CHAPTER 2

EXPERIMENTAL

2.1 Chemicals and instruments

All chemicals used in the experiments are analytical grade or better as shown in Table 2.1

Table 2.1 Chemicals, Molecular weight, Purity and Company

Chemical	**Molecular weight (g/mol)**	**Purity**	**Company/ CAS NO.**
Al_2O_3 substrates/ interdigitated with Au electrodes(Au/Al_2O_3)	101.96	96%	Semiconductor Wafer, Inc. NECTEC, THAILAND
Ethanol	46.07	99.9%	Merck / CAS No. 64−17−5
Ethyl cellulose	454.8	48-49.5%	Sigma/ CAS No. 9004−57−3
Hydrochloric acid	36.46	36.5-38.0%	Sigma/ CAS No. 7647−01−0
Platinum (II) acetyacetonate	393.29	97%	Aldrich/ CAS No. 15170−57−7

Table 2.1 (Cont.) Chemicals, Molecular weight, Purity and Company

Chemical	Molecular weight (g/mol)	Purity	Company/ CAS NO.
Sodium tungstate	329.86	99.0%	Ajax/ CAS No. 10213−10−2
Sodium chloride	58.44	99.0%	Sigma/ CAS No. 7647−14−5
Terpineol	154.25	90%	Aldrich/ CAS No. 10482−56−1
Tungsten (VI) ethoxide 5% w/v in ethanol 99.8%	454.21	5% w/v in ethanol 99.8%	Alfa Aesar / CAS No. 62571−53−3

2.2 Instruments

The instruments employed in the experiments are summarized in Table 2.2

Table 2.2 Instrument used in the experiments

Instrument	Model/ Company/ Country
X-ray diffractometer (XRD)	Rigaku, TTRAXIII, JAPAN
Scanning electron microscope (SEM) and energy dispersive X-ray spectroscope (EDS)	JEOL, JSM-6335F, Japan
Transmission electron microscopy (TEM, HRTEM)	JEOL, JEM-2010, Japan
Brunauer-Emmett-Teller (BET)	Micromeritics Tristar, 3000, Germany

2.3 Sample preparations

2.3.1 Unloaded WO_3 and Pt-loaded WO_3 nanoparticles synthesized by FSP

Tungsten ethoxide (Alfa Aesar, 5% w/v in ethanol 99.8%) and platinum (II) acetylacetonate (Pt $(acac)_2$, Aldrich, 97% Pt) were used as tungsten and platinum precursors, respectively. 0.0624 g of platinum (II) acetylacetonate ($Pt(acac)_2$) was dissolved in 6 mL of ethanol solution under vigorous stirring. Then, the solution was added into 50 mL of tungsten ethoxide in the amount of 0.5, 1.0, 1.5 and 2.0 mL for Pt loading of 0.25, 0.5, 0.75 and 1.0 wt.%, respectively. The experimental setup for the synthesis of Pt-loaded WO_3 nanoparticles was shown in Figure 2.1. The liquid precursor mixture was rapidly dispersed by a gas stream and ignited by a premixed CH_4/O_2 flame. The precursor solutions were fed into a FSP reactor by a syringe pump at a rate of 5 mL/min while 5 L/min of O_2 was distributed around the injection nozzle (5/5 flame condition) while supporting flamelet was produced with CH_4 and O_2 flow rates of 1.19 and 2.46 L/min, respectively. The flame height was observed to be approximately 10−12 cm, and was slightly increased by increasing the combustion enthalpy. The combustion enthalpies are directly dependent on the particular solvent, starting materials and dopants. All samples showed a yellowish-orange flame as seen in Figure 2.2. The pressure drop at the capillary tip was kept constant at 1.5 bars by adjusting the orifice gap area at the nozzle. After evaporation and combustion of precursor droplets, nanopowders were formed by nucleation, condensation, coagulation, coalescence and Pt deposition on WO_3 support. Finally, nanoparticles were collected on glass microfibre filters (Whatmann GF/A, 25.7 cm in diameter) with an aid of a vacuum pump. The flame-made WO_3 nanoparticles was designated as

P0 while the WO_3 nanoparticles with 0.25−1.0 wt.% Pt loading were designated as P0.25-P1, respectively.

