the pure ZnO sensor testing with 0.005 vol.% concentration of NO₂ and SO₂ under the operating temperature of 300°C.

3.2.2 Flammable and Explosive gases

3.2.2.1 Gas sensing of Pt-doped ZnO nanoparticle towards hydrogen (H₂) gas

The response and response time of the thin films of ZnO nanoparticles as a function of H₂ concentration between 0.02 and 1.0 vol.% of concentration at 200, 300 and 350°C are shown in Figure 3.13. The response increased considerably by doping the ZnO nanoparticles with 0.2 at% Pt from 98 at 200°C to 164 at 300°C (as shown in Figure 3.13 (a,b)). On the other hand, the response decreased by doping the ZnO nanoparticles with 0.2 at% Pt was 126 at 350°C as show in Figure 3.13(c). Therefore, doping the ZnO nanoparticles with 0.2 at% Pt sensor at 300°C had better response than 350° C and 200° C, respectively. In Figure 3.13 (a), the response increased considerably with increasing concentration of H₂ doping the ZnO nanoparticles with 0.2 at% Pt. In Figure 3.13 (b) the response of 164 and response time of 6 s at 300 °C were obtained at 1.0 vol.% of H₂ concentration for doping the ZnO nanoparticles with 0.2 at% Pt. Thus, in this study 0.2 at% Pt-doped ZnO showed good response for H₂ gas as compared to the other literatures. In the present study the response for reducing gase, however decreased considerably by doping ZnO nanoparticles with 1.0 and 2.0 at% Pt at any temperature. It is important to note that the pure and 0.2 at% Pt-doped ZnO nanoparticles behave as an n-type semiconductor with the resistance decreased during increasing concentration of H₂ reducing gas exposure, a typical behavior of ZnO material [133].

The sensor characteristics of sensing films are affected by the film structure, morphology, and film thickness, which are determined by the film preparation procedure. In addition, the sensing temperature and film thickness are important parameters, which affect the gas sensing properties in terms of response value, response time and recovery time. In gas sensors, small-sized particles decrease the response time and increase the gas response, while a low degree of agglomeration facilitates the production of thin or thick films [134]. The response and response time of the thin films of ZnO nanoparticles as a function of H₂ concentration are between 0.02 and 1 vol.% of concentration at 200, 300 and 350°C as shown in Figure 3.13. It is evident that the response of 0.2 at% Pt-doped ZnO nanoparticles increased by more than one order of magnitude compared to the pure ZnO for all operating temperatures from 200 to 350°C. As the operating temperature increased from 200°C to 300°C, the response increased from 98 to 164 (shown in Figure 3.13 (a, b) for 1.0 vol.% of H₂).

However, the response decreased to 126 as operating temperatures increases beyond to 350° C as shown in Figure 3.13(c). Therefore, 0.2 at% Pt-doped ZnO nanoparticles gas sensor had optimum response at operating temperature of 300° C, which was lower than optimum operating temperature of the pure ZnO at around $350-400^{\circ}$ C. This lower optimum operating temperature is attributed to Pt catalyst's behavior that can be best reduced hydrogen at relatively low temperature. The response of 164 and response time of 6 s were obtained at 1 vol.% of H₂ concentration and 300°C operating temperature with doping the ZnO nanoparticles with 0.2 at% Pt. In addition, a low detection limit of 0.005 vol.% was obtained at 300°C operating temperature to be around 0.005 vol.%. It was at this concentration which the response was ~1.1, corresponding to 10% change of resistance.

Figure 3.13 shows the response was decreased considerably by doping ZnO nanoparticles with 1.0 and 2.0 at% Pt and they were even less than the pure ZnO. The sensor behaviors versus the H₂ concentrations ranging from 0.02 to 1.0 vol.% of concentration plot for S1, S2, S3 and S4 sensors based on an as-prepared flame-made (5/5) ZnO nanoparticles towards H₂ gas at sensing operating temperature 300°C is shown in Figure 3.14 (a) and changes in resistance of S0 and S1 are shown in Figure 3.14 (b). The response as a function of the gas concentration follows the well-known power law behavior. It can be seen again that 0.2 at% was an optimum Pt doping concentration and higher concentration significantly degraded gas sensing behavior. The semiconducting and gas-sensing behaviors are thus depending strongly on the doping level of Pt on ZnO nanoparticles. The observed gas-sensing dependence on Pt concentration may be explained as follows:



Figure 3.13 Variation operating temperature of response with concentration of H₂ (0.02–1 vol.% concentration) for S1, S2, S3 and S4 at (a) 200°C, (b) 300°C and (c) 350° C.



