



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 P-25 TiO_2 (J.J. Degussa Hüls 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. Acid Yellow 23 (AY, $\text{C}_{16}\text{H}_9\text{N}_4\text{Na}_3\text{O}_9\text{S}_2$) (analytical grade, Nacalai Tesque)
6. Acid Black 1 (AB, $\text{C}_{22}\text{H}_{14}\text{N}_6\text{Na}_2\text{O}_9\text{S}_2$) (analytical grade, Nacalai Tesque)
7. Hydrochloric acid (HCl) (37% analytical grade, Lab Scan)
8. Sodium hydroxide (NaOH) (analytical grade, Labscan Asia CO., Ltd.)
9. Calcium chloride (CaCl_2) (analytical grade, Ajax Finechem)
10. Magnesium chloride (MgCl_2) (analytical grade, Ajax Finechem)
11. Distilled water

3.2 Equipments

Equipments used in this research were as follows:

1. X-ray diffractometer (XRD, Rigaku/Rint 2200 HV)
2. Surface area analyzer (SSA, Quantachrome/Autosorb 1)
3. Transmission electron microscope (TEM, JEOL 2000 CX)
4. TOC analyzer (Shimadzu TOC-5000A)
5. UV-Visible 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 Photocatalyst Synthesis by a Sol-Gel Process with the Aid of Structure-Directing Surfactant

The mesoporous-assembled TiO₂ photocatalyst was synthesized according to the following procedure:

- a. A specified amount of analytical grade ACA was first introduced into TIPT with the molar ratio of unity.
- b. The mixed solution was then smoothly shaken until homogeneous mixing. Afterwards, 0.1 M LAHC aqueous solution with pH of 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 kept continuously stirring at 40°C for 8 h to obtain transparent yellow sol.
- d. Then, the sol-containing solution was placed into an oven at 80°C for a week in order to obtain complete gel formation.
- e. 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.
- f. The dried gel was finally calcined at 500°C for 4 h to remove LAHC template, and consequently, the desired TiO₂ photocatalyst was produced.

The preparation flow chart for the synthesis of mesoporous-assembled TiO₂ photocatalyst is shown in Figure 3.1:

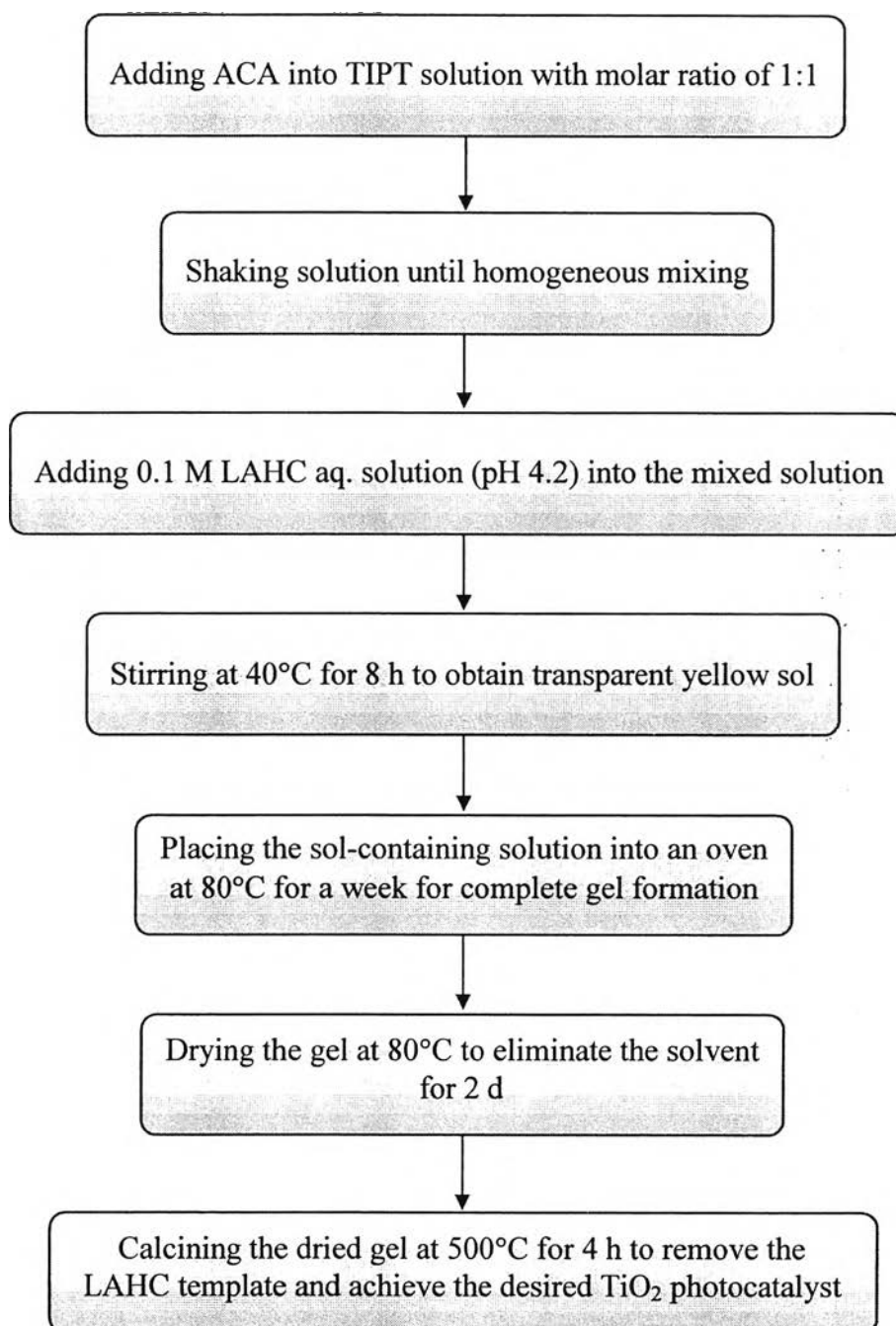


Figure 3.1 Synthesis procedure for mesoporous-assembled TiO₂ photocatalyst.

3.3.2 Photocatalyst Characterizations

- a. The surface area of the synthesized photocatalyst 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 the photocatalyst surface, and then the quantity of gas adsorbed onto or desorbed from their solid surface at some equilibrium vapor pressures by static volumetric method was measured. The solid sample was maintained at a constant temperature of the sample cell until the equilibrium was established. This volume-pressure data was used to calculate the BET surface area.
- b. X-ray diffraction (XRD) was used to identify phases present in the sample 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. The 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 20 to 60° in the continuous mode with the rate of 5°/min. The XRD results show peak parameters, including the centroid 2θ , the full line width at half the maximum of intensity (β), d-value, and intensity. The mean crystallite size was calculated from the XRD data from X-ray line broadening.
- c. The sample morphology was observed by a transmission electron microscope (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. However, electron beams can be easily scattered by air

- molecules, and TEM columns must be kept under high vacuum. Additionally, the electromagnetic lens was used for focusing the electron beam.
- d. UV-Visible spectrophotometer was used to identify light absorption ability of the photocatalyst. The analysis was operated under scanning wavelength range of 200-600 nm. And, it was also be used to measure the quantity of dyes by using absorbance mode under scanning wavelength range of 300-700 nm and to follow the degradation of dyes due to the cleavage of N=N bond.
 - e. The point of zero charge (PZC) of the photocatalyst was determined by suspending a desired amount of the photocatalyst sample in deionized water with different initial pHs. The mixture was shaken for an hour. It was found that this time interval was sufficient for stable pH readings, indicating that the adsorption-desorption equilibrium was reached. Finally, the pH was