

CHAPTER III EXPERIMENTAL



3.1 Preparation of Photocatalysts

3.1.1 Materials

Hydrogen tetrachloroaurate (III) trihydrate ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$) obtained from Aldrich, silver nitrate (AgNO_3) and tetraethylorthotitanate ($(\text{C}_2\text{H}_5\text{O})_4\text{Ti}$) or TEOT supplied by Fluka, were used as precursors for gold, silver and titania (TiO_2), respectively. The hydrolysis of TEOT was achieved with 37% hydrochloric acid (HCl), 99.7% ethanol from BDH, 65% nitric acid (HNO_3) from Lab-Scan and deionized water. The activity of the photocatalyst prepared by the sol-gel method was compared with commercially available titania (P25) obtained from Degussa Corporation.

3.1.2 Preparation Procedures

3.1.2.1 *TiO₂ Particles*

The pure TiO_2 catalysts used in this experiment were prepared by using the same method as described by Anderson and Bard (1995). TEOT was dissolved in ethanol and then nitric acid was added dropwise to obtain a solution pH of 5.5 at room temperature. Water was added dropwise to the prepared solution with vigorous stirring. The gelation was allowed to proceed slowly and completed within an hour. The mixture was allowed to age at room temperature in a covered beaker for 10 hours. The gel was dried at 100 °C for 5 hours to become a glassy material and then calcined at 400 °C. The mole ratio of alkoxide to water, acid, and alcohol was 1:52:13:0.8.

For the Au/TiO_2 , Ag/TiO_2 and Au-Ag/TiO_2 preparation, the calculated amounts of hydrogen tetrachloroaurate (III) trihydrate and silver nitrate were dissolved in ethanol. Then, Au/TiO_2 and Au/Ag/TiO_2 were prepared by the same method as that for TiO_2 .

3.1.2.2 *TiO₂ on Glass Plates*

TEOT was dissolved in ethanol and then nitric acid was added dropwise to obtain a solution pH of 5.5 at room temperature. The molar ratio of TEOT to ethanol and nitric acid was 1:52:0.8. A glass plate was dipped into the prepared solution and dried 100 °C for 2 min, followed by three more dippings. The glass plate was finally dried at 100 °C for 5 hours to obtain a glassy material and then calcined at 400 °C.

3.2 Catalyst Characterizations

3.2.1 Crystal Structures

X-ray diffraction patterns of all catalysts were obtained by using the Rigaku Dmax-2200 diffractometer equipped with a graphite monochromator and a Cu tube for generation a CuK α radiation (wavelength 1.5406 Å). The particles were spread on a glass slide specimen holder and its diffraction angles were examined between 5-90° at a scanning rate of 2 θ of 1.5° per minute with 0.02° increments. CuK α radiation of the X-ray source at $\lambda = 0.154$ nm was operated at 40 kV, 30 mA, and 1.20 kW. The digital output of the proportional X-ray detector and the goniometer angle measurements were transmitted to an online microcomputer for storing the data and the data were analyzed using PC-APD version 3.5B. The peak positions of the samples were compared with the standard files to identify crystalline phases.

X-ray diffraction is based on the fact that an X-ray diffraction pattern is unique for each crystalline substance. Thus, if an exact match can be found between the patterns of an unknown and an authentic sample, chemical identity can be assumed. It is also possible to make a relatively quantitative analysis by comparing the intensity of the diffraction lines. When comparing the same crystalline substance of two different samples, the higher intensity shows the higher content.

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

$$d = k\lambda / b\cos\theta \quad (3.1)$$

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)

3.2.2 Surface Area Measurement

The Brunauer-Emmett-Teller (BET) method was utilized for determining the surface area of the prepared catalysts. The characterization is based on the physical adsorption of an inert gas using Autosorb-1 Gas Sorption system (Quantachrome Corporation). It operates by measuring the quantity of gases adsorbed onto or desorbed from a solid surface at some equilibrium vapor pressures. Nitrogen gas with cross sectional area of $16.2 \times 10^{-2} \text{ m}^2/\text{molecule}$ was employed as an adsorbate at a liquefied nitrogen temperature (77 K).

The catalyst amount of 0.2 grams was dried and outgassed in the sample cell at 300 °C for at least three hours before adsorption. The specific surface area of each catalyst was evaluated from five points adsorption isotherm. The results were analyzed using Autosorb ANAGAS software Version 2.10. To ensure the accuracy of the data, BET method was employed to measure surface area of each catalyst at least twice.

3.2.3 Atomic Absorption Spectrophotometer (AAS)

An atomic absorption spectrophotometer (Varian Model 300/400) was employed to determine actual gold and silver loadings on the prepared catalysts.

A known weight of catalyst was dissolved in an aqua regia solution (hydrochloric acid and nitric acid with a ratio of 3:1). The metal solution was diluted to the measuring range. The concentrations of gold and silver were obtained by comparing their absorbance values with the calibration curve of standard solutions.

