CHAPTER 3

EXPERIMENTAL

3.1 Materials and instruments

All chemicals used in the experiments are shown in Table 3.1. Also, the instruments used in the experiments are summarized in Table 3.2.

Table 3.1 Category of chemicals: Purity, Molecular weight/Density and Company

Chemical Name	Purity	Molecular formula	Molecular weight (g/mol)/ Density (g/ml)	Company
Zinc naphthenate	< 8 wt% Zn; ≤50% in mineral spirits	$2(C_{11}H_7O_2).Zn$	0.962 g/ml at 25°C (lit.)	Aldrich
Tin (II) 2-ethylhexanoate	~95%	$[CH_3(CH_2)_3CH(C_2H_5)CO_2]_2Sn$	405.12 g/mol	Sigma
Xylenes	~80% Xylene Isomers	$C_6H_4(CH_3)_2$	106.17 g/mol	Aldrich
Ethyl cellulose	48.0−49.5% (w/w) ethoxyl basis	$[C_6H_7O_2(OC_2H)_3]n$	1.14 g/ml at 25°C (lit.)	Fluka

Table 3.1 (Continued)

Chemical Name	**Purity**	**Molecular formula**	**Molecular weight (g/mol)/ Density (g/ml)**	**Company**
Alpha-terpineol	90%	$C_{10}H_{18}O$	154.25 g/mol	Aldrich
Alumina substrate	96%	Al_2O_3	-	Semiconductor Wafer, Inc., 96%
Sodium hydroxide	98.8%	NaOH	40 g/mol	Labscan
Methanol	99.8%	CH_3OH	32.04 g/mol	Labscan
Phenol	99%	C_6H_5OH	94.11 g/mol	Labscan
ZnO nanoparticle (≤ 100 nm)	79.1 - 81.5%	ZnO	81.39 g/mol	Aldrich

Table 3.2 Instruments used in the experiments

Instrument	**Model**	**Company**
Transmission electron microscope (TEM)	JEM-2010	JEOL
X-ray diffractometer (XRD)	D8 Advance	Bruker
Glass microfiber filters	GF/A; 25.7 cm in diameter	Whatmann

Table 3.2 (Continued)

Instrument	**Model**	**Company**
Scanning electron microscope (SEM) and energy dispersive X-ray spectroscope (EDS)	JEM-6335F	JEOL
Vacuum pump (Flame spray pyrolysis reactor)	Seco SV 1040C	Busch
Surface area analyzer	Autosorb 1MP	Quantachrome
Spin coater	WS-400B-6NPP/LITE	Laurell
Picoammeter	6487	Keithley
UV-A lamp	Blacklight blue, 18 W	Philip
Conductivity meter	PC 5500	Eutech
Conductivity probe	EC 620161	Eutech
UV-vis absorption spectrometer	UV Lamda 650	Perkin Elmer

3.2 Nanostructure synthesis and characterization

Undoped ZnO and Sn-doped ZnO nanostructures were synthesized by using a flame spray pyrolysis reactor, at Nanoscience Research Laboratory, Department of Chemistry, Faculty of Science, Chiang Mai University, with various Sn concentrations in the range of 0.5−5 at% as dopant. The set-up and principle composition of an FSP reactor were shown in the schematic diagram of Figure 3.1. Precursor solutions of 0.5 M in Zn and Sn were prepared by dissolving the appropriate amounts of zinc naphthenate and tin (II) 2-ethylhexanoate with xylene as a solvent.

In nanostructure synthesis process, the liquid precursor of 5 ml/min was fed to the flame by a syringe pump and dispersed with 4.3 ml/min oxygen, forming fine spray droplets. The pressure drop at the capillary tip was maintained at 1.5 bars by adjusting the orifice gap at the nozzle [134]. The flame was ignited by mixing methane and oxygen supporting gases with the flow rate of 1.1 l/min and 2.4 l/min, respectively. The flame issued from an annular gap (0.15 mm spacing, at a radius of 6 mm from the center of nozzle). A sintered metal plate ring (8 mm wide, at inner radius of 9 mm from center of nozzle) provided additional 3.9 l/min of oxygen as sheath for the supporting flame. The product nanostructures were collected on a glass microfiber filters with the assist of a vacuum pump. The appearance of the flames was light orange color with ~11 cm of the flame height (Figure 3.2).