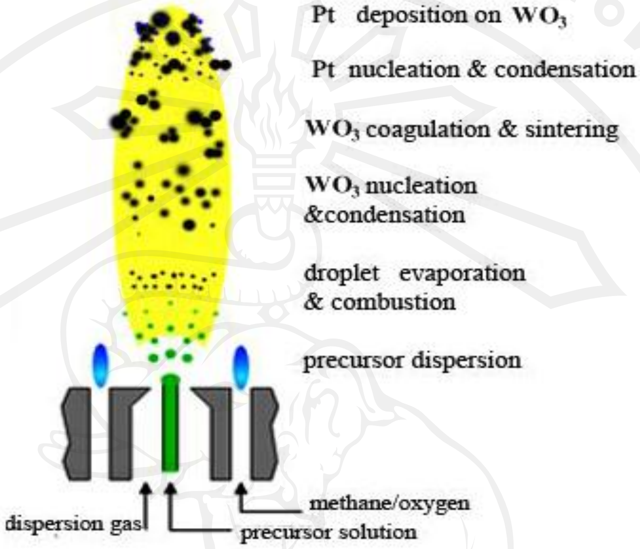

Figure 2.1 The experimental setup for the synthesis of Pt-loaded WO_3 nanoparticles by FSP.

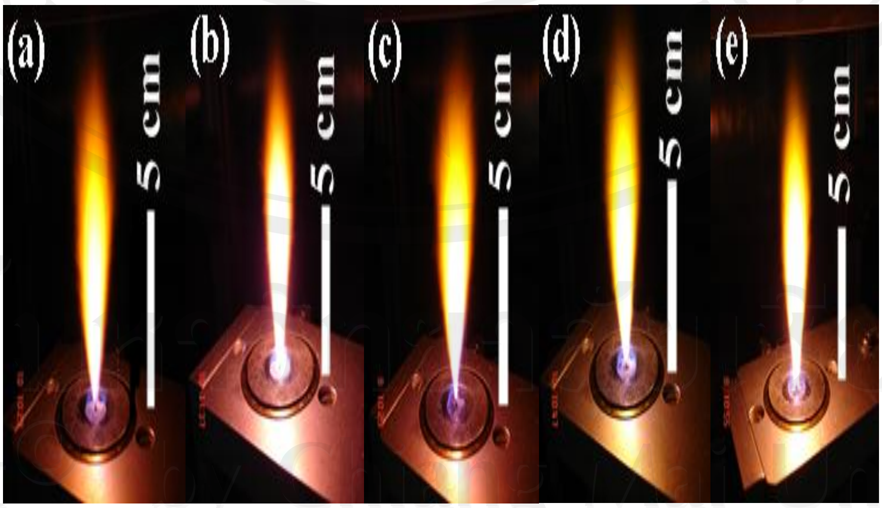

Figure 2.2 Spray flame of (a) unloaded WO_3 (P0), (b-e) 0.25, 0.5, 0.75, and 1.0 wt.% Pt-loaded WO_3 nanoparticles (P0.25-P1).

2.3.2 Unloaded WO_3 and Pt-loaded WO_3 nanoparticles synthesized by hydrothermal/impregnation methods

The process steps in the preparation of Pt-loaded WO_3 nanoparticles by hydrothermal/impregnation techniques were shown in Figure 2.3. Unloaded WO_3 nanoparticles were synthesized by the hydrothermal method. Sodium tungstate dihydrate ($Na_2WO_4 \cdot 2H_2O$), hydrochloric acid (HCl), and sodium chloride (NaCl) aqueous solution were used as the precursors. In a typical procedure to synthesize unloaded WO_3 nanoparticles, 0.825 g of $Na_2WO_4 \cdot 2H_2O$ and 1.160 g of NaCl were dissolved in 19 mL of deionized (DI) water under stirring. Subsequently, 3 M HCl was slowly dropped into the solution under continuous stirring until the pH value of the solution reached 2.0. Then, the solution was transferred into a Teflon-lined autoclave and the hydrothermal reaction proceeded at 180^{o}C for 24 h in an oven. After the autoclave cooled to room temperature, the final products were washed with DI water and ethanol several times by centrifugation. The obtained powder was subsequently dried at 80^{o}C in air. Pt-loaded WO_3 nanoparticles were prepared by the impregnation method. 0.0624 g of platinum (II) acetylacetonate ($Pt(acac)_2$) was dissolved in 6 mL of ethanol solution under vigorous stirring. Then, the solution was added into 1 g of WO_3 nanoparticles in the amount of 0.5, 1.0, 1.5 and 2.0 mL for Pt loading of 0.25, 0.5, 0.75 and 1.0 wt.% respectively. The contents were mixed until they formed smooth slurry and dried in an oven at 80^{o}C for 2 h. The yellowish-brown color powder was obtained. The powders were grinded in an agate motar and calcined at 300^{o}C for 2 h. The five Pt/WO_3 samples with different Pt contents were named as H0, H0.25, H0.5, H0.75 and H1.0.

