

CHAPTER III

EXPERIMENT

Referring to the objective of this work, the synthesized particulate composites of ZnO and carbon nanoparticles by single-step gas phase reaction were required. Within the gas phase reaction of the composites, the composites were expected to be combination of the ZnO and carbon nanoparticles. However, the combination of those major compounds for the formation of the composites was found to be more complexity than both isolated synthesis of the ZnO nanoparticles and carbon nanoparticles due to complex thermochemical oxidation at high temperature range of related elements in the system including Zn, C and Fe.

For controlling the formation of the composites, both of isolated synthesis of the ZnO nanoparticles and carbon nanoparticles were investigated before the synthesis of the composites. The carbon nanoparticles, especially MWCNTs with high purity, were synthesized by CVD of glycerol and ferrocene. Furthermore, to truly understand the formation of the MWCNTs, parallel study of synthesis of SWCNTs by laser ablation was revealed. While, the ZnO nanoparticles were synthesized by oxidation of pure Zn. After the studies of the isolated synthesis of the SWCNTs, MWCNTs and ZnO nanoparticles, the ZnO/MWCNT composites were then investigated under controlling conditions for decrease in the thermochemical oxidation of undesired products.

Therefore, experiment of this work were separated into 4 parts including the synthesis of SWCNTs by laser ablation, the synthesis of carbon nanoparticles by CVD of glycerol and ferrocene, the synthesis of ZnO nanoparticles by oxidation of Zn and the synthesis of composites of ZnO/MWCNT composites by gas phase reaction. Various parameters which affected on the synthesis of each part were carefully investigated.

3.1 Synthesis of the SWCNTs by laser ablation

3.1.1 Raw materials and experiment

C/Ni/Co target rod (Toyo Tanso Company) with a diameter of 6 mm and length of 30 mm prepared from particulate mixture of carbon and 0.6% atomic of nickel and cobalt, respectively was used as C, Ni and Co sources of this work, respectively as shown in Figure 3.1.

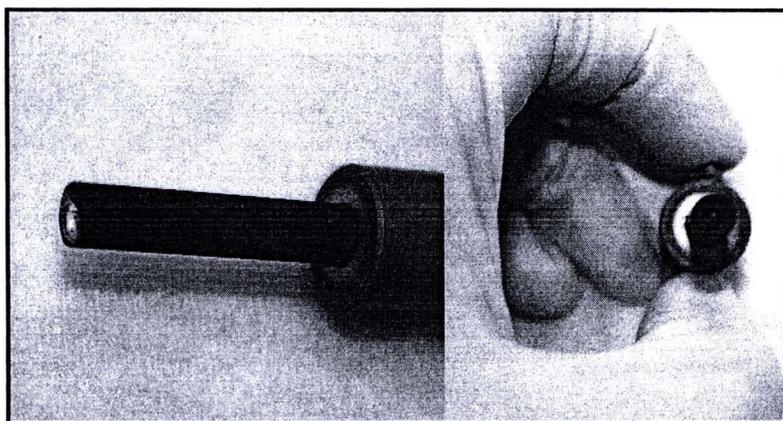


Figure 3.1 C/Ni/Co target rod.

The SWCNTs were synthesized by pulsed Nd:YAG laser ablation of the C/Ni/Co target rod within a quartz tube reactor which is schematically shown in Figure 3.2. The experimental set up consists of an electrical furnace, a quartz tube (outer diameter of 28 mm, inner diameter of 25 mm and length of 700 mm), a mass flow controller (MFC), a pressure transducer, a vacuum pump, and a rotating motor with a speed of 7 rpm.

