



CHAPTER III EXPERIMENTAL

3.1 Materials

All chemicals were of analytical grade and used as received. Poly(vinyl alcohol) powder having molecular weight of $72,000 \text{ g mol}^{-1}$ and a degree of hydrolysis of min. 99% was purchased from Merck (Germany) and was used as a particle stabilizer and a fiber forming material. Chloroplatinic acid hexahydrate ($\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$), a platinum precursor, was a product of Sigma-Aldrich (USA). Trisodium citrate purchased from Ajax Finechem (Australia) was applied as a reducing agent. A surfactant, Sodium dodecyl sulfate, in order to decrease surface tension of electrospinning solution, was purchased from Fluka (Japan).

3.2 Equipment

3.2.1 Electrospinning Apparatus

The electrospinning apparatus consisted of a high-voltage DC power supply (D-ES30PN/M692, Gamma High Voltage Research, USA), a standard 20 ml syringe attached with a gauge 20 flat-tipped stainless steel needle (outer diameter = 0.91 mm), used as a nozzle, and the grounding electrode to a home-made rotating metal drum, used as the fibre-collecting device. A prepared viscous solution was poured into the syringe, then high voltage was applied in order to fabricate super fine fibers on the collecting drum (outer diameter = 15 cm).

3.2.2 Conductivity Meter

A viscosity value of prepared electrospinning solution was measured by a Suntex SC-170 conductivity meter. The system was calibrated with standard conductivity solution having conductivity of $1,413 \mu\text{S cm}^{-1}$ at 25°C .

3.2.3 Viscosity Meter

A Brookfield Digital (Model DV-111) was used to investigate the solution viscosity at the room temperature. Spindle used was number 21.

3.2.5 UV-visible Spectrophotometer

The surface plasmon resonance of the stabilized platinum nanoparticles in PVA viscous solution was studied by using UV-visible spectrophotometer (SHIMADZU UV2550). The scanning range was 200-800 nm.

3.2.4 Scanning Electron Microscope (SEM)

Morphology of fibers and fiber diameters of nanocomposites nanofibers were investigated by using JEOL/JSM 5200 scanning electron microscope (SEM) at 15 kV with the magnification of 5,000x and 10,000x. Histogram, mean diameter, and standard deviation of each condition were obtained by sampling 100 fiber cross-section in SEM images, then analyzing by SemAfore.

3.2.6 Fourier Transformation Infrared Spectroscopy (FTIR)

Qualitative Fourier transform infrared spectra of the nanocomposites nanofiber mats were obtained from Bruker Equinox 55/S with 32 scans at a resolution of 4 cm^{-1} . A frequency range of 4000-400 cm^{-1} was observed using a deuterated triglycinesulfate detector with a specific detectivity, D^* , of $1 \times 10^9 \text{ cm.Hz}^{1/2} \text{ w}^{-1}$.

3.2.7 X-ray Diffraction (XRD)

The formation of platinum nanoparticles from the chemical reduction of chloroplatinic acid hexahydrate was confirmed by X-ray diffraction (Rigaku, model Dmax 2002) with Ni-filtered $\text{CuK}\alpha$ radiation operated at 40 kV and 20 mA. Samples were scanned from $2\theta = 20^\circ$ to $2\theta = 80^\circ$ at a scanning rate of $2^\circ 2\theta/\text{min}$ and from $2\theta = 30^\circ$ to $2\theta = 50^\circ$ at a scanning rate of $1^\circ 2\theta/\text{min}$.

3.2.8 Transmission Electron Microscope (TEM)

Transmission electron microscopy (TEM) observations were carried out on a instrument operated at 80 kV accelerating voltage. The TEM samples were prepared on a 400 mesh copper grid coated with carbon.

3.2.9 Thermogravimetric/differential thermal analyser (TG/DTA)

A Perkin Elmer Pyris Diamond was used to investigate thermal behavior of the PVA matrix and the Pt-loaded as-spun PVA mats (each sample weighed 3–5 mg). The heating rate of $10^\circ \text{C min}^{-1}$ was applied to heat the samples from 30°C to 600°C under nitrogen atmosphere (200 ml min^{-1}).