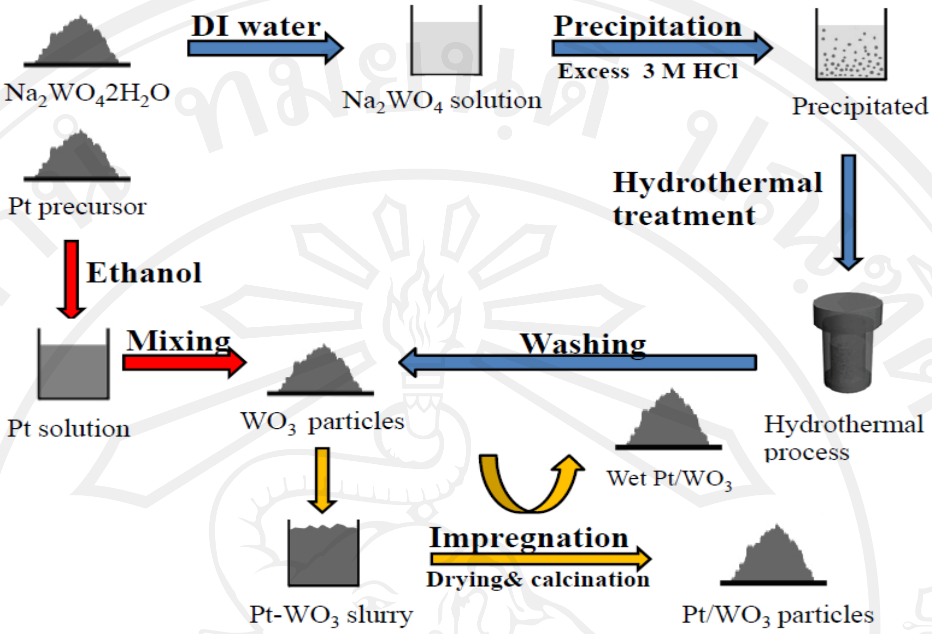

Figure 2.3 The process steps in the preparation of Pt-loaded WO_3 nanoparticles by hydrothermal/impregnation techniques.

2.4 Characterization of nanopowders

The unloaded WO_3 nanopowders and Pt-loaded WO_3 nanoparticles were characterized by using X-ray diffraction (XRD), Brunauer-Emmett-Teller (BET) analysis, scanning electron microscopy (SEM), energy-dispersive X-ray spectrometry (EDS) and high resolution transmission electron microscopy (HRTEM). XRD was used to confirm the phase and crystalline structure of unloaded WO_3 and Pt-loaded WO_3 nanoparticles. BET was a method of choice to evaluate the specific surface area of unloaded WO_3 and Pt-loaded WO_3 nanoparticles. SEM and EDS elemental mapping were used to analyze the morphology and chemical compositions of the samples. HRTEM was selected to determine the accurate size and morphology.

2.4.1 X-ray Diffraction (XRD)

The crystalline structure and phase transformation of unloaded WO_3 and Pt-loaded WO_3 nanoparticles were analyzed by XRD using CuKα radiation. The detection of 2θ values was 10−80°. Identification of crystalline phases were carried out by comparison of the obtained XRD patterns with JCPDS standards.