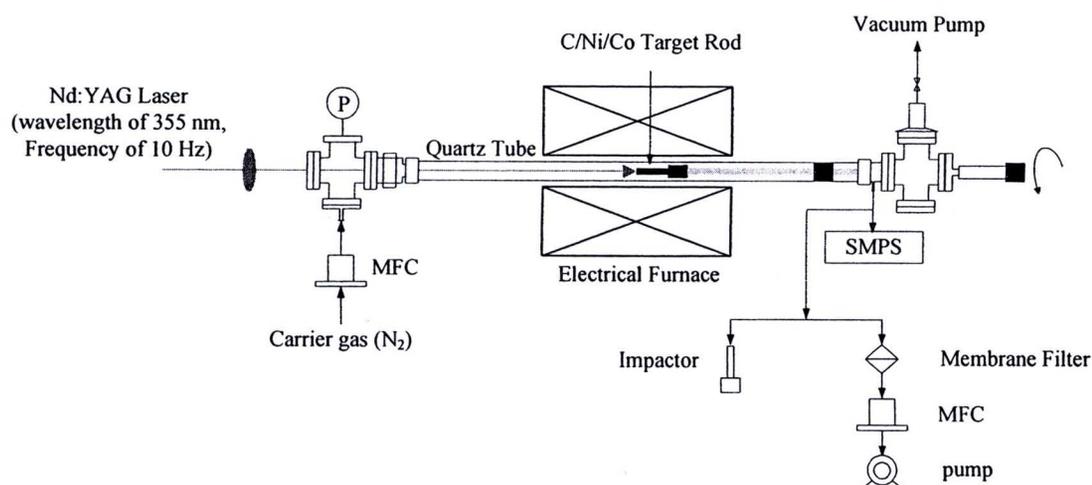


Figure 3.2 Schematic diagram of experimental apparatus for aerosol generation of the SWCNTs by pulsed Nd:YAG laser ablation.

Before the laser ablation, the C/Ni/Co target rod was heated to a desired temperature. The Nd:YAG laser beam (wavelength of 355 nm, repetition rate of 10 Hz, pulse width of 10 ns) with desired laser power irradiated perpendicularly to the target surface which was steadily rotated for uniform ablation. All experiments were carried out under atmospheric pressure and nitrogen flow rate of 1.5 L/min. The airborne products were collected on a polycarbonate membrane filter (filter size of 25 mm and pore size of 100 nm, ADVANTEC) for characterizing their morphology and crystallinity by Scanning Electron Microscope and Raman Spectroscopy, respectively. The detailed morphology of the synthesized SWCNTs was analyzed by a Transmission Electron Microscopy. The TEM specimens were prepared by depositing aerosol on a TEM microgrid (200 mesh) using an impactor. Furthermore, the size distribution of the airborne SWCNTs was also determined by a computer controlled Scanning Mobility Particle Sizer (SMPS) system equipped with a Differential Mobility Analyzer and a Condensation Particle Counter.

3.1.2 Experimental procedures

The experimental procedures of this work were separated into 2 parts as following;

3.1.2.1 Variation of laser intensity

In this part, effect of laser intensity was investigated on morphology, particle size distribution and crystallinity of the synthesized carbon nanoparticles at the laser intensity of 0.4, 0.5 and 0.6 W. The experiments were fixed at temperature of 25 °C under atmospheric pressure and nitrogen flow rate of 1.5 L/min.

3.1.2.2 Variation of temperature

Referring to many previous reports, the temperature could affect on the formation of the SWCNTs including their quality and quantity. Therefore, in this part, effect of temperature on the morphology, size distribution and crystallinity of the synthesized SWCNTs was studied at the reaction temperature of 25, 200, 400, 600, 800, 1000 and 1080 °C. It should be noted that the temperature was controlled not higher than 1080 °C due to limitation of the electrical furnace. The dimensions (diameter and length) of the monodispersed SWCNTs by DMA with mobility-based diameters of 100 and 200 nm were also analyzed by SEM. The experiments were controlled under laser intensity of 0.6 W, atmospheric pressure and nitrogen flow rate of 1.5 L/min.