Powder X-ray diffraction (XRD) analysis on the samples was carried out at 2θ (CuKα) = 20−80°, step = 0.02° and scan speed = 1.2°/min to obtain the structure and phase composition. Brunauer Emmett and Teller (BET) adsorption isotherms and specific surface area (SSA_{BET}) analysis was performed after degassing in nitrogen for 4h at 120°C. The BET equivalent particle diameter was calculated using the following formula:

$$d_{BET} = 6 / SSA \times \left(\left(\rho_{Sn} \times wt\%Sn \right) + \left(\rho_{ZnO} \times wt\%ZnO \right) \right) \tag{3.1}$$

where ρ_{ZnO} and ρ_{Sn} are the weighted density of ZnO and Sn dopant as 5.61 g/cm^3 and 7.30 g/cm^3 [135], respectively. Images of the nanostructures were analyzed from transmission electron microscope (TEM) operated at 200 kV. The crystallite morphologies and sizes of undoped ZnO and Sn-doped ZnO nanoparticles were analyzed. Field emission scanning electron microscope-energy dispersive spectroscope (FESEM-EDS) operated at 200 kV, was utilized for confirming the presence of Sn doped in ZnO samples, coated with Au.

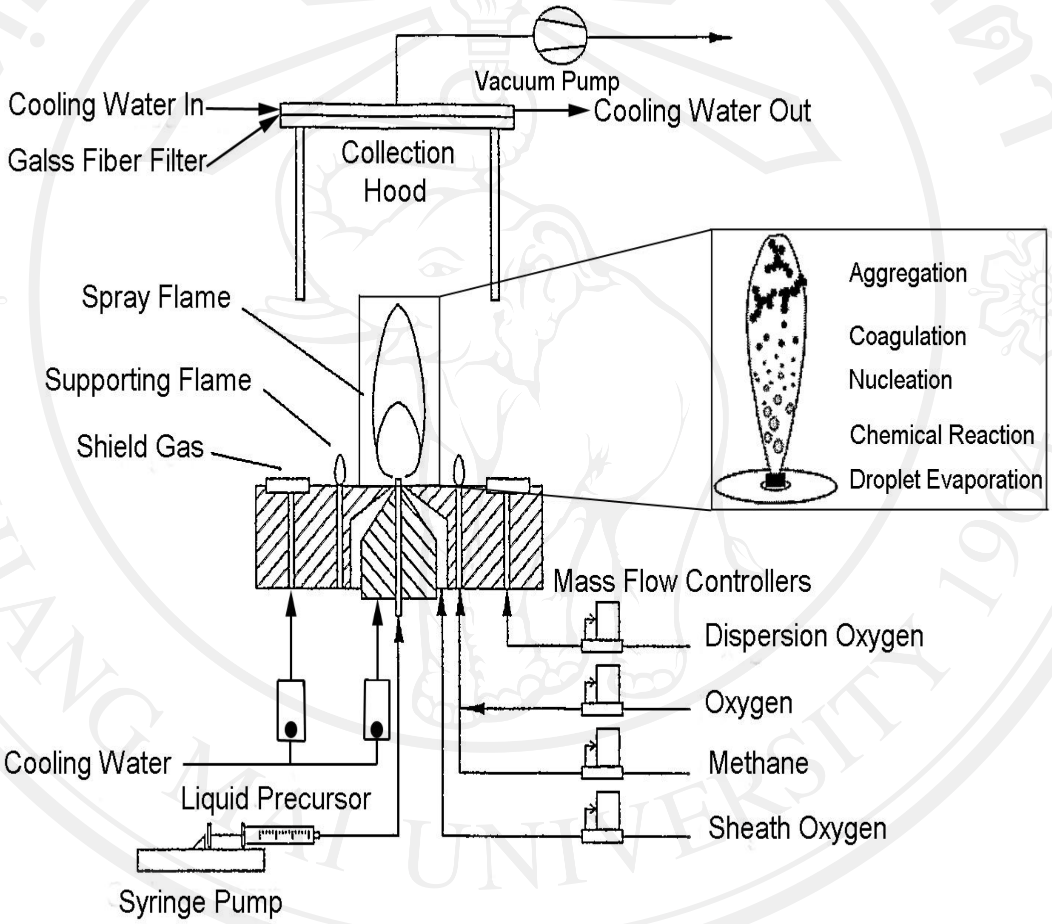

Figure 3.1 Schematic diagram of an FSP reactor set-up

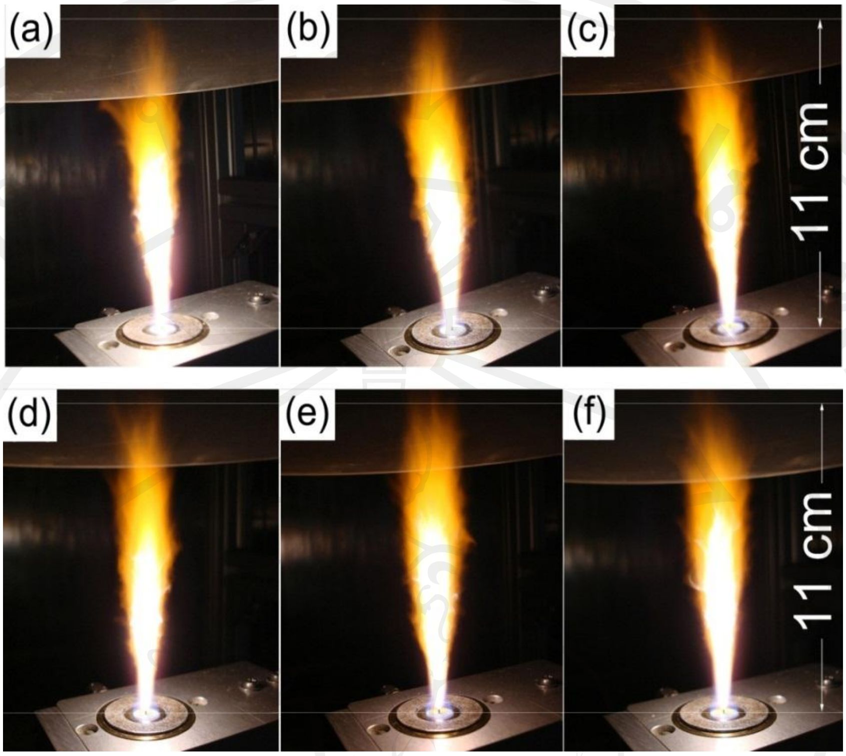

Figure 3.2 Spray flame appearances of (a) undoped ZnO and (b) 0.5 at% (c) 1 at% (d) 2 at% (e) 3 at% and (f) 5 at% Sn-doped ZnO

3.3 Preparation of sensing films

