

## CHAPTER III

### EXPERIMENTAL

The synthesis of zinc oxide nanostructure using combined electrospinning and solvothermal techniques is explained in this chapter. The chemicals, sample preparation and characterization are also explained.

#### 3.1 Materials

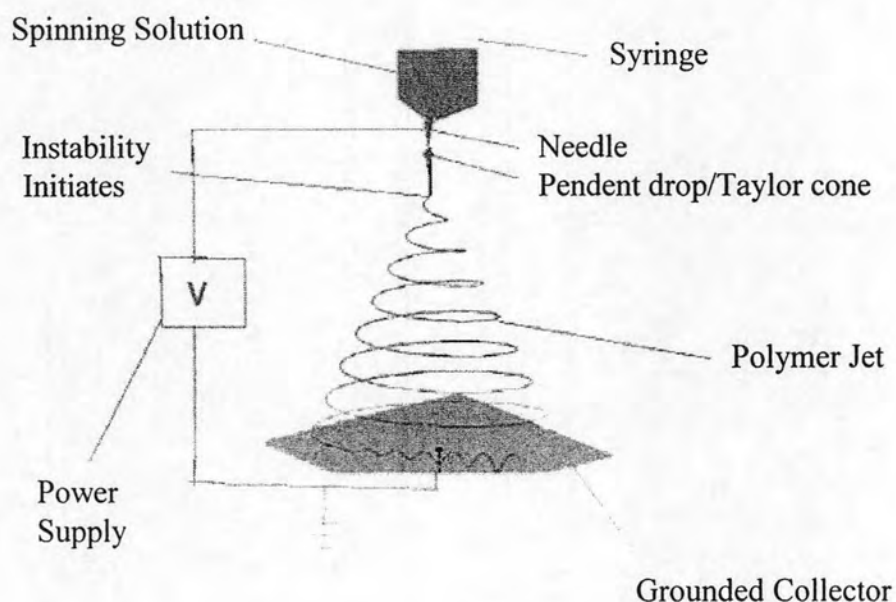
1. Zinc acetate ( $\text{Zn}(\text{CH}_3\text{COO})_2$ ), 99.99%, available from Sigma-Aldrich.
2. Poly(vinyl alcohol) (PVA) (MW = 72,000), available from Fluka.
3. 1-Octanol ( $\text{C}_8\text{H}_{18}\text{OH}$ ), 99%, available from Panreac.

#### 3.2 Equipments

##### 3.2.1 Electrospinning System

The schematic diagram of the electrospinning apparatus used in this work is shown in Figure 3.1. The components of the apparatus and their functions are described as follows.

- A high voltage power supply (ES30PN, Gamma High Voltage Research Inc., Ormond Beach, Florida) was used to generate either positive or negative DC voltage up to 30 kV, with very low electrical current of 166 microamperes.
- A 5 ml syringe is used as a container for electrospinning solution. The syringe is made from plastic and it was set in vertical orientation.
- A stainless steel needle (guage number 20 and the outside diameter of 0.90 mm) was used as a nozzle and as an electrode to conduct the electrical energy from the power supply to the solution. The tip of the needle was cut into a flat shape and the length of the needle was 2 cm.
- Aluminum foil and aluminum sieve were used as a ground collector and were placed on a wood stand.

