CHAPTER 4

CONCLUSIONS

In this research, unloaded TiO_2 and metal-loaded (metal = Pt, Au and Ag) TiO_2 nanoparticles were successfully synthesized by FSP method. Characterization of these nanoparticles and the sensing films were elucidated and investigated by XRD, BET, SEM with EDS–dot mapping mode and HRTEM. Gas sensing films of all samples were tested towards various flammable gases (H_2, C_2H_5OH and $(CH_3)_2CO$) and environmentally hazardous gases (CO and SO_2).

4.1 Nanoparticles synthesized by FSP

Unloaded TiO_2 and metal-loaded TiO_2 (0.25, 0.50, 0.75, 1.0, 2.0 and 3.0 mol%) nanoparticles were successfully synthesized by FSP and structurally characterized by XRD, SEM, EDS and HRTEM. The BET surface area (SSA_{BET}) of the nanoparticles was measured by nitrogen adsorption micromeristic technique. From BET measurement, it was found that the calculated particle sizes of all samples were in the same range of ~10−38 nm. XRD patterns revealed that metal-loaded TiO_2 nanoparticles and their corresponding sensing films were crystalline with anatase and rutile phase of TiO_2. The XRD peaks of Pt and Ag peaks were not found in these patterns, but Au peaks were found in these patterns.

From SEM and EDS data, it can be seen that nanoparticles were spherical in shape, the surface of the nanopowders was porous, and well dispersed without evidence of aggregation. The EDS spectra showed the elemental histograms

corresponding to Ti and O of TiO_2, Pt, Au and Ag of metal loading. From this observation, it was found that the rough morphology and the rough particle sizes were not changed with increasing Pt, Au and Ag loading levels. HRTEM characterization showed the nanoparticles having clear spherical morphology. The crystallite sizes of spherical unloaded TiO_2 and Pt, Au and Ag-loaded TiO_2 nanoparticles were found to be ranging of 10−80 nm. For Pt, Au and Ag-loaded TiO_2 powder, very small spherical Pt and Ag nanoparticles with diameter of ~2 nm, Au nanoparticles with diameter of ~5−15 nm were found to disperse over the surface of TiO_2 matrix and the presence of Pt, Au and Ag element was confirmed by EDS analysis.

4.2 Comparison of characteristics of unloaded TiO_2 and metal-loaded TiO_2 nanoparticles synthesized by FSP

Table 4.1 shows the summary of characteristics of unloaded TiO_2 and metal-loaded TiO_2 nanoparticles.

Table 4.1 Summary of characteristics of unloaded TiO_2 and metal-loaded TiO_2 nanoparticles

Material characterization method	**Unloaded TiO_2**	**Pt-loaded TiO_2**	**Au-loaded TiO_2**	**Ag-loaded TiO_2**
XRD	TiO_2 (anatase, rutile)	TiO_2 (anatase, rutile), Pt (cubic face centered)	TiO_2 (anatase, rutile), Au (cubic face centered)	TiO_2 (anatase, rutile), Ag (cubic face centered)

Table 4.1 (Cont.) Summary of characteristics of unloaded TiO_2 and metal-loaded TiO_2 nanoparticles

Material characterization method	**Unloaded TiO_2**	**Pt-loaded TiO_2**	**Au-loaded TiO_2**	**Ag-loaded TiO_2**
BET	Size : 9−10 nm	Size : 14−38 nm	Size : 14−27 nm	Size : 14−24 nm
TEM	Size : ~9−25 nm	Size : ~10−50 nm	Size : ~10−60 nm	Size : ~10−80 nm

4.3 Gas sensing properties

Unloaded TiO_2 film on alumina substrates interdigitated with gold electrodes were prepared by spin-coating technique and tested for gas sensing towards reducing gas such as H_2 and different reducing gases including $(CH_3)_2CO$, CO, C_2H_5OH and SO_2. For the reducing gases, the unloaded TiO_2 synthesized by the FSP method was selective to H_2 with relatively low response (S = ~2.37 at 1 vol% H_2, 400 ^oC) compared with Pt, Au and Ag-loaded TiO_2 synthesized by FSP. On the other hand, reducing gases like $(CH_3)_2CO$ and C_2H_5OH, unloaded TiO_2 exhibited $(CH_3)_2CO$ and C_2H_5OH sensing performances with response (S = ~19.4 at 0.20 vol% (350 ^oC) of $(CH_3)_2CO$ and S = ~21.7 at 0.10 vol% (400 ^oC) of C_2H_5OH).

