CHAPTER III
METHODOLOGY

3.1 Materials and Equipment

3.1.1 Chemicals

3.1.1.1 Catalysts Preparation

Titanium tetraisopropoxide (TTIP, 97%) and titanium butoxide (TBT, 97%) obtained from Sigma-Aldrich; and titanium ethoxide (TEOT) supplied by Fluka were used as Ti-precursors for the electrospinning process. Ethanol anhydrous (99.8%) obtained from Carlo-Erba and glacial acetic acid (99.7%) from Lab-Scan were used as received. Polyvinylpyrolidone (PVP), mw ~ 1,300,000, from Sigma-Aldrich was used as polymer for adjusting the viscosity of spinning solution. Silver nitrate ($AgNO_3$, 99.8%) supplied by Carlo-Erba was used as a precursor for metal doping. TiO_2 (Degussa P25) from JJ-Degussa was used as a commercial TiO_2.

3.1.1.2 Photocatalytic Experiments

4-chlorophenol (99+ %) from Sigma-Aldrich was used as a model pollutant. Hydroquinone (HQ, 99.8%) from Ajax and hydroxyhydroquinone (HHQ, 99%) from Aldrich were used for analysis of intermediate products. HPLC grade of acetonitrile (CH_3CN) and methanol (CH_3OH) from Lab-Scan were used as a mobile phase for a High Pressure Liquid Chromatography (HPLC). High purity of oxygen was from Thai Industrial Gases Public, Co.Ltd.

3.1.2 Equipment

X-ray Diffractometer (XRD): Rikaku
BET surface area analysis: Quantachrome Autosorb-1
Scanning Electron Microscope (SEM): JSM5800
High Pressure Liquid Chromatograph (HPLC): Hewlett Packard HPLC
Total Organic Carbon analyzer (TOC): Shimazu TOC-V_{CSH}

3.2 Experimental

3.2.1 Catalysts Preparation

3.2.1.1 Spinning Solution Preparation

Each titanium precursor was mixed with acetic acid and ethanol with the molar ratio of precursor to acetic acid to ethanol 1:10:10 (Table 3). The solution was rest for 10 minutes before added into 7.5 ml of 9% polyvinylpyrolidone (PVP) in ethanol, and the resulting mixture was constantly stirred for 10 minutes. The as-prepared solution is the spinning solution.

Table 3.1 Three types of titanium alkoxide precursor with ethanol and acetic acid

Precursor	Precursor (g)	Ethanol (ml)	Acetic acid (ml)
TTIP	1.5	3	3
TBT	1.8	3	3
TEOT	1.2	3	3

3.2.1.2 Metal doped TiO_2

Metal doped TiO_2 was prepared by adding the calculated amount of $AgNO_3$ into the mixture of a titanium precursor and PVP solution. For Ag doping, $AgNO_3$ was dissolved in EtOH before adding acetic acid and Ti-precursor. The amount of Ag was varied between 0 and 4 wt% based on the amount of TiO_2.

3.2.1.3 Spinning of the Composite Nanofibers

The spinning solution was immediately loaded into a plastic syringe. A blunt ended 20-guage stainless steel needle was used as the nozzle, which was set in a 45° orientation. The emitting electrode from a high voltage Protek DF1730SB3A 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, which was used as the collector plate. The aluminum foil was placed below the tip of the needle (Figure 3.1). The distance between the collector plate and the tip of the needle was set at 15 cm. During the application of a high voltage (20.5 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 exposed to moisture for approximately 16 hours to allow complete hydrolysis of titanium precursor.

