



CHAPTER III EXPERIMENTAL

3.1 Materials

Materials and reagents used in this research were as follows:

1. Tetraisopropyl orthotitanate (TIPT, $\text{Ti}(\text{OCH}(\text{CH}_3)_2)_4$) (analytical grade, Merck)
2. Commercial TiO_2 : P-25 (J.J. Degussa Hüls Co., Ltd.), ST-01 (Ishihara Sangyo Co., Ltd.), and JRC-03 (Ishihara Sangyo Co., Ltd.).
3. Laurylamine hydrochloride (LAHC, $\text{CH}_3(\text{CH}_2)_{11}\text{NH}_2\cdot\text{HCl}$) (analytical grade, Merck).
4. Acetylacetone (ACA, $\text{CH}_3\text{COCH}_2\text{COCH}_3$) (analytical grade, Carlo Erba Reagents).
5. Methyl orange (MO) (analytical grade, Nacalai Tesque).
6. Hydrogen hexachloroplatinate(IV) hydrate ($\text{H}_2\text{PtCl}_6\cdot 6\text{H}_2\text{O}$) (analytical grade, Aldrich).
7. Hydrochloric acid (HCl) (37% analytical grade, Lab Scan)
8. Hydrogen peroxide (H_2O_2) (solution 30% in water, Carlo Erba Reagents)
9. Distilled water

3.2 Equipments

Equipments used in this research were as follows:

1. Thermogravimetric-differential thermal analyzer (TG-DTA, Perkin Elmer/Pyris Diamond)
2. Surface area analyzer (SSA, Quantachrome/Autosorb 1)
3. Transmission electron microscope (TEM, JEOL 2000 CX)
4. Scanning electron microscope (SEM, JOEL JSM-6400)
5. UV-VIS spectrophotometer (Shimadzu UV-2550)

6. UV light source (11-Watt low-pressure mercury lamp, Philips)
7. Oven (CARBOLITE/CWE 1100)
8. pH meter (HANAA/pH 211)
9. Microcentrifuge (Spectrofuge 24D)
10. Magnetic stirrer
11. Thermostat bath

3.3 Methodology

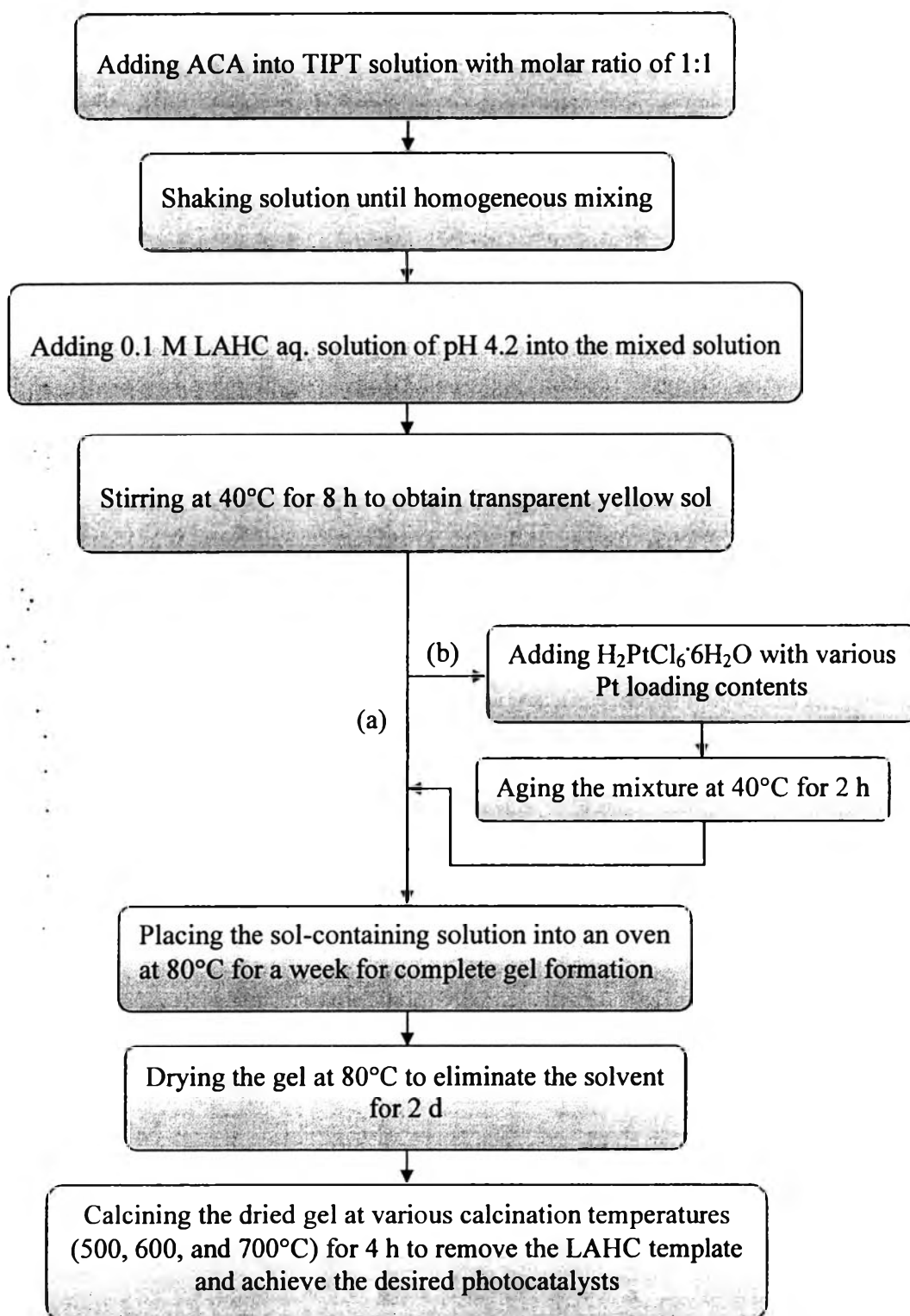
3.3.1 Mesoporous-Assembled TiO₂ Nanocrystal Photocatalyst Synthesis by a Sol-Gel Process with the Aid of Structure-Directing Surfactant and Pt-Loaded Mesoporous-Assembled TiO₂ Nanocrystal Photocatalyst Synthesis by Single-Step Sol-Gel (SSSG) Method

