CHAPTER 2

EXPERIMENTAL

2.1 Chemicals and instruments

All chemicals used in the experiments are shown in Table 2.1

Chemical	Molecular weight (g/mol)	Purity	Supplier/ CAS NO.
Al ₂ O ₃ substrates/ interdigitated with Au electrodes (Au/Al ₂ O ₃)	101.96	96%	Semiconductor Wafer, Inc/ (NECTEC, THAILAND)
Ethyl cellulose	454.8	48-49.5%	Sigma/ CAS No. 9004–57–3
Platinum (II) acetylacetonate	393.29	97%	Aldrich/ CAS No. 15170–57–7
Terpineol	154.25	90%	Aldrich/ CAS No. 10482–56–1
Xylene	106.16 5	98.5%	Carlo Erba/ CAS No. 1330–20–7
Zinc naphthenate	319.71	8 wt% Zn	Aldrich/ CAS No. 12001–85–3

 Table 2.1 Chemicals, Molecular weight, Purity and Suppliers.

2.2 Instrument

The instrument used in the experiments are summarized in Table 2.2.

Table 2.2	Instrument	used in	the	experiments
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Instrument	Model/ Company/ Country
X-ray diffractometer (XRD)	Brand/Mode;Panalytical/Expert
Scanning electron microscope	JEOL JSM-6335F, Japan
(SEM) and energy dispersive	
X-ray spectroscope (EDS)	-30%
Transmission electron microscope	JEOL, JEM-2010, Japan
(TEM, HRTEM)	
Brunauer-Emmett-Teller (BET)	Micromeritics Tristar, 3000,
	Germany

2.3 Sample preparations

2.3.1 Precursor preparation

Zinc naphthenate and platinum (II) acetylacetonate $(Pt(acac)_2)$ were used as precursors because the zinc naphtenate had a high heat of combustion and $Pt(acac)_2$ dissolves well in xylene which also has a high heat of combustion. The precursors were dissolved in xylene to obtain a 0.5 M precursor solution. Table 2.3 presented the precursors calculation of the flame synthesis of 0–2.0 at% Pt-doped ZnO data.

2.3.2 Nanoparticles synthesis

The experimental setup for the synthesis of pure ZnO and Pt-doped ZnO nanoparticles by FSP was shown in Figure 2.1. In a typical run, the precursor was fed into a FSP reactor by a syringe pump with a rate of 5 ml/min while 5 l/min O_2 is being dispersed (5/5 flame). The gas flow rates of methane and O_2 supporting flamelets were 1.19, and 2.46 l/min, respectively. The pressure drop at the capillary tip was kept constant at 1.5 bar by adjusting the orifice gap area at the nozzle.

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 temperatures for the spray flame were typically in the range of 2000 K to 2500 K [125]. The liquid precursor mixture was rapidly dispersed by a gas stream and ignited by a premixed methane/oxygen flame. After evaporation and combustion of precursor droplets, particles are formed by nucleation, condensation, coagulation, coalescence, and Pt deposited on ZnO support. Finally, the nanoparticles were collected on glass microfibre filters with the aid of a vacuum pump. Undoped ZnO nanopowder was designated as P0 while the ZnO nanopowders doped with 0.2–2.0 at% Pt were designated as P0.2–P2.0, respectively.

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 Table 2.3 presented the precursors calculation of the flame synthesis of 0–2 at% Pt/ZnO.

			Z	nO - PRECURSO	DR (at%)	50	
		Doping					
Precursor	CAS	density (g.cm ⁻³)		molar weight	(g.mol ⁻¹)	at%Pt-do]	oed ZnO
Zn naphthenate 8wt% Zn	12001-85-3	0.962			4		0.0
Pt(II)-acetylacetonate	15170-57-7			393	31		12
							5
				4			0.
Oxide		7		molar weight	(g.mol ⁻¹)		.5
Zn				65	38		0.
0		J		15.5	- 666		
Ρ	h S	J		195	60.		
ZnO			8	81			
				いい			
molarity precursor	0.50) mol/l	87 9			b . / \/	
volume	200 20	lmi	Child I				
# mol	0.0250	lom				2	
	la	Pt (II)		Zn	Zn	~	
Precursor	Pt (II)	acetylacetonate	Zn naphthenate (g)	naphthenate	naphthenate	xylene (ml)	Total powder on
	acetylacetonate (g)	(Inol)		(Iml)	(Inol)		filter (g)
ZnO	0.0	0.0000	20.43	21.24	0.025000	28.76	2.03
0.2at%Pt:ZnO	0.0203	0.000050	20.39	21.20	0.024950	26.40	2.04
0.5at%Pt:ZnO	0.0507	0.000125	20.33	21.13	0.024875	22.87	2.05
1.0at%Pt:ZnO	0.1014	0.000250	20.23	21.03	0.024750	16.97	2.06
1.5at%Pt:ZnO	0.1521	0.000375	20.12	20.92	0.024625	11.08	2.08
2.0at%Pt:ZnO	0.2027	0.000500	20.02	20.81	0.024500	5.19	2.09

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Figure 2.1 The experimental setup for the synthesis of Pt-doped ZnO nanoparticles by FSP.