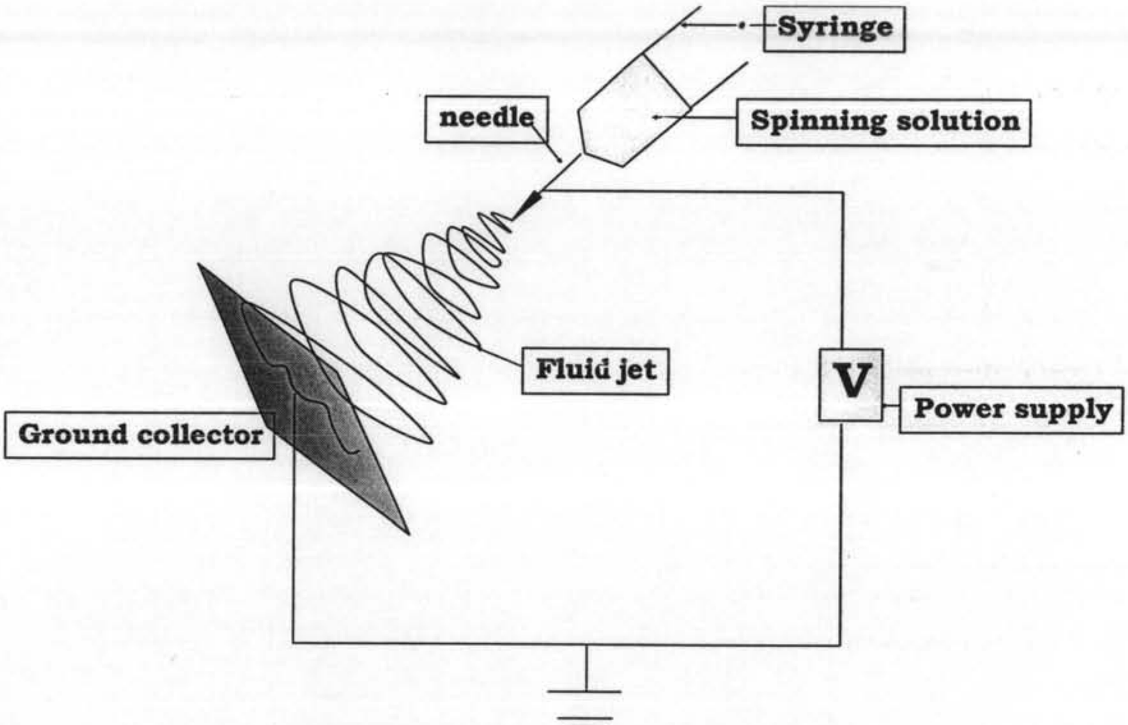

Figure 3.1 Experimental set up for the electrospinning process.

3.2.1.4 Calcination of the Composite Nanofibers

The electrospun TiO_2 composite fibers were calcined by varying the temperatures at 500, 600, and 700°C for 3 hours at heating rate of 1°C/min to remove the residual polymer.

3.2.2 Photocatalysis Experiments

3.2.2.1 Experimental Set-Up

Batch Operation

A 650 ml reactor with a cooling water jacket was used as a batch reactor. The UV light source, an 11-watt low-pressure mercury lamp (Philips PL-S 11W TUV) with a wavelength in the range of 200-280 nm, was dipped into the bottle in order to illuminate throughout the solution. A thermostat bath and magnetic stirrer were used to control the temperature and continuously mix the solution during the experiment. The reactor was covered by an opaque PVC box to prevent the outer effect and for UV protection (Figure 3.2).