Figure 3.13 (Cont.) Variation operating temperature of response with concentration of H₂ (0.02–1.0 vol.% concentration) for S1, S2, S3 and S4 at (a) 200° C, (b) 300° C and (c) 350° C.



Figure 3.14 (a) Variation of response (left) with concentration of H_2 (0.02–1.0 vol.% concentration) and variation of response times (right) for S1, S2, S3 and S4 at 300°C. (b) change in resistance of sensor S1 and S2 under exposure to reducing gas H_2 during forward cycle.

It is widely believed that Pt catalyst enhances reducing gas sensing of metal oxide via spillover mechanism [135]. This interaction is a chemical reaction by which additives assist the redox process of metal oxides. The term spillover refers to the process, illustrated in Figure 3.15, namely the process where the metal catalysts dissociates the molecule, then the atom can 'spillover' onto the surface of the semiconductor support. At appropriate temperatures, reactants are first adsorbed on to the surface of additive particles and then migrate to the oxide surface to react there with surface oxygen species, affecting the surface conductivity. For the above processes to dominate the metal oxide resistance, the spilled-over species must be able to migrate to the interparticle contact. Thus, for a catalyst to be effective there must be a good dispersion of the catalysts so that catalyst particles are available near all contacts. Only then can the catalysts affect the important interparticle contact resistance.

From the experimental results, the response of Pt-doped ZnO at 2 at% is lower than that at 0.2 at% but the d_{BET} of 2 at% Pt-doped ZnO nanoparticles is smaller. This can be explained from Figure 3.15. In Figure 3.15 (a), it can be seen that small Pt particles for the case of low Pt concentration (0.2 at%) can cause agglomeration so that two or more ZnO nanoparticles are connected. As a result, the low Pt concentration case will have larger average particle diameter, d_{BET} , than high Pt concentration one (Figure 3.15 (b)). However, spillover effect for the case of low concentration, which has larger d_{BET} , is considerably more effective than the other case. For low Pt concentration (0.2 at %), Pt nanoparticles are very small compared to ZnO ones and they can be well dispersed on ZnO nanoparticles as shown in Figure 3.14 (a). Thus, Pt nanoparticles are very effective catalyst via spillover mechanisms. In contrast, larger Pt nanoparticles, which are formed at higher Pt concentrations, can not be well dispersed and cause possible separation among ZnO nanoparticles as shown in Figure 3.15 (b). Therefore, catalytic action of Pt becomes considerably less effective. This is the reason why gas sensitivity significantly decreased at higher Pt concentration even though the average particle size measured by d_{BET} decreased at higher Pt concentration (recall that the average particle size decreases because of less agglomeration as Pt nanoparticle size increased).

The gas sensing selectivity of ZnO gas sensor has been characterized towards two other common reducing gases, carbon monoxide (CO) and methane (CH₄) as shown in Figure 3.16. Figure 3.16 shows that 0.2 at% Pt-doped ZnO gas sensor has a good gas selectivity for 0.1 vol.% of H₂ concentration of 8.2 at 300°C. The response of 0.2 at% Pt-doped ZnO gas sensor of CO and CH₄ were 2.1 and 1.0 at 0.1 vol.% of concentration at 300°C operating temperature. Thus, the gas response of 0.2 at% Ptdoped ZnO to H₂ is higher than those of CO and CH₄. The hydrogen selectivity of 0.2 at% Pt-doped ZnO is also substantially higher than pure ZnO gas sensor whose hydrogen response is on the same order as those of CO and CH₄. Table 3.1 sumarized the sensing materials to various gases with responses at different temperatures.



Figure 3.16 Variation of response with concentration of H_2 , CO and CH_4 (at 300°C, 0.1 vol.% concentration) for sensor S1 (pure ZnO) as compared to S2 (0.2 at% Pt-doped ZnO).