3.2 Synthesis of the carbon nanoparticles by CVD of glycerol and ferrocene

3.2.1 Raw materials and experiment

In this work, glycerol (Ajax Chemicals) and ferrocene (Sigma-Aldrich) were used as sources of carbon and iron catalyst for the synthesis of the carbon nanoparticles by CVD, respectively. Boiling points of glycerol and ferrocene are 290 and 249 °C, respectively. Experimental set up shown in Figure 3.3 consists of an

electrical furnace, a quartz tube reactor with inner diameter of 34 mm and length of 600 mm, a boat of glycerol-ferrocene mixture, silicone stoppers and a dust collector.

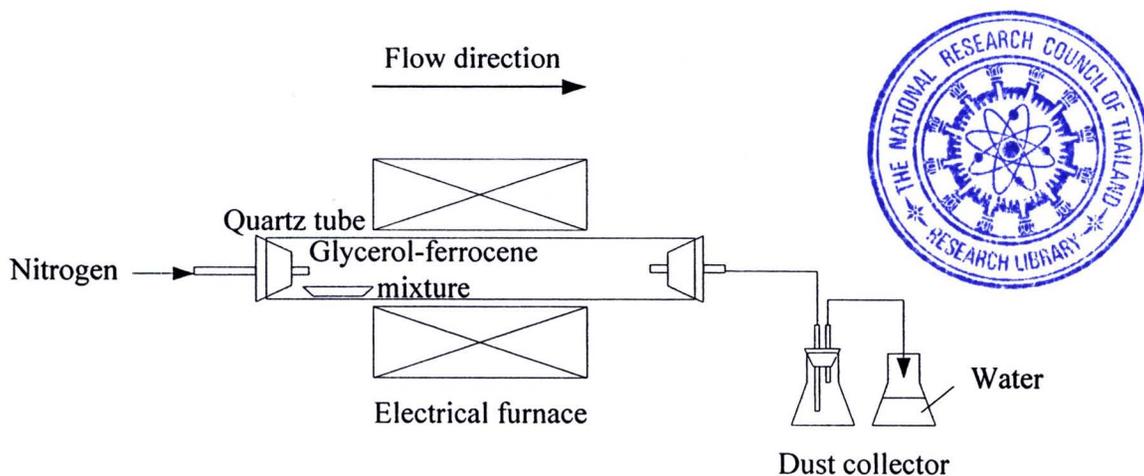


Figure 3.3 Experimental set up for synthesizing carbon nanoparticles by CVD of glycerol and ferrocene.

Glycerol and ferrocene were mixed with desired molar ratio and loaded into the boat. After that, the boat of the glycerol-ferrocene mixture was inserted inside the tube reactor at position of 5 cm from inlet of the reactor. From temperature profile as shown in Appendix A, it could be assured that temperature of the position of 5 cm from the inlet was high enough for vaporization of the mixture of glycerol-ferrocene. Before heating the furnace up, residual air inside the tube reactor was eliminated by supplying nitrogen gas with flow rate of 200 mL/min for 20 min. The furnace was then heated up until desired temperature under controlling desired nitrogen flow rate. The process was controlled for 1 hr. The tube was then naturally cooled down to room temperature. The synthesized black products on inner wall of the tube reactor were kept and characterized their morphology, crystallinity and phase.

3.2.2 Experimental procedures

The experimental procedures of this work were separated into 3 parts as following;

3.2.2.1 Variation of nitrogen flow rate

Referring to many previous reports, the nitrogen flow rate could affect on the formation of the carbon nanoparticles including their quality and quantity. In this part, the nitrogen flow rate was found to be controlled not higher than 500 mL/min because, at the nitrogen flow rate higher than 500 mL/min, the carbon nanoparticles could not be formed on inner wall of the quartz tube reactor. Therefore, effect of nitrogen flow rate on the morphology, crystallinity and yield of the synthesized carbon nanoparticles was investigated by varying flow rate at 50, 200, 350 and 500 mL/min under the same condition of synthesizing temperature of 800 °C and glycerol to ferrocene molar ratio of 5 to 1.