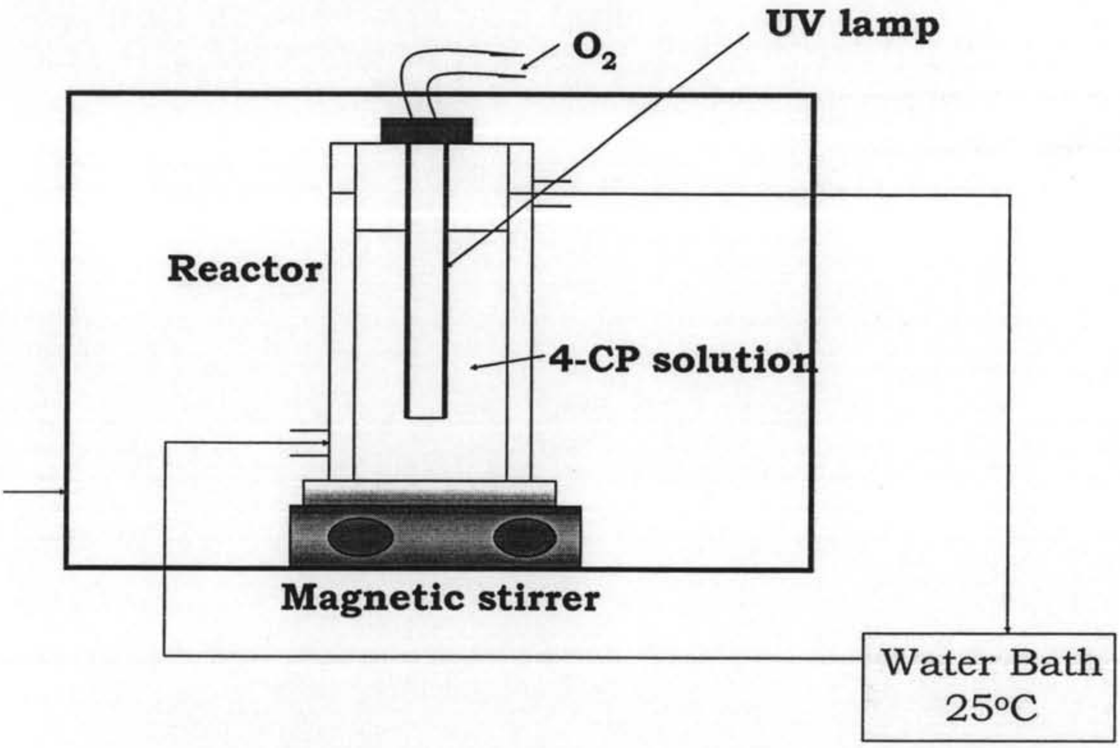

Figure 3.2 Schematic diagram of the photocatalytic reactor used in the batch operation.

3.2.2.2 Experimental Procedure

Batch Operation

500 ml solution containing 0.5 mM of 4-CP and 0.4 g/l of a catalyst were added into the reactor. Before the irradiation, the solution was stirred

for 30 minutes to allow equilibrium adsorption of the solute on the catalyst with a constant feed of O_2 to saturate the solution in the dark. O_2 was also continuously fed into the system during the experiment. The temperature was maintained at about 25°C by a thermostat bath. The experiment started when the UV lamp was turned on. The concentration of the substance in the bulk solution at this point was used as the initial value. Approximately 25 ml of the solution was taken every 20 minutes for 1 hour. After that, the solution was taken every 60 minutes for 5 hours.

3.2.3 Analytical Methods

3.2.3.1 Scanning Electron Microscopy (SEM)

The surface morphology and size of the resulting electrospun TiO_2 composite fibers (TiO_2/PVP composite fibers, pure TiO_2 fibers, metal doped TiO_2 fibers (Si or Ag doping)) were observed by a JSM5800 Scanning Electron Microscope (SEM), which was operated at 20 kV, at the Scientific and Technological Reseach Equipment Center (STREC), Chulalongkorn University. Samples were coated by a thin layer of gold prior to the analysis.

3.2.3.2 X- ray Diffractometry (XRD)

The crystalline phase of pure TiO_2 and metal doped TiO_2 fibers were determined by using a Rigaku X-ray diffractometer. CuKα radiation of X-ray source at $\lambda = 0.154$ nm was operated at 40 kV, 30 mA, and 1.20 kW.

X-ray diffraction patterns were used for the crystallite size (d) estimation by line broadening measurements with the Debye-Scherrer equation:

$$d = \frac{k\lambda}{b\cos\theta}\ , \tag{3.1}$$

where

λ = the wave length (nm)

k = the Debye-Scherrer constant (1.0)

b = the full width at half maximum (FWHM) of the broadened peak

θ = the Bragg angle of the reflection (degree)

d = the crystallite size (nm)

3.2.3.3 Brunauer-Emmett-Teller (BET)

The surface areas of the catalysts were measured by using the Quantachrome Autosorb-1. It measures the quantity of gases adsorbed onto or desorbed from a solid surface at some equilibrium vapor pressures. Nitrogen gas with cross sectional area 16.2×10^{-2} m^2/molecule was employed as an adsorbate at the liquidfied nitrogen temperature (77K).

The catalyst amount of 0.2 g was dried and out gassed in the sample cell at 250°C for at least 3 hours before the adsorption. The specific surface area of each catalyst was evaluated from the five points adsorption isotherm. The results were analyzed using the Autosorb-1 ANAGAS software Version 2.10.

3.2.3.4 High Pressure Liquid Chromatography (HPLC)

The sample solutions were analyzed for their composition of 4-CP and intermediate products using a Hewlett Packard High Pressure Liquid Chromatography (HPLC) equipped with an Alltech Apollo C18 column (150-mm length, 4-mm internal diameter, and 5 µm particle diameters) and UV detector adjusted to 270 nm. The mobile phase was a mixture of 40:60 volume ratio of acetonitrile to deionized water with the flow rate of 0.5 ml/min. By comparison of the retention times with standard substances, all chemicals can be identified. The concentration of any compounds can be calculated by using the calibration factor obtained from the calibration curve of a known concentration of that compound. Before the analysis, samples were centrifuged and filtered through a nylon filter membrane (0.2-µm pore size, 25-mm diameter) to remove all solid particles.

3.2.3.5 Total Organic Carbon (TOC)

The total organic carbon (TOC) was determined by a Shimatzu TOC-V_{CSH} analyzer.