Sensing material	Method	Gas concentration	Response	Reference
0.5 wt% Pt 0.5 wt% Ru 0.5 wt% Rh 0.5 wt% Ag	Chemical precipitation	0.2 % in air 0.2 % in air 0.2 % in air 0.2 % in air	2 at 330°C 6 at 230°C and 2 at 400°C 115 at 300°C 9 at 400°C	[7]
0 at % Pt 1.0 at % Pt 0 at % Pt 1.0 at % Pt	ZnO nanowires and ZnO nanotubes by electrochemical deposition	1000 ppm in air 1000 ppm in air 1000 ppm in air 1000 ppm in air	43 at 150°C 825 at 150°C 18 at 150°C 740 at 150°C	[9]
Pt-coated	ZnO nanorods deposited by Molecular Beam Epitaxy(MBE)	500 ppm in N ₂	Relative response of up to 8 % H ₂ at room temperature	[10]
Pt-coated	ZnO nanorods / thin films deposited by Molecular Beam Epitaxy (MBE)	500 ppm in N ₂	Response of Pt-coated nanorods was 3 times of thin films as prepared ZnO	[11]

Table 3.1 A summary comparing H₂ sensing with metal-doped ZnO

In comparison with the same doping material there were many reports with other preparation methods such as Xu *et al.* [7], Rout *et al.* [9], Wang *et al.* [10] and Tien *et al.* [11]. In addition, for comparison with other doping material was Xu *et al.* [7]. The summary on comparisons of metal-doped ZnO with several synthetic methods for H_2 sensing is shown in Table 3.1.

3.2.2.2 Gas response of Pt-doped ZnO nanoparticle towards acetylene (C₂H₂) gas

In this study, the gas sensing properties of Pt-doped ZnO sensing films are characterized in terms of response, response time, and recovery time as a function of operating temperature, gas concentration and Pt doping.

Figures. 3.17 (a), (b) and (c) show the response and response time of Pt-doped ZnO sensing films as a function of C_2H_2 concentration between 0.02 and 1.0 % at 200, 300 and 350°C, respectively It is evident that the response of 2.0 at% Pt-doped ZnO nanoparticles increased by more than samples order of magnitude compared to pure ZnO, 0.2 at% Pt-doped and 1 at% Pt-doped one for all operating temperatures ranging from 200 to 350° C.

As the operating temperature increased from 200°C to 300°C, the response increased from 520 to 836 (as shown in Figs. 3.17 (a, b)). However, the response decreased to 720 as operating temperatures increased further to 350°C as shown in Figure 3.17(c). Therefore, 2.0 at% Pt-doped ZnO nanoparticles gas sensor has optimum response at operating temperature of 300°C, which is lower than optimum operating temperature of the pure ZnO sample at around 350–400°C. This lower optimum operating temperature is attributed to Pt catalyst's behavior that can be best reduced C_2H_2 at relatively low temperature. However, the ultimate optimal Pt content for C_2H_2 sensing cannot yet be determined from this study. From the result trend, the response for C_2H_2 should be further increased if Pt content increases more than 2.0 at% and it should eventually maximize at an optimal concentration. A 2.0 at% Pt doping was chosen as the limit of this study because most other reports found that the optimal Pt doping on ZnO for various gases at Pt content below 2.0 at%. Further study will be conducted to determine the ultimate optimal Pt content of Pt-doped ZnO nanoparticles for C_2H_2 sensing.

It is widely believed that Pt catalyst enhances the reducing gas sensing of metal oxide via spillover mechanism [135] as mentioned in 3.2.1.1. From the experimental results, the response of Pt-doped ZnO at 2 at% is higher than that 0.2 at% and the d_{BET} of 2.0 at% Pt-doped ZnO nanoparticles is smaller. From TEM images in Figure 3.6, the size of Pt nanoparticles are not considerably depending on Pt doping concentration. Thus, the density of Pt nanoparticle increases with Pt concentration as depicted in Figure 3.15. It can be seen that the low Pt concentration case will have larger average Pt-doped ZnO particle diameter, d_{BET} , than high Pt concentration one because the average particle size of Pt and ZnO mixed nanoparticles will decrease as the number of smaller Pt nanoparticles increases. For low Pt concentration, the number of Pt nanoparticles is low and spill-over mechanism is not effective because Pt catalyst particles are not available near all contacting points. The spill-over action of Pt becomes considerably more effective when the number of Pt nanoparticles is sufficiently high enough so that they can control interparticle contact resistance. This is the reason why gas response significantly decreases and the average particle size measured by d_{BET} decreases as Pt concentration increases.