3.3 Photocatalysis Experiment

3.3.1 Materials

4-chlorophenol (4-CP) with 98% purity obtained from BDH was used as a model pollutant in this study. Hydroquinone obtained from Ajax and Hydroxyhydroquinone from Aldrich were used for the analysis of intermediate products. HPLC grade of acetonitrile (CH_3CN) purchased from Lab-Scan was used as a mobile phase in running HPLC. High purity of oxygen obtained from Thai Industrial Gases Public, Co. Ltd. was used to aerate the 4-chlorophenol solution.

3.3.2 Experimental Setup

A 1000 ml reagent bottle was used as a batch reactor in the study. The UV light source was an 11-watt low-pressure mercury lamp (Philips PLS 11 W) with a wavelength in the range of 200-280 nm. This wavelength range gives high energy enough to activate the photocatalysts. The UV lamp was dipped into the reactor in order to illuminate throughout the solution. The solution in the reactor was well mixed using a magnetic stirrer. A thermostat cooling-heating circulating unit was used to control the solution temperature at 25 °C throughout the experiment. The reactor was covered by an opaque PVC box to prevent the outer effects and for UV protection. The setup of the photocatalytic reactor is shown in Figure 3.1.

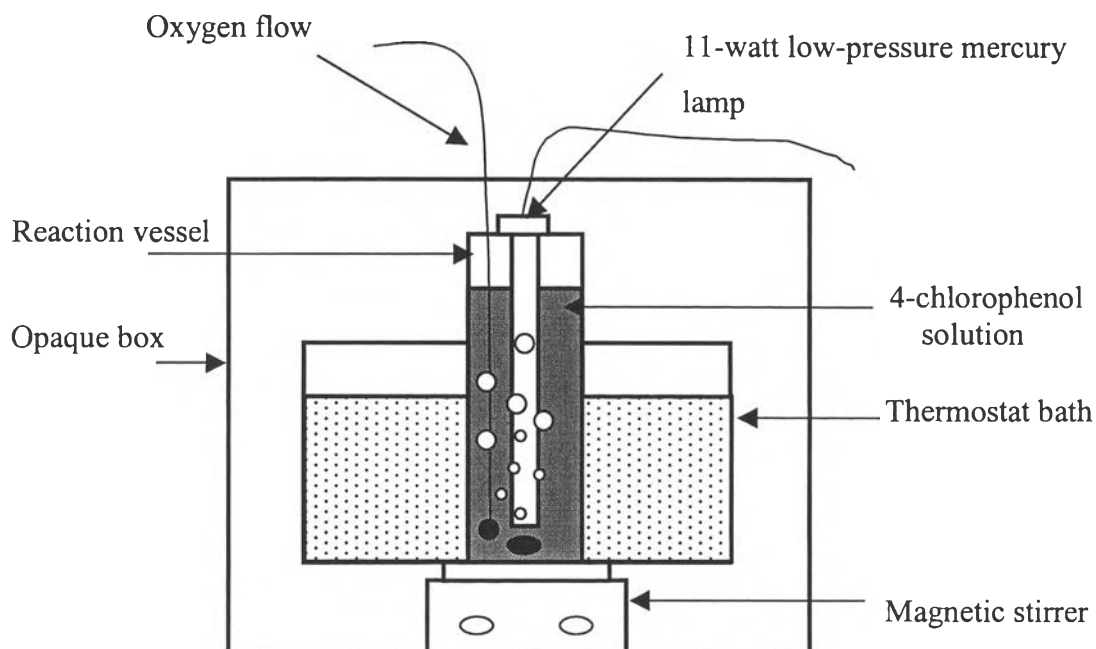


Figure 3.1 A schematic diagram of the photocatalytic reactor used in this experiment.

3.3.3 Experimental Procedure

For the irradiation experiment, a 450 ml solution containing 0.5 mM 4-CP and 0.5 g/l catalyst were added into the reactor. Before the irradiation, the solution was stirred well and saturated with oxygen for 1 hour to allow for the equilibrium adsorption of the system. The solution temperature was maintained at room temperature (about 25 °C) by using a the thermostat bath in conjunction with a cooling/heating unit. The experiment started when the UV lamp was turned on. A 25 ml sample was taken every 30 min for 360 min during the irradiation. Every experiment was carried out carefully and repeated at least twice.

3.3.4 Analytical Methods

Before analysis, a solution sample taken from the reactor was centrifuged and filtered with a nylon filter membrane (0.2- μm pore size, 25-mm

diameter) to remove all solid particles. The concentrations of 4-CP and intermediate products in the filtered sample were determined by a Hewlett Packard HPLC equipped with an ODS-2 spherisorb column (125-mm length, 4-mm internal diameter, and 5 μm particle diameter) and an UV detector adjusted to 270 nm for the detection of 4-CP. The mobile phase was a mixture of 40:60 volume ratio of acetonitrile to deionized water with a flow rate of 1.0 ml/min. Total organic carbon of the solution was also determined by a TOC analyzer (Shimadzu TOC-5000A).