3.2.2.2 Variation of synthesizing temperature

From preliminary study, it should be noted that, at the synthesizing temperature lower than 800 °C, some of vaporized glycerol could not be decomposed and then condensed into liquid droplets of glycerol and deposited on inner wall of the quartz tube reactor. However, the synthesizing temperature could not be controlled higher than 900 °C due to limitation of the electrical furnace and, especially poisoning from the silicone stoppers. Therefore, in this part, the effect of synthesizing temperature on the morphology, crystallinity and yield of the synthesized carbon nanoparticles was studied at 800, 850 and 900 °C. The nitrogen flow rate and glycerol to ferrocene molar ratio were fixed at 350 mL/min and 5/1, respectively.

3.2.2.3 Variation of glycerol to ferrocene molar ratio

In this part, the effect of glycerol to ferrocene molar ratio on the quality and quantity of the synthesized carbon nanoparticles was studied by varying the molar ratio in a range of 5/1, 10/1 and 20/1 under the same condition of synthesizing temperature of 800 °C and nitrogen flow rate of 350 mL/min.

3.3 Synthesis of the ZnO nanoparticles by oxidation of Zn

3.3.1 Raw materials and experiment

In this work, zinc powder (Sigma-Aldrich, purity > 98%) with its boiling point of 907 °C was used as Zn source for the synthesis of the ZnO nanoparticles by oxidation of the Zn. Experimental set up for the synthesis of the ZnO nanoparticles shown in Figure 3.4 was modified from the experimental set up for the synthesis of the carbon nanoparticles as shown in Figure 3.3 by changing position of a boat of Zn powder to 15 cm from the inlet and adding oxygen to react with vaporized Zn to form ZnO nanoparticles.

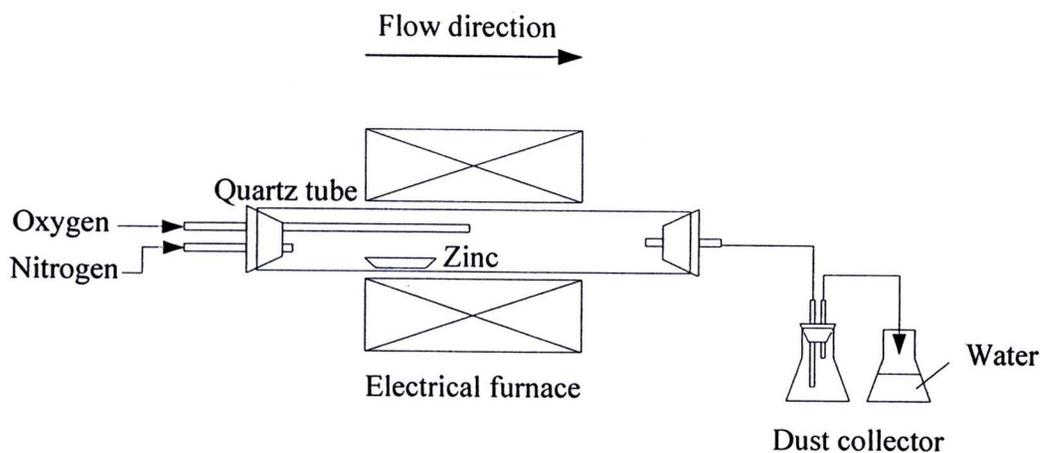


Figure 3.4 Experimental set up for synthesizing ZnO nanoparticles by oxidation of Zn.

Zinc powder was loaded into the boat and inserted inside the tube reactor at position of 15 cm from the inlet. From temperature profile as shown in Appendix A, it could be also assured that temperature of the position of 15 cm from the inlet was high enough for evaporation of the Zn powder. Before heating the furnace up, residual air inside the tube reactor was eliminated by supplying nitrogen gas with flow rate of 200 mL/min for 20 min. The furnace was then heated up until desired temperature under controlling desired nitrogen and oxygen flow rates. The process was controlled for 1 hr. The tube was then naturally cooled down to room temperature. The synthesized white products on inner wall of the tube reactor were kept and characterized their morphology, size and phase.