Gas sensor films were prepared by mixing the nanoparticles and an organic solution composing of ethyl cellulose and alpha-terpineol in the ratio of 1:41.86, which acted as a vehicle binder and solvent, respectively. The mixtures were spin-coated on Al_2O_3 substrates with interdigitated Au electrodes. The Al_2O_3 substrate had a dimension of 0.4 cm × 0.5 cm × 0.04 cm. Interdigit width, 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 three steps of spinning were fixed in order of the spin rates of 500 rpm for 10 s, 1,000 rpm for 30 s and 6,000 rpm for 30 s. The films were dried and annealed at 80°C for 5 min then at 400°C for 2h (with heating rate of 2°C/min for binder removal) respectively. Cross-section FESEM images and EDS analysis of the sensing films under the same condition of spinning were used for determining the thickness and elemental composition of the prepared films, respectively.

3.4 Gas sensing measurement

Gas sensing measurements of undoped ZnO and Sn-doped ZnO sensors were performed in a stainless steel chamber. The chamber had 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. All measurements were conducted in a temperature-stabilized sealed chamber at 20°C in dry air. The Pt-heater was heated by a regulated direct (dc) power supply to different operating temperatures. The gas-sensing characteristics of undoped ZnO and Sn-doped ZnO films were characterized toward ethanol, acetone, hydrogen and methane.