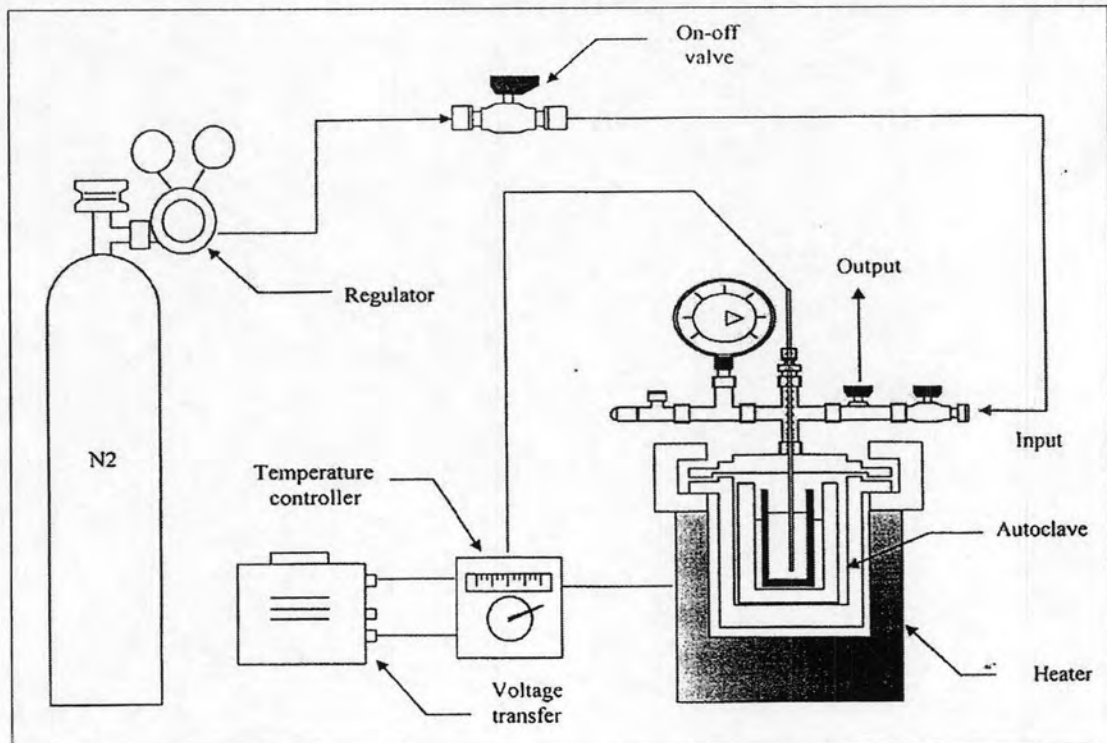


**Figure 3.1** Experimental set up for electrospinning process.

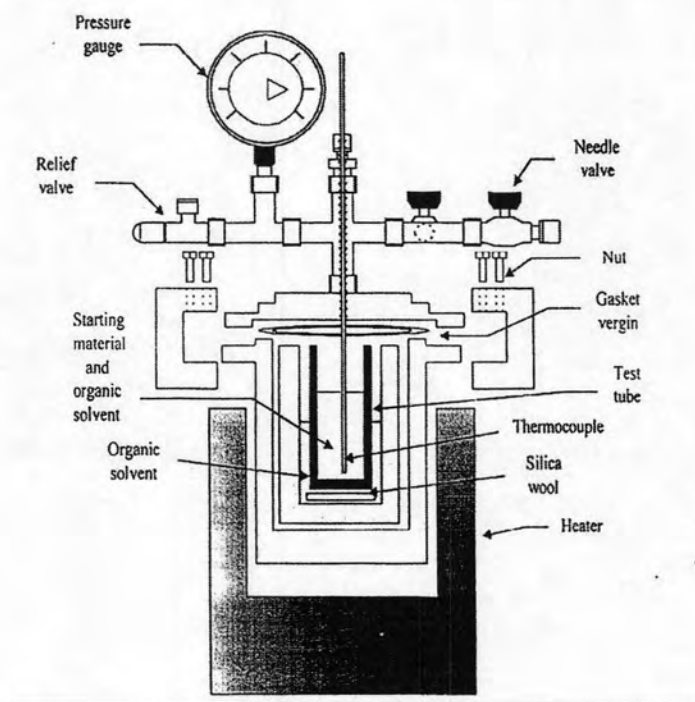
### 3.2.2 Solvothermal System

The detailed schematic diagram of the equipment used for ZnO synthesis is shown in Figure 3.2. The system is mainly consisted of an autoclave reactor as shown in Figure 3.3. The reactor has the following features.

- Made from stainless steel
- Volume of 1000 cm<sup>3</sup>
- 10 cm inside diameter
- Maximum temperature of 350°C
- Pressure gauge in the range of 0-140 bar
- Relief valve used to prevent runaway reaction
- Iron jacket was used to reduce the volume of autoclave to be 300 cm<sup>3</sup>
- Test tube was used to contain the reagent and glycol



**Figure 3.2** Diagram of the solvothermal system.



**Figure 3.3** Autoclave reactor.

### 3.3 Procedures

#### 3.3.1 Preparation of Spinning Solution

PVA (MW = 72,000) and zinc acetate were used as starting materials. An aqueous solution of PVA was first prepared by dissolving PVA in deionized water and heating at 90 °C with vigorous stirring for 1 hour. Zinc acetate was added slowly to the PVA solution and it was stirred vigorously about 3 hours. Then it was kept at room temperature for 8 hours for the reaction between PVA and  $\text{Zn}(\text{CH}_3\text{COO})_2$  to proceed. A viscous gel of PVA/zinc acetate composite was obtained at the end of the process.