3.3.2 Experimental procedures

Because of the objective of this work was to synthesize the ZnO/MWCNT composites. Therefore, various parameters including the nitrogen flow rate and synthesizing temperature which also affected on the formation of the ZnO nanoparticles were also controlled as same as those for the isolated synthesis of the carbon nanoparticles by CVD.

3.3.2.1 Variation of nitrogen flow rate

In this part, effect of nitrogen flow rate on the morphology, size and yield of the synthesized ZnO nanoparticles was investigated by varying flow rate at 200, 350 and 500 mL/min under the same condition of synthesizing temperature of 800 °C and oxygen flow rate of 100 mL/min. From preliminary study, it should be noted that the oxygen flow rate could not be controlled lower than 100 mL/min due to not enough for the formation of the ZnO nanoparticles.

3.3.2.2 Variation of synthesizing temperature

Effect of synthesizing temperature on the morphology, size and yield of the synthesized ZnO nanoparticles was studied in a range of 800, 850 and 900 °C. The nitrogen and oxygen flow rates were fixed at 500 and 100 mL/min, respectively.

3.3.2.3 Variation of oxygen flow rate

Referring to many previous reports, the oxygen flow rate could affect on the formation of the ZnO nanoparticles including their quality and quantity. From preliminary study, the oxygen flow rate was found to be controlled not lower than 100 mL/min. When preliminary study of thermodynamics was investigated, the oxygen flow rate was considerably controlled not higher than 150 mL/min for avoiding thermochemical oxidation of Zn, C, Fe elements within the system of the composite synthesis. Therefore, in this part, effect of oxygen flow rate on the formation of the synthesized ZnO nanoparticles was studied in at the rate of 100 and 150 mL/min

under the same condition of N_2 flow rate of 500 mL/min and synthesizing temperature of 800 °C.

3.4 Synthesis of the ZnO/MWCNT composites by gas phase reaction

3.4.1 Raw materials and experiment

Raw materials of this work were glycerol, ferrocene and Zn powder as C, Fe and Zn sources. Experimental set up for the synthesis of the composites shown in Figure 3.5 was combined from the experimental set up for the synthesis of the carbon nanoparticles as shown in Figure 3.3 and the experimental set up for the synthesis of the ZnO nanoparticles as shown in Figure 3.4.

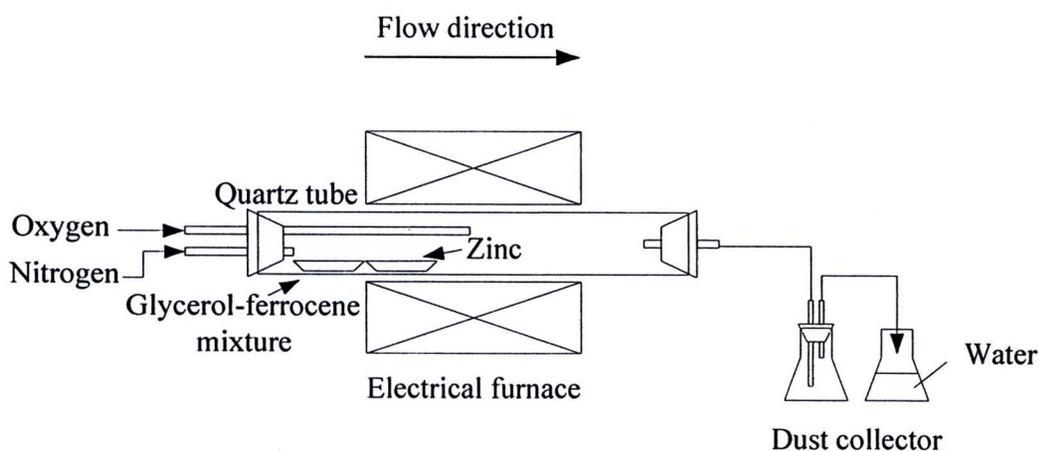


Figure 3.5 Experimental set up for synthesizing ZnO/MWCNT composites.