The resistances of various sensors were continuously monitored with a LabView based software from the computer through the measuring circuit. The resistances of various sensors were also continuously monitored with a computer-controlled system by voltage-amperometric technique with 10 V dc bias and current measurement through a picoammeter. For gas testing, purified air and target gases were mixed with different ratios and made to flow through the testing chamber. The gas flow rates were precisely manipulated using a computer controlled multi-channel mass flow controller. Purified air was used at a constant flux of 0.5 l/min. The ethanol and acetone vapors were obtained by passing Air Zero through 99.9% ethanol and acetone. The operating temperature was varied from 200°C to 400°C. The experimental set up for gas testing was shown in Figure 3.3.

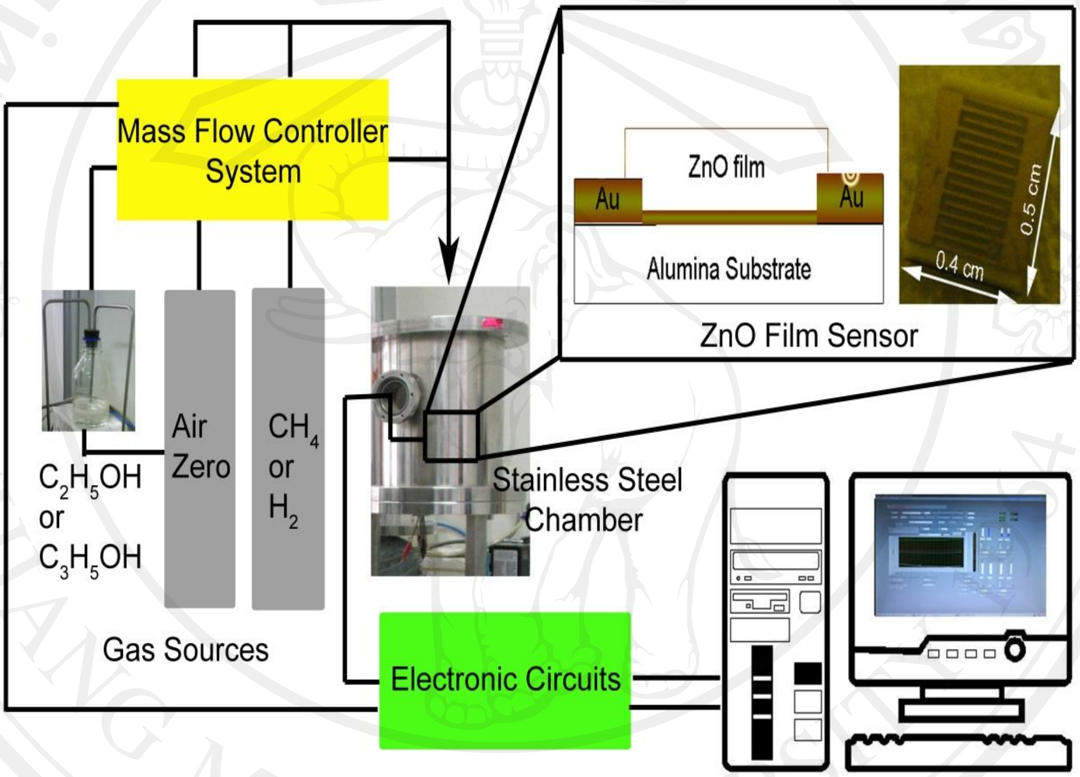

Figure 3.3 Schematic diagram of gas-sensing measurement

3.5 Photocatalytic activity testing

The photocatalytic studies were conducted in a 200 ml closed-system slurry-type spiral reactor as described by Teoh et al. [136−137], at Nanoscience Research Laboratory, Department of Chemistry, Faculty of Science, Chiang Mai University. A schematic diagram of the set-up for measuring the photocatalytic degradation of organic compounds was given in Figure 3.4. Photocatalyst suspension of 1 g/l undoped ZnO and Sn-doped ZnO, adjusted to pH 9 ± 0.1 using NaOH was used in all experiments. An impurity carbon burn-off step was carried out by illuminating the slurry with a UVA lamp at ambient condition until no further CO_2 could be detected. The slurry was then air-equilibrated before any injection of organic compounds. An organic compound aliquot equivalent to 10 mg of carbon atom per liter (mg C/l) was then injected into the suspension and mixed for a further 30 min to allow for a dark adsorption of the organic compound on the photocatalyst surface.