The concentration of PVA in solution was 8 wt.%, while the ratio between PVA and zinc acetate was varied from 3, 1.5 and 1.

#### 3.3.2 Spinning of the PVA/Zinc Acetate Composite Fibers

The spinning solution was immediately loaded into a plastic syringe. A blunt-ended 20-gauge stainless steel needle was used as the nozzle. The emitting electrode from a Gamma High Voltage Research ES30PN power supply capable of generating DC voltages up to 30 kV was attached to the needle. The grounding electrode from the same power supply was attached to a piece of aluminum foil and aluminum sieve which were used as the collector plate and were placed approximately 15 cm below the tip of the needle. Upon the application of a high voltage of 19 kV across the needle and the collective plate, a fluid jet was ejected from the nozzle. As the jet accelerated towards the collector, the solvent evaporated, leaving only ultrathin fibers on the collector. The obtained fibers were left exposing to the ambient atmosphere for approximately 1 day.

### *3.3.3 Conversion of the Composite Fibers into ZnO Nanostructure by Solvothermal Technique*

PVA/zinc acetate composite fibers were used as starting material in the solvothermal process. The excess zinc acetate, which was used in the range of 0.1 – 10 g, was also added into the solvothermal system. They were suspended in 100 ml of 1-octanol, which was employed as solvent, contained in a test tube. The test tube was then placed in an autoclave. In the gap between the test tube and autoclave wall, 30 ml of the same solvent was added. After the autoclave was completely purged with nitrogen, the autoclave was heated to desired temperature, in the range of 170-250 °C at the rate of 2.5°C min<sup>-1</sup> and held at that temperature for 2 hours. Pressure in the autoclave reactor gradually increased autogeneously as the temperature was raised and the reaction proceeded. After the holding period, the autoclave was cooled to room temperature. The resulting products were collected after repeatedly washed with methanol.

### *3.3.4 Conversion of the Composite Fibers into ZnO Nanostructure by Conventional Method*

In the conventional method, the electrospun PVA/zinc acetate composite fibers were subjected to heat treatment at a high temperature 600 °C for 2 hours under heating rate of 10°C/min by using a box furnace to oxidize zinc acetate to ZnO, as well as remove residual PVA.

For some experiments which were designed to compare between the products from solvothermal technique and from conventional method, the residual PVA in the zinc oxide nanostructure synthesized via solvothermal technique was intentionally removed by using box furnace in the same manner as mentioned.

### 3.4 Sample Characterizations

#### 3.4.1 X-ray Diffraction Analysis (XRD)

X-ray diffraction (XRD) analysis of zinc oxide was performed by a SIEMENS D5000 X-ray diffractometer connected with a personal computer with Diffract AT version 3.3 program at the Center of Excellence on Catalysis and Catalytic Reaction Engineering, Chulalongkorn University. The measurement was carried out by using Ni filtered  $\text{CuK}\alpha$  radiation. The condition of the measurement is shown as followed:

$2\theta$  range of detection :  $10 - 80^\circ$

Scanning step :  $0.04^\circ$

Number of scan cycle : 10

#### 3.4.2 Scanning Electron Microscopy (SEM)

The surface morphology and size of the electrospun PVA/zinc acetate composite fibers as well as ZnO nanostructure were observed by a JSM 5800 Scanning Electron Microscopy (SEM), which operated at 20 kV, at the Scientific and Technological Research Equipment Center (STREC), Chulalongkorn University. Samples were coated by thin film of gold prior to the analysis.

#### 3.4.3 Thermogravimetric and Differential Thermal Analysis (TG-DTA)

The as-spun PVA/zinc acetate composite fibers and the ZnO nanostructure were subjected to the thermogravimetric and differential thermal analysis (Diamond Thermogravimetric and Differential Thermal Analyzer, TG-DTA, Perkin-Elmer) to determine the PVA content in the sample, as well as their thermal behaviors. The furnace was heated from  $50^\circ\text{C}$  to  $800^\circ\text{C}$  at a constant rate of  $10^\circ\text{C}/\text{min}$ .

#### *3.4.4 Fourier Transform Infrared Spectroscopy (FT-IR)*

Transmittance spectra of particles were determined by FT-IR using a Nicolet model Impact 400 spectrophotometer. Each sample was mixed with KBr with ratio of sample: KBr equal to 1:100 and then pressed into a thin disk. Infrared spectra were recorded between 400 – 4000  $\text{cm}^{-1}$  on a microcomputer. The residual solvent from solvothermal technique was also determined by FT-IR.

Scan resolution : 0.4  $\text{cm}^{-1}$