3.2.10 X-Ray Fluorescence (XRF)

X-ray Fluorescence Spectrometer, Oxford model ED2000 was used to detect Pt content contained in each fiber mat. The measurement was carried out under 35 keV electrical potential.

3.2.11 Temperature-Program Reduction (TPR)

PVA flakes 0.05 g was filled in a long glass cell and connect to the TPR apparatus which equipped with a thermal conductivity detector and connected to continuous flow of hydrogen. Non-isothermal (30-700 °C) mode was applied to the samples. The temperature ramp used was 10 C° min⁻¹ and the gas flow rate was 8.7 ml s⁻¹.

3.3 Methodology

3.3.1 Preparation of Pt/PVA Electrospinning Solution

All glassware was rinsed with distilled water and acetone prior to the use. An electrospinning solution was prepared simultaneously with chemical reduction process of platinum precursor to platinum metal. For this study, four conditions were prepared. The first condition, 8 %(w/v) pure PVA solution, 8 g PVA powder was added into 10 ml distilled water in a round-bottomed flask. The mixture was stirred at a speed of 400 rpm for 3 hours under 85 °C (in an oil bath). The second condition, 1% Pt loading, a gram of PVA was added in a 100 ml round-bottomed flask, also 21.485 ml of distilled water was pour into the same flask. The mixture was stirred at about 400 rpm in an oil bath at for 2 hours. Afterwards, 8 ml of 15 %(w/v) sodium citrate and 1 ml of 0.643M chloroplatinic acid hexahydrate (CPAH) were added into the mixture. A clear yellow solution was then obtained. The mixture was stirred vigorously (about 700 rpm) under 95-100 °C for about two hours until the solution became dark brown. Then, 1.4388 g PVA was added, and the system was kept stirred for another 6 hours. Afterwards, the flask was removed from the oil bath and the system was cooled down at room temperature. Later, some surfactant, 1ml of 0.05 M sodium dodecyl sulfate (SDS), was added. For the 3% and 5% conditions, 3 ml CPAH + 19.246 ml distilled water + 1.4197 g PVA and 5 ml CPAH + 17.478 ml

distilled water + 1.4382 g PVA were added into the viscous reaction mixtures, respectively.

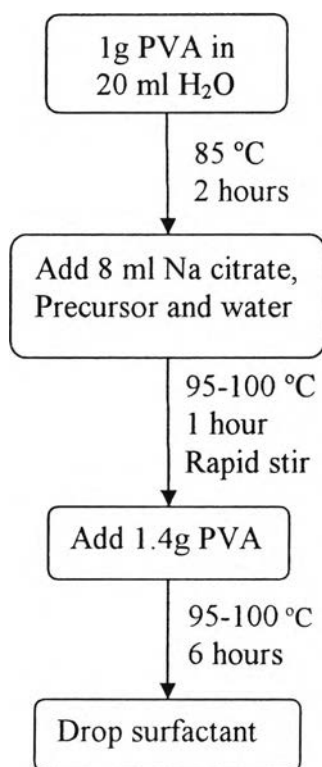


Figure 3.1 Flow chart shows the electrospinning solution preparation.

3.3.2 Fabrication of Pt/PVA Nanofiber Nanocomposites

Electrospinning of the as-prepared solutions was carried out by connecting the emitting electrode of positive polarity from a high-voltage DC power supply (D-ES30PN/M692, Gamma High Voltage Research, USA) to the solutions contained in a standard 10 ml syringe, the open end of which was attached with a gauge 20 flat-tipped stainless steel needle (outer diameter = 0.91 mm), used as a nozzle, and the grounding electrode to a home-made rotating metal drum, used as the fibre-collecting device. The electrostatic field strength was fixed at 17 kV. The distance between the nozzle tip and the collecting drum was 15 cm. For morphological study, the collection time was about 5 min, while samples collected for other analysis were collected from 24 h electrospinning period. The drum (outer diameter = 15 cm) rotated at a speed of about 50–65 rpm.