CHAPTER 4

CONCLUSIONS

In this research unloaded WO_3 and Pt-loaded WO_3 were successfully synthesized by FSP and the hydrothermal method. Characterization of these nanomaterials and the sensing films were elucidated and investigated by XRD, BET, SEM with EDS–dot mapping mode, HRTEM. Gas sensing films of all samples were tested towards various flammable gases (H_2, C_2H_5OH, C_2H_4 and CO); and environmentally hazardous gas (NO_2).

4.1 Nanoparticles synthesized by FSP

Unloaded WO_3 and Pt-loaded WO_3 (0.25−1.0 wt.% Pt loading) nanoparticles were successfully produced by FSP and structurally characterized by XRD, SEM and HRTEM. The BET surface area (SSA_{BET}) of the nanoparticles was measured by nitrogen adsorption micromeristic technique. XRD patterns revealed that Pt-loaded WO_3 nanoparticles and their corresponding sensing films were crystalline with a monoclinic phase of WO_3. From BET measurement, it was found that the calculated particle sizes of all samples were in the same range of 9−11 nm. From SEM data, the nanoparticles were spherical like, and well dispersed without evident aggregation. The average particles size ranges from 10 to 20 nm. From this observation, it was found that the rough morphology and the rough particle sizes were not changed with the increasing Pt loading levels. HRTEM characterization, showed the nanoparticles having clear spherical morphology. The crystallite sizes of spherical unloaded WO_3 and Pt-loaded WO_3 were found to be ranging of 5−20 nm. For Pt-loaded WO_3 powder, very small spherical Pt nanoparticles with diameter of ~1 nm were found to disperse over the surface of WO_3 matrix and the presence of Pt element was confirmed by EDS analysis.

4.2 Nanoparticles synthesized by the hydrothermal method

Unloaded WO_3 nanoparticles were synthesized by the hydrothermal method and then impregnated with different Pt contents (0.25−1.0 wt.% Pt loading). The nanoparticles were characterized by XRD, BET, SEM, EDS and HRTEM. The XRD characterizations showed that all samples were highly crystalline and all peaks can match to the monoclinic structure of WO_3 (JCPDS No. 04−006−7123). Pt peaks were not found in these patterns. It can be assumed that the size of Pt particles were very small. From BET measurement, it was found that the calculated particle sizes of all samples were in the same range of 50−80 nm. From SEM characterization, it can be seen that the powders were seen as loose agglomerations with a plate size ranging from roughly 40 to 500 nm in width and 20−40 nm in thickness. Moreover, the presence of Pt element was confirmed by EDS analysis. From HRTEM data, it was observed that platelet particle having the average size of 80±10 nm in length and 50±5 nm in thickness. HRTEM show that very small Pt nanoparticles were uniformly dispersed on the surface of larger WO_3 particles. The size of Pt nanoparticles was smaller than 1 nm for 1.0 wt.% Pt-loaded WO_3.

4.3 Comparison of characteristics of unloaded WO_3 and Pt-loaded WO_3 nanoparticles synthesized by FSP and the hydrothermal method

Table 4.1 shows the summary of characteristics of unloaded WO_3 and Pt-loaded WO_3 nanoparticles.

Table 4.1 Summary of characteristics of unloaded WO_3 and Pt-loaded WO_3 nanoparticles.

Material characterization method	**Unloaded WO_3 and Pt-loaded WO_3 nanoparticles**	
	FSP	**Hydrothermal**
XRD	Monoclinic structure (JCPDS No.83−0950)	Monoclinic structure (JCPDS No.04−006−7123)
BET	Size : 9−10 nm	Size : 50−80 nm
SEM	Size : 10−20 nm (nanoparticles)	Size : 40−500 nm in width and 20−40 nm in thickness (nanoplates)
TEM	Size : 5−20 nm	Size : 80±10 nm in length and 50±5 nm in thickness

4.4 Gas sensing properties

4.4.1 Comparison of the performance of the unloaded WO_3 sensor

Unloaded WO_3 film on alumina substrates interdigitated with gold electrodes were prepared by spin-coating technique and tested for gas sensing towards oxidizing gas such as NO_2 and different reducing gases including H_2, C_2H_4 , C_2H_5OH and CO. For the reducing gases, the unloaded WO_3 synthesized by the hydrothermal method was the most selective to H_2 with relatively high response (S = ~102.44 at 1 vol.% H_2) when compared with unloaded WO_3 synthesized by FSP. On the other hand, oxidizing gas like NO_2, unloaded WO_3 synthesized by FSP exhibited excellent NO_2 sensing performances with a very high response (S = ~326 at 20 ppm NO_2), low operating temperature and shorter response time than unloaded WO_3 synthesized by the hydrothermal method. Therefore, it was important to note that the sensor response of WO_3 depended significantly on the preparation method.

4.4.2 Influence of Pt nanoparticles

Unloaded WO_3 sensor showed highly response to oxidizing gas, NO_2, but very weak response to reducing gas. It is well known that the sensor properties can be boosted by activation with some metals such as Au, Pd and Pt. Among various metal tested, Pt is the most effective catalyst that can greatly promote sensing of reducing gas including hydrogen, carbon monoxide and hydrocarbon by chemical sensitization via 'spillover' effect. It can be effectively used to increase response and selectivity as well as to reduce response and recovery times.