2.4.2 BET-Specific surface areas analysis (BET)

The specific surface areas (SSA_{BET}) of unloaded WO_3 and Pt-loaded WO_3 nanoparticles were determined by 5-point nitrogen adsorption from the Bruneauer-Emmett-Teller (BET) measurements at 77^{o}K. All samples were controlled with degassing at 150°C for 1 h prior to analysis. The particle diameters (d_{BET}) of unloaded WO_3 and Pt-loaded WO_3 nanoparticles were calculated from specific surface areas and density of Pt and WO_3 as;

$d_{\mathrm{BET}} = 6/[(\rho \mathrm{wo}_3 \times \mathrm{SSAwo}_3 \times (\mathrm{wt.\%\ of\ WO_3})) + (\rho_{\mathrm{Pt}} \times \mathrm{SSA}_{\mathrm{Pt}} \times (\mathrm{wt.\%\ of\ Pt}))]$ equation, where $\rho \mathrm{wo}_3 = 7.16\ \mathrm{g/cm}^3$ and $\rho_{\mathrm{Pt}} = 21.45\ \mathrm{g/cm}^3$.

2.4.3 Scanning Electron Microscopy (SEM)

The morphology of unloaded WO_3 and Pt-loaded WO_3 nanopowders were observed and analyzed by SEM [JSM-6335F, JEOL] and the elemental compositions of the pulp were investigated by EDS [JSM-6335F, JEOL]. The powders samples were dispersed in absolute ethanol using ultrasonic probe for 20 min. The suspension was dropped onto a gold conductive tape attached to the surface of the SEM brass stub. The stub was then coated with gold by plasma sputtering for 2 min, and an acceleration voltage of 20 kV was used.

2.4.4 High Resolution Transmission Electron Microscopy (HRTEM)

The morphology and accurate particle sizes of WO_3 and Pt-loaded WO_3 nanopowders were analyzed by HRTEM) [JEM-2010, JEOL] at an acceleration voltage of 200kV. The powders samples were dispersed in absolute ethanol using ultrasonic probe for 20 min. The suspension was dropped onto carbon-copper grid. The deposit was dried in air prior to imaging.

2.5 Preparation and characterization of sensors

The sensing films were prepared by mixing nanoparticles into an organic paste composed of ethyl cellulose (Fluka, 30−60 mPaS) and terpineol (Aldrich, 90%), which acted as a vehicle binder and a solvent, respectively. The resulting paste was spin-coated on Al_2O_3 substrates (Semiconductor Wafer, Inc, 96%) with interdigitated Au electrodes as shown in Figure 2.4. Figure 2.5 shows SEM images of Al_2O_3 substrates interdigitated with Au electrodes. The alumina substrate had a dimension of 0.4 cm × 0.55 cm × 0.04 cm. Interdigit width, interdigit spacing and area of the electrode were 100 µm, 100 µm and 0.24 cm × 0.4 cm, respectively. The electrode pattern was made by DC sputtering of 50 nm-thick Cr and 200 nm-thick Au layers and lift-off process. The sensing films were subsequently annealed at 400°C for 2 h with heating rate of 2°C/min for binder removal. The particle size was found to be slightly changed after annealing at 400°C. The fabricated sensors using unloaded WO_3, 0.25 wt.% Pt, 0.5 wt.% and 1.0 wt.% Pt-loaded WO_3 powders were labeled as S0, S0.25, S0.5, and S1, respectively. The morphologies and cross section of sensing films were examined by scanning electron microscope (SEM, JEOL JEM-2010).