The gas sensing selectivity of ZnO gas sensor has been characterized toward three other common reducing gases, hydrogen (H₂), carbon monoxide (CO) and methane (CH₄) as shown in Figure 3.18. Figure 3.18 shows that 2.0 at% Pt-doped ZnO gas sensor has a good gas selectivity for 0.1 vol.% of C_2H_2 concentration of 43 at 300°C. The response of 2.0 at% Pt-doped ZnO gas sensor of H₂, CO and CH₄ were

8.2, 2.4 and 1.4 at 0.1 vol.% of concentration respectively and at 300°C operating temperature. Thus, the C₂H₂-sensing response of 2.0 at% Pt-doped ZnO was higher than that to H₂, CO and CH₄. The C₂H₂ selectivity of 2.0 at% Pt-doped ZnO is also substantially higher compared to the pure ZnO gas sensor whose acetylene response was on the same order as those of H₂, CO and CH₄. The results indicate that Pt has higher catalytic activity with C₂H₂ than H₂, CO and CH₄.

The reproducibility, stability and reversibility of the sensor were also assessed. Five sensors from the same batch were found to have response variation of less than 15 %. The sensors were also seen to have good stability with less than 20 % drift in response over 1 months of operation. Moreover, the sensor was highly reversible with baseline shift of less than 5 % after recovery from several repeated gas sampling at high concentration.



Figure 3.17 Variation operating temperature of response with concentration of C_2H_2 (0.02–1.0 vol.% of concentration) for S1, S2, S3 and S4 at (a) 200°C, (b) 300°C and (c) 350°C.



Figure 3.17 (Cont.) Variation operating temperature of response with concentration of C_2H_2 (0.02–1.0 vol.% of concentration) for S1, S2, S3 and S4 at (a) 200°C, (b) 300°C and (c) 350°C.



Figure 3.18 Variation of response with concentration of C_2H_2 , H_2 , CO and CH₄ (at 300°C, 0.1 vol.% concentration) for sensor S1 (pure ZnO) as compared to S2 (0.2 at% Pt-doped ZnO).

3.2.2.3 Gas response of Pt-doped ZnO nanoparticle towards

Methane (CH₄) gas

The response and response time of the thin films of the pure ZnO and Pt-doped ZnO with different doping levels nanoparticles as a function of CH₄ concentration between 0.02 and 0.5 vol.% of concentration at 200, 300 and 350 °C were performed. The response increased considerably by doping the ZnO nanoparticles with 0.2 at% Pt to be ~1.5 at 350°C for 0.5 vol.% of CH₄ concentration as shown in Figure 3.19. On the other hand, the sensitivity decreased when doping the ZnO nanoparticles with 1.0, 2.0 at% Pt and the pure ZnO respectively, which the

response decreased and the operating temperature decreased from 300°C to 200°C. The response couldn't measure at the operating temperature beyond 350°C. Moreover, the response of the pure ZnO and the ZnO nanoparticles doped with 1.0 and 2.0 at% Pt sensing films could not detect, due to much small response signals.



Figure 3.19 Variation operating temperature of response with concentration of CH₄ (0.02–1.0 vol.% concentration) for S1 and S2 at 350° C.

3.2.3 Other gases

3.2.3.1 Gas response of Pt-doped ZnO nanoparticle towards

Ethylene (C₂H₄) and Ammonia (NH₃) gases

The response and response time of the thick films of the pure ZnO and Pt-doped ZnO with different doping levels nanoparticles as a function of C_2H_4 and NH₃ concentration between 0.02 and 1.0 vol.% concentration at 200, 300 and 350°C were performed. The response of C_2H_4 and NH₃ gases increased considerably by doping the ZnO nanoparticles with 1 at% Pt to be ~0.89 and 0.53 for 1.0 vol.% of C_2H_4 and NH₃ concentration, respectively at 350 °C. On the other hand, the response decreased by doping the ZnO nanoparticles with 0.2, 2.0 at% Pt and the pure ZnO respectively, when the response decreased as the operating temperature decreased from 300°C to 200°C. The response couldn't be measured at the operating temperature beyond 350°C. Moreover, the response of the pure ZnO and the ZnO nanoparticles doped with 0.2 and 2.0 at% Pt sensing films could not be determined, due to weak response signals. The summary comparing gases sensing with the pure ZnO and Pt-doped ZnO as shown in Table B.2 (Page 154).