For the gas response behavior of Pt-loaded WO_3 sensing films several gases have been tested namely NO_2, H_2, C_2H_4, C_2H_5OH, and CO. The results showed that the gas sensing properties of the Pt-loaded WO_3 sensors were superior to those of the unloaded WO_3. Especially, both of 1.0 wt.% Pt-loaded WO_3 synthesized by FSP and the hydrothermal method showed higher response, better selectivity, faster response/recovery and better longer term stability usage to especially H_2 than the other gases. In addition, 1.0 wt.% Pt-loaded WO_3 synthesized by FSP exhibits the extremely high response of ~1.34 $x10^5$ at 1 vol.% H_2, which much higher than 1.0 wt.% Pt-loaded WO_3 synthesized by the hydrothermal method (S= ~2.16 $x10^4$ at 1 vol.% H_2 (Temp.= 250°C)) and with low working temperature (150°C). In relation to this study the gas sensing properties of materials were related to the surface states and morphology of the material. The gas response could be increased by decreasing the grain size due to high surface/volume ratio.

4.5 Comparison of gas sensing response of unloaded WO_3 and Pt-loaded WO_3 nanoparticles synthesized by FSP and the hydrothermal method

Table 4.2 shows the summary of gas sensing performances of unloaded WO_3 sensor.

Table 4.2 Summary of gas sensing performances of unloaded WO_3 sensor.

Methods	Materials	Gas concentration	Response (S=R_a/R_g or R_g/R_a)
FSP	Unloaded WO_3	H_2 (0.01−1 vol.%)	No response
Hydrothermal	Unloaded WO_3		~102.44 to 1 vol.% at 250^{o}C
FSP	Unloaded WO_3	C_2H_5OH (0.005−0.1 vol.%)	~4.48 to 0.1 vol.% at 200^{o}C
Hydrothermal	Unloaded WO_3		~4.53 to 0.1 vol.% at 250^{o}C
FSP	Unloaded WO_3	CO (0.005−0.2 vol.%)	No response
Hydrothermal	Unloaded WO_3		No response
FSP	Unloaded WO_3	C_2H_4 (0.005−0.1 vol.%)	~1.12 to 0.1 vol.% at 150^{o}C
Hydrothermal	Unloaded WO_3		~7.28 to 0.1 vol.% at 350^{o}C
FSP	Unloaded WO_3	NO_2 (1−50 ppm)	~326 to 20 ppm at 150^{o}C
Hydrothermal	Unloaded WO_3		~15.38 to 50 ppm at 250^{o}C

Table 4.3 show the summary of gas sensing performances of 0.25–1.0 wt.% Pt-loaded WO_3 sensors.

Table 4.3 Summary of gas sensing performances of 0.25–1.0 wt.% Pt-loaded WO_3 sensors.

Methods	**Materials**	**Gas concentration**	**Response (S=R_a/R_g or R_g/R_a)**
FSP	1.0 wt.% Pt-loaded WO_3	H_2 (0.01−1 vol.%)	~$1.34x10^5$ to 1 vol.% at 150°C
Hydrothermal	1.0 wt.% Pt-loaded WO_3		~$2.16x10^4$ to 1 vol.% at 250°C
FSP	1.0 wt.% Pt-loaded WO_3	C_2H_5OH (0.005−0.1vol.%)	~$2.4x10^3$ to 0.1 vol.% at 200°C
Hydrothermal	1.0 wt.% Pt-loaded WO_3		~$1.4x10^3$ to 0.1 vol.% at 350°C
FSP	1.0 wt.% Pt-loaded WO_3	CO (0.005−0.2vol.%)	~$1.2x10^2$ to 0.05 vol.% at 200°C
Hydrothermal	1.0 wt.% Pt-loaded WO_3		~469 to 0.2 vol.% at 250°C
FSP	1.0 wt.% Pt-loaded WO_3	C_2H_4 (0.005−0.1vol.%)	~9.9 to 0.1 vol.% at 150°C
Hydrothermal	1.0 wt.% Pt-loaded WO_3		~388 to 0.1 vol.% at 350°C
FSP	0.25wt.% Pt-loaded WO_3	NO_2 (1−50 ppm)	~954 to 20 ppm at 150°C
Hydrothermal	0.25wt.%Pt-loaded WO_3		~8.21 to 50 ppm at 250°C

4.6 Suggestions for future work

4.6.1 The gas sensing properties of the unloaded WO_3 and Pt-loaded WO_3 sensors for other gases (such as H_2S, NH_3, O_2, C_2H_2 and CH_4) will be further investigated.

4.6.2 Unloaded WO_3 and Pt-loaded WO_3 nanoparticles will be investigated for catalysts, electrochromic devices, and possibility for use as photocatalytic catalysts.

4.6.3 The sensor may be prepared by several methods such as screen-printing, sputtering and chemical vapor deposition.