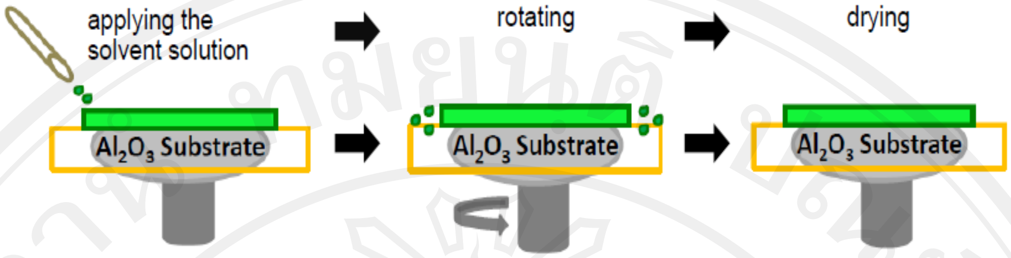

Figure 2.4 The sensors preparation by spin coating technique**.**

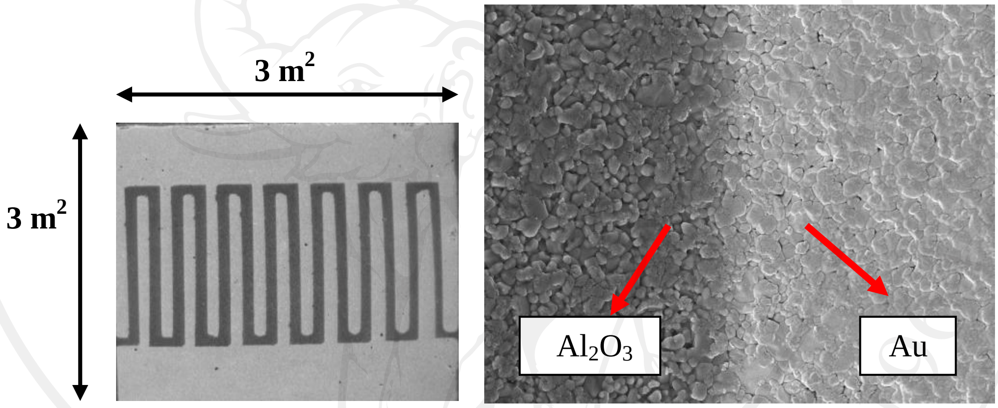

Figure 2.5 SEM images of Al_2O_3 substrates interdigitated with Au electrodes.

Gas sensing measurements of unloaded WO_3 and Pt-loaded WO_3 sensors were performed in a stainless steel chamber. The chamber has a cylindrical shape with diameter of ~12 cm and height of ~15 cm. In addition, there was a conical gas distributor with diameter of ~9 cm and height of ~8 cm, spreading gas to all sensors. A standard flow through technique was used to test gas-sensing properties of these sensors. A constant flux of synthetic air of 2 L/min was mixed with desired concentrations of target gases. All measurements were conducted in a temperature-stabilized sealed chamber at 20°C under controlled humidity. The external NiCr heater was heated by a regulated DC power supply to various operating temperatures.

The operating temperature was varied ranging from 150°C to 350°C. The resistances of various sensors were continuously monitored with a computer-controlled system by voltage-amperometric technique with 5 V dc bias and current measurement through a 6487 Keithley picoammeter. The schematic of sensing test set up as shown in Figure 2.6. The gas sample exposure time and the clean air restoring time were fixed at 5 min and 15 min, respectively. For selectivity performance, the sensors were characterized towards NO_2, C_2H_5OH, CO, C_2H_4 and H_2 gases.

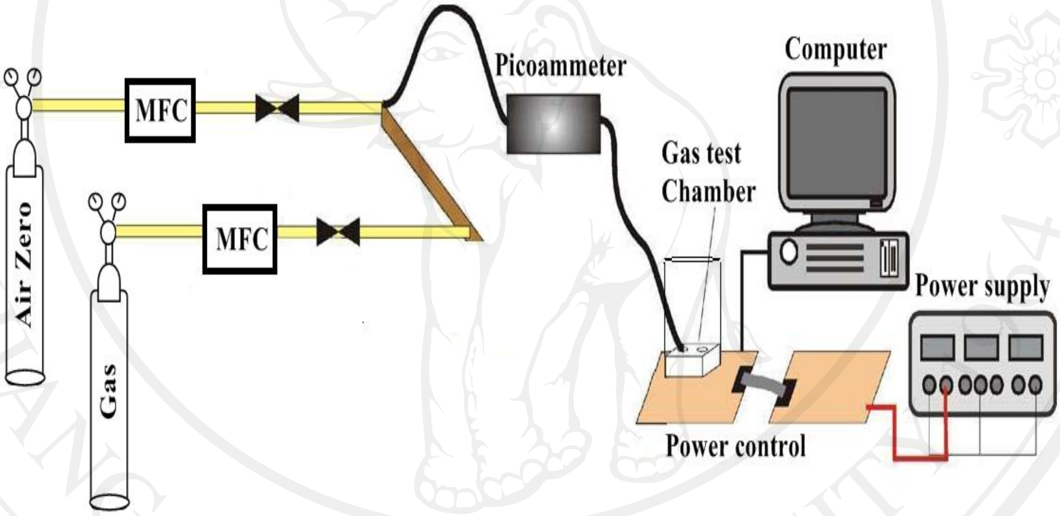

Figure 2.6 The experimental set up of sensing test.