Figure 2.2 Spray flame of (a) pure ZnO, (b-f) 0.2, 0.5, 1.0, 1.5 and 2.0 at% Ptdoped ZnO nanoparticles, the flame heights were observed ranging from 10–12 cm with slight increasing the combustion enthalpy and Pt concentration.

2.4 Characterization of nanopowders

The ZnO nanoparticles and Pt-doped ZnO nanoparticles were characterized by using a field emission-scanning electron microscopy (FE-SEM), energy-dispersive Xray spectrometry (EDS), X-ray diffraction (XRD), transmittion electron microscopy and high resolution transmission electron microscopy (TEM, HTEM) and Brunauer-Emmett-Teller (BET) analysis. FE-SEM and EDS elemental mapping were used for analyzing the morphology and chemical compositions of the samples. XRD was used for confirmation the phase and crystalline structure of ZnO and Pt-doped ZnO nanoparticles. TEM was selected to determine the accurate size and morphology. BET was a method of choice to evaluate the specific area of ZnO and Pt-ZnO nanoparticles.

2.4.1 X-ray Diffraction (XRD)

The crystalline structure and phase transformation of pure ZnO synthesized and Pt-doped ZnO were analyzed by X-ray diffraction using CuK α radiation. The detection of 2 θ values was 20–60°. Identification of crystalline phases was carried out by comparison of XRD patterns with JCPDS standards.

2.4.2 Scanning Electron Microscopy (SEM)

The morphology of pure ZnO nanopowders, Pt-doped ZnO nanopowders were observed and analyzed by a field emission-scanning electron microscopy (FE-SEM) [JSM-6335F, JEOL] and the elemental compositions of the pulp were investigated by energy-dispersive X-ray (EDS) spectrometry [JSM-6335F, JEOL]. The powders samples were dispersed in absolute ethanol using ultrasonic probe for 20 minutes. 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 minutes, and an acceleration voltage of 20 kV was used.

2.4.3 Transmission Electron Microscopy (TEM, HRTEM)

The morphology and accurate particle sizes of pure ZnO and Pt-doped ZnO nanopowders were analyzed by transmission electron microscopy (TEM) [JEM-2010] at an acceleration voltage of 200kV. The powders samples were dispersed in absolute ethanol using ultrasonic probe for 20 minutes. The suspension was dropped onto carbon-copper grid. The deposit was dried in air for prior to imaging.

2.4.4 BET-Specific surface areas analysis (BET)

The specific surface areas were analyzed from the BET measurements. The specific surface areas (*SSA*) of pure ZnO and Pt–doped ZnO nanoparticles were calculated and the approximate particle sizes (d_{BET}) were determined by 5-point nitrogen adsorption from the BET measurements at 77 K. All samples were controlled with degassing at 150°C for 1h prior to analysis. The particle diameters of pure ZnO and Pt-doped ZnO were calculated from specific surface areas and density of Pt and ZnO as $d_{BET} = 6/[(\rho_{ZnO} \times SSA_{ZnO} \times (at\% \text{ of } ZnO))+(\rho_{Pt} \times SSA_{Pt} \times (at\% \text{ of } Pt))]$ equation, where $\rho_{ZnO} = 5.61 \text{ g/cm}^3$ and $\rho_{Pt} = 21.45 \text{ g/cm}^3$.

2.5 Preparation and characterization of sensors

Sensing films were prepared by mixing the nanoparticles into an organic paste composed of ethyl cellulose and terpineol, which acted as a vehicle binder and solvent, respectively. The resulting paste was spin-coated on Al₂O₃ substrates with predeposited interdigitated Au electrodes as shown in Figure 2.3 and Figure 2.4 shows SEM images of Al₂O₃ substrates interdigitated with Au electrodes. The films were then annealed at 400°C for 2h (with heating rate of 2 °C/min) for binder removal. The particle size of films was slightly grown after the films were annealed at 400°C. The fabricated sensors using P0, P0.2, P1.0, and P2.0 powders were now labeled as S1, S2, S3, and S4, respectively. The morphology and the cross section of sensing films were analyzed by SEM. The surface morphology, elemental compositions, and accurate size of the ZnO and Pt nanoparticles were further investigated by the EDS line scan mode.



Figure 2.3 The sensors preparation by spin coating technique



Figure 2.4 SEM images of Al₂O₃ substrates interdigitated with Au electrodes.

The gas-sensing characteristics of metal oxide nanoparticles were characterized towards several gases. The flow through technique was used to test the gas-sensing properties of thin films. A constant flux of synthetic air of 2 l/min was mixed with desired concentrations of pollutants. 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 different operating temperatures. The operating temperature was varied from 200°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 picoammeter. The schematic of sensing test set up as shown in Figure 2.5. The sensor was exposed to a gas sample ~5 minutes for each gas concentration testing and then the air flux was restored to recovery for 15 minutes.



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