Glycerol-ferrocene mixture and Zn powder were loaded into separated boats and then inserted inside the quartz tube reactor at position of 5 and 15 cm from the inlet, respectively. Before heating the furnace up, residual air inside the tube reactor was eliminated by supplying nitrogen gas with flow rate of 200 mL/min for 20 min. The furnace was then heated up until desired temperature under nitrogen and oxygen flow rates of 500 and 100 mL/min, respectively. The process was controlled for 1 hr. The tube was then naturally cooled down to room temperature. The synthesized gray products on inner wall of the tube reactor were kept and characterized their morphology and size and phase.

3.4.2 Experimental procedures

In this part, thermodynamic data for oxidation of related elements including Zn, C and Fe was firstly investigated by using Ellingham diagram. From the diagram, the synthesizing temperature of 800 and 900 °C was carefully considered to be major parameter for the synthesis of the composites under controlling of the nitrogen flow rate, oxygen flow rate and glycerol to ferrocene molar ratio at 500 mL/min, 100 mL/min and 5/1, respectively.

3.5 Analytical instruments

The instruments were used to characterize morphology, structure, and phase of the synthesized carbon nanoparticles, ZnO nanoparticles and their composites are Scanning Electron Microscope (SEM), Transmission Electron Microscope (TEM), and X-Ray Diffraction (XRD), respectively. Purity and crystallinity of the synthesized carbon nanoparticles were characterized by Raman Spectroscopy, while size distribution and classification of the synthesized airborne SWCNTs were investigated by Scanning Mobility Particle Sizer (SMPS). The composites were further characterized their absorption, elements and bonding by UV-Visible Spectrophotometer (UV-Vis), Energy Dispersive X-Ray Spectroscopy and Fourier Transform Infrared Spectrophotometer, respectively to confirm their structures.

3.5.1 Scanning Electron Microscopy (SEM)

Morphology and size of the synthesized carbon nanoparticles, ZnO nanoparticles and their composites were investigated by SEM (Hitachi, model S4500 and JEOL model JSM-6400).

3.5.2 Transmission Electron Microscope (TEM)

Structure of the synthesized carbon nanoparticles, ZnO nanoparticles and their composites were investigated by TEM (JEOL model JEM 2100).

3.5.3 Raman Spectroscope

Purity and crystallinity of the synthesized carbon nanoparticles were characterized by Raman Spectroscope (Perkin Elmer model Spectrum GX).

3.5.4 Scanning Mobility Particle Sizer (SMPS)

The SMPS (TSI model 3081) was used to analyze particle size distribution of airborne SWCNTs synthesized by laser ablation, and classify their size. The SMPS consists of differential mobility analyzer (DMA) as the main component for generating or sizing aerosol. For example given a polydisperse input aerosol, the instrument output can be a stream of monodisperse aerosol of known particle size. The number of monodisperse aerosol was counted by condensation particle counter (CPC).

3.5.5 X-Ray Diffraction (XRD)

The XRD (Bruker model X8APEX) was used to characterize phase of the synthesized carbon nanoparticles, ZnO nanoparticles and their composites.

3.5.6 UV-Visible Spectrophotometer (UV-Vis)

The UV-Vis spectrophotometer (Shimadzu model UV-1700) was used to measure absorbance of the synthesized carbon nanoparticles, ZnO nanoparticles and their composites.

3.5.7 Fourier Transform Infrared Spectrophotometer (FT-IR)

The FT-IR spectrometer (Thermo model 470 FT-IR) was used to measure bonding of the composite of carbon nanoparticles and ZnO nanoparticles.