Unloaded TiO_2 sensor showed response to reducing gases, H_2, $(CH_3)_2CO$ and C_2H_5OH while showed no response to CO and SO_2. It is well known that the sensor properties can be boosted by activation with some metals such as Pt, Au and Ag. Among various metal tested, Pt, Au and Ag, are the most effective catalysts that can greatly promote sensing of reducing gas including H_2, CO, $(CH_3)_2CO$ and C_2H_5OH 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, Au and Ag-loaded TiO_2 sensing films several gases have been tested namely H_2, $(CH_3)_2CO$, CO, C_2H_5OH, and SO_2. The results showed that the gas sensing properties of the metal-loaded TiO_2 sensors were superior to those of the unloaded TiO_2. Especially, metal-loaded TiO_2 showed higher response, better selectivity, faster response/recovery and better longer term stability usage to especially H_2 than the unloaded TiO_2. In addition, 2.0 mol% Pt-loaded TiO_2 exhibits the extremely high response of 470 at 1.0 vol% (300 ^oC) towards H_2, which much higher than Au and Ag-loaded TiO_2. 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.

4.4 Comparison of gas sensing response of unloaded TiO_2 and metal-loaded TiO_2 nanoparticles synthesized by FSP

Table 4.2 shows the summary of gas sensing performances of unloaded TiO_2 and metal-loaded TiO_2 sensor.

Table 4.2 Summary of gas sensing performances of unloaded TiO_2 and metal-loaded TiO_2 sensor

Materials	**Gas concentration**	**Response ($S=R_a/R_g$)**
Unloaded TiO_2	H_2	~2.37 at 400 ºC
2.0 mol% Pt-loaded TiO_2	(1.0 vol%)	~470 at 300 ºC
0.75 mol% Au-loaded TiO_2		~41.2 at 400 ºC
1.0 mol% Ag-loaded TiO_2		~12.0 at 350 ºC
Unloaded TiO_2	$(CH_3)_2CO$	~19.4 at 350 ºC
0.50 mol% Pt-loaded TiO_2	(0.20 vol%)	~244 at 400 ºC
0.75 mol% Au-loaded TiO_2		~194 at 350 ºC
0.75 mol% Ag-loaded TiO_2		~161 at 350 ºC
Unloaded TiO_2	CO	NO response
1.0 mol% Pt-loaded TiO_2	(0.10 vol%)	~5.39 at 350 ºC
0.50 mol% Au-loaded TiO_2		~8.60 at 350 ºC
Ag-loaded TiO_2		NO response
Unloaded TiO_2	C_2H_5OH	~21.7 at 400 ºC
0.25 mol% Pt-loaded TiO_2	(0.10 vol%)	~14.5 at 400 ºC
0.75 mol% Au-loaded TiO_2		~425 at 350 ºC
0.25 mol% Ag-loaded TiO_2		~20.7 at 400 ºC
Unloaded TiO_2	SO_2	No response
Pt-loaded TiO_2	(0.05 vol%)	No response
Au-loaded TiO_2		No response
Ag-loaded TiO_2		No response

4.5 Suggestions for future work

4.5.1 The gas sensing properties of the unloaded TiO_2 and Pt, Au and Ag-loaded TiO_2 sensors for other gases (such as H_2S, NH_3, NO_2, C_2H_2 and CH_4) will be further investigated.

4.5.2 The photocatalytic activity of unloaded TiO_2 and metal-loaded TiO_2 nanoparticles for several organic compounds under UV and/or visible light irradiation will be further investigated as a function of pH.