3.2.3.2 Gas response of the pure ZnO nanoparticle towards ethanol (C_2H_5OH) gas

The response and response time of the thick films of the pure ZnO nanoparticles as a function of C_2H_5OH concentrations at 300°C and 350°C are shown in Figure 3.20(a) and (b). The response of the pure ZnO of ~ 29 with the response time of 11s were obtained at 0.1 vol.% of C_2H_5OH , respectively at 300°C. The sensor behaviors under the operating temperature of 300°C versus the C_2H_5OH

concentrations ranging from 0.005–0.1 vol.% of C_2H_5OH concentration for the flame-made pure ZnO nanoparticles were plotted as shown in Figure 3.20 (a). The changes in resistance of the pure ZnO sensor for C_2H_5OH gas under exposure to 0.005–0.1 vol.% of C_2H_5OH during forward cycle at 350°C are shown in Figures 3.20 (b). The response, however, increased considerably by testing the pure ZnO sensor with C_2H_5OH gas at 0.1 vol.% concentration of C_2H_5OH gas. The response of ~ 19 with the response time of 11s was obtained at 0.1 vol.% of C_2H_5OH , respectively.



Figure 3.20(a) Variation operating temperature of response with concentration of C_2H_5OH (0.005–0.1 vol.% of concentration) for S1, S2, S3 and S4 at 300°C.



Figure 3.20(b) Variation operating temperature of response with concentration of C_2H_5OH (0.005–0.1 vol.% of concentration) for S1, S2, S3 and S4 at $350^{\circ}C$.

It is well known that the response of a semiconductor gas sensor is highly influenced by its operating temperature [131–132]. In order to determine the optimum operating temperatures, the response of the pure ZnO gas sensor towards 0.005 vol.% concentration of nitrogen dioxide, ethanol and sulfur dioxide in air was tested as a function of operating temperature, as shown in Figure 3.21. It is clear that the responses of three gases tested varied with operating temperature. The response to NO₂ first increased with temperature, up to 300°C, and then gradually decreased. The maximum response towards NO₂ was 33 at 300°C. For C_2H_5OH and SO₂, the

response continuously increased when operating temperatures varied from 200 to 300° C, and then decreased. The maximum responses obtained were 7 and 3 at 300° C. Therefore, optimal operating temperatures of 300° C were chosen for NO₂, ethanol and SO₂ respectively, to further examine the characteristics of the gas sensor. It can be concluded from the results that the pure ZnO sensor can act as a multifunctional selective gas sensor for detecting NO₂, C₂H₅OH and SO₂ gases. In other words, the above mentioned sensor can be used as an excellent NO₂ sensor at an operating temperature of 300° C.



Figure 3.21 The response *versus* variation of the operating temperature of NO_2 , C_2H_5OH and SO_2 (at 0.005 vol.% concentration) for the pure ZnO sensor.

The gas sensing selectivity of the pure ZnO gas sensor has been characterized towards one common oxidizing gas, NO₂, and two other common reducing gases, C_2H_5OH and SO₂ as shown in Figure 3.22. In Figure 3.22, the responses towards NO₂, C_2H_5OH 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 the synthesized pure ZnO gas sensor.



Variation of gas type at 50 ppm



For sensors comparison with the same material, there were many reports with other preparation methods. A summary on the response properties towards NO_2 , C_2H_5OH and SO_2 gases of the pure ZnO prepared by several synthetic methods is shown in Table 3.2. Great interest in improving the gas response as well as selectivity and in decreasing the working temperature has been witnessed. NO_2 is considered a common air pollutant produced during combustion in automotive engines, industrial factories, and power plants. Therefore, the development of stable NO_2 gas sensors that can detect extremely low concentrations of NO_2 with high sensitivity is highly desirable [136]. In this study, the 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.

The NO₂, C_2H_5OH and SO₂ sensing behaviors reported by other researchers are summarized in Table 3.2

Sensing materials	Method	Gas concentration	Response	Reference
Pure ZnO	Hydrothermal	1 ppm of NO ₂ , at 300°C	~ 1.8	[14]
Pure ZnO	Electrostatic spray deposition (ESD) technique.	1 ppm of NO ₂ , at 300°C	~ 1.84	[13]
Pure ZnO	Conventional solid-state method	10 ppm of NO ₂ , at 350°C	~ 1.81	[15]
Pure ZnO	A simple chemical route,	250 ppm of ethanol, at 400, 600 and 800°C	~ 6.5, 5.6 and 4,	[20]
Pure ZnO	Thermal evaporation	500 ppm of ethanol, at 300°C	5.3	[23]
Pure ZnO	A solution method	100 ppm of SO ₂	< 0.5	[18]

Table 3.2. A summary on the gas sensing properties of differently–prepared undoped ZnO for NO₂, ethanol (C_2H_5OH) and SO₂ gases.

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