Methanol and phenol were used as the model organic compounds. Photocatalytic reaction was initiated by illuminating the suspension with the UVA lamp. Evolution of CO_2 during the catalytic degradation of organic compounds was monitored online based on conductivity meter and conductivity probe. Conversation of monitored conductivity value of pure water ($\Delta k = k_t - k_0$) to amount of CO_2 or carbon atom of decomposed organic compound relating with irradiation time (C_t) was evaluated through the calibration equation:

$$\ln\left(\Delta k\right) = 0.4526\ln(C_t) - 2.1974\ , \qquad (3.1)$$

having high correlation coefficient value (R^2) of 0.9999 (Appendix B.1). FSP-made undoped ZnO was used as a sample for calibrating. Re-testing of phenol degradation (four times) under UVA irradiation using commercial ZnO nanoparticles as photocatalysts was needed for confirming the technical operation accuracy (Appendix B.2).

For UV-vis absorption measurements, the powder samples were dispersed in deionized water with a fixed concentration (5 mg/ 4 ml).

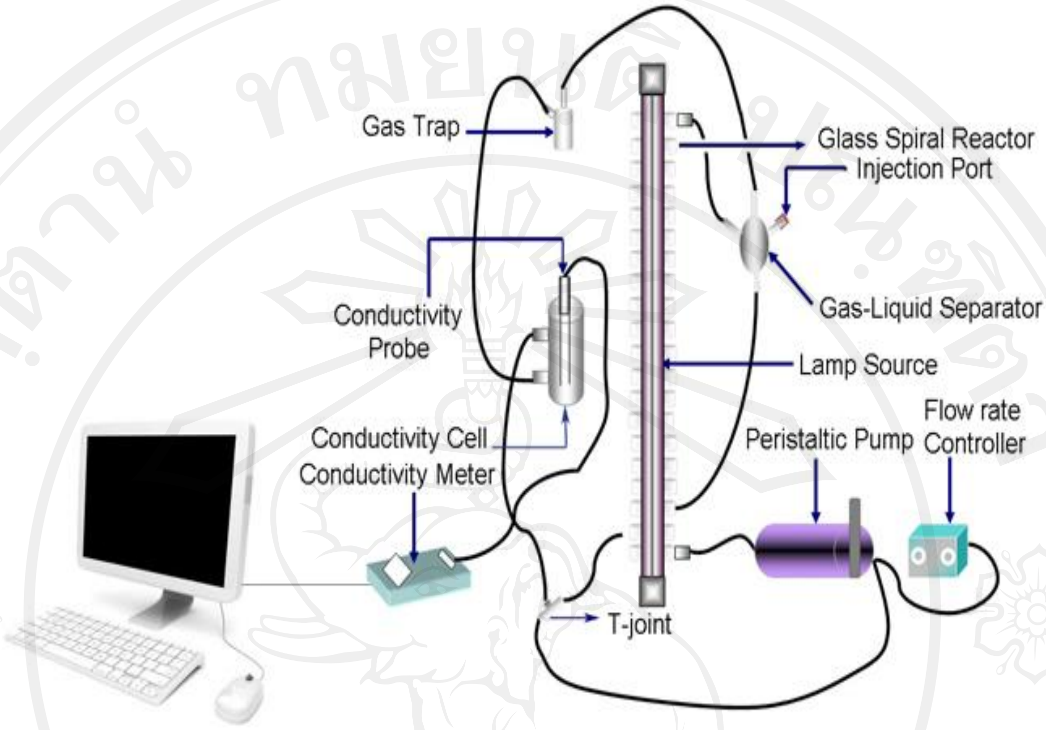

Figure 3.4 Schematic diagram of photocatalytic activity measurement