The mesoporous-assembled TiO₂ and Pt-loaded mesoporous-assembled TiO₂ photocatalysts were synthesized according to the following procedure:

- a. A specified amount of analytical grade ACA was introduced into TIPT with the molar ratio of unity.
- b. The mixed solution was smoothly shaken until homogeneous mixing. Afterwards, 0.1 M LAHC aqueous solution of pH 4.2 was added into the ACA-modified TIPT solution, in which the molar ratio of TIPT to LAHC was tailored to a value of 4.
- c. The mixture was continuously stirred at 40°C for 8 h to obtain transparent yellow sol.
- (d. and e. were the additional steps for the preparation of Pt-loaded mesoporous-assembled TiO₂ by single-step sol-gel, SSSG, method)
- d. To the aged TiO₂ sol solution, a necessary amount of hydrogen hexachloroplatinate(IV) hydrate for desired Pt loadings of 0.2-1.0 wt.% was incorporated (Sreethawong and Yoshikawa, 2005)
- e. The final mixture was further aged at 40°C for 2 h to acquire homogeneous solution.

- f. Then, the sol-containing solution was placed into an oven at 80°C for a week in order to obtain complete gel formation.
- g. The gel was dried at 80°C to eliminate the solvent for 2 d, which was mainly the distilled water used in the preparation of surfactant aqueous solution.
- h. The finally dried gel was calcined at various calcination temperatures (500, 600, and 700°C) for 4 h to remove LAHC template and consequently produce the desired TiO₂ photocatalysts.

The preparation flow chart for the mesoporous-assembled TiO₂ and Pt-loaded mesoporous-assembled TiO₂ photocatalyst preparation is shown below:



Flow diagram Synthesis procedure for mesoporous-assembled TiO_2 photocatalyst (a) for mesoporous-assembled TiO_2 and (b) for Pt-loaded mesoporous-assembled TiO_2 by SSSG method.

3.3.2 Photocatalyst Characterizations

- a. Simultaneous thermogravimetry and differential thermal analysis (TG-DTA) was used to study the thermal decomposition behavior of the as-synthesized dried TiO₂ gel and obtain suitable calcination temperature for removing LAHC template. The dried gel of 5-15 mg was heated from 30 to 700°C with a heating rate of 10°C /min in a static air atmosphere with α -Al₂O₃ as the reference.
- b. The surface area was measured by BET surface area analyzer. The photocatalyst sample was first outgassed to remove the humidity and volatile adsorbents adsorbed on surface under vacuum at 150°C for 4 h prior to the analysis. Then, N₂ was purged to adsorb on surface, measuring the quantity of gas adsorbed onto or desorbed from their solid surface at some equilibrium vapor pressure by static volumetric method. The solid sample was maintained at a constant temperature of the sample cell until the equilibrium was established. This volume-pressure data were used to calculate the BET surface area.
- c. X-ray diffraction (XRD) was used to identify phases present in the samples by using a Rigaku RINT 2000 diffractometer equipped with a Ni filtered CuK α radiation source ($\lambda = 1.542 \text{ \AA}$) of 40 kV and 30 mV. A photocatalyst sample was pressed into a hollow of glass holder and held in place by glass window. Then, it was scanned in the 2θ range of 15 to 70° in the continuous mode with the rate of 5°/min. The XRD results showed peak parameters, including the centroid 2θ , the full line width at half the maximum of intensity, d-value, and intensity. The mean crystallite size was calculated from the XRD data from X-ray line broadening.
- d. The sample morphology was observed by a transmission electron microscope (TEM) and a scanning electron microscope (SEM). For TEM, the photocatalyst sample was ground into fine powder and ultrasonically dispersed in ethanol. A small droplet of the suspension was deposited on a copper grid with polyvinyl desiccate, and the solvent was evaporated prior to loading the sample into the microscope. TEM was carried out in a JEOL 2000 CX

operating at an accelerating voltage of 200 kV in bright field mode. A beam was passed through a series of lenses to form a magnified image of a sample that was inserted in the area of the objective lens. The image from selected area was viewed through projection onto a view of screen. Because electron beams can be easily scattered by air molecules, TEM columns must be kept under high vacuum. Additionally, the electromagnetic lens were used for focusing the electron beam. For SEM, the sample was coated with Au before measurement for improving conductivity of sample. The accelerating voltage for the SEM operation was 15 kV.

- e. UV-VIS spectrophotometer was used to identify light absorption ability of the photocatalysts. The analysis was performed under scanning wavelength range of 200-800 nm. And, it was also used to measure the quantity of dye by using absorbance mode and to follow the decolorization and degradation of MO dye.

3.3.3 Photocatalytic Activity Testing

Photocatalytic decomposition of MO dye was performed in an open system with UV light irradiation, as shown in Figure 3.1.

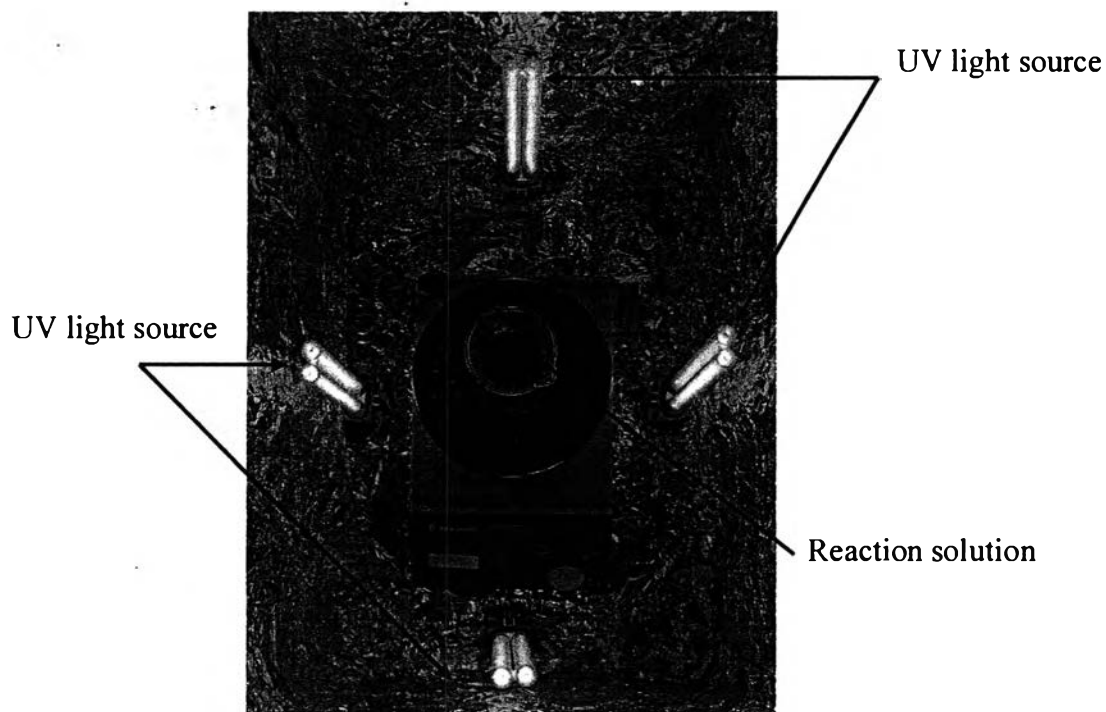


Figure 3.1 UV light irradiation system for photocatalytic activity test.

The photocatalytic decomposition of MO dye was carried out according to the following procedure:

- a. A specified amount of all prepared photocatalysts, namely synthesized mesoporous-assembled TiO₂, Pt-loaded mesoporous-assembled TiO₂, P-25 TiO₂, ST-01 TiO₂, and JRC-03 TiO₂, was suspended in an aqueous MO solution with different initial MO concentrations and solution pHs, by means of magnetic stirrer within a Pyrex glass reactor.
- b. Prior to the photocatalytic activity test, the continuously suspended mixture was left for 1 h in dark environment to establish the adsorption equilibrium.
- c. The reaction was started by exposing the mixture with UV light irradiation from 11 W low-pressure mercury lamps.
- d. The suspension was withdrawn every 1 h and then centrifuged by a centrifugal machine to separate the photocatalyst powder out.
- e. The liquid samples were analyzed for MO concentration by UV-VIS spectrophotometer to follow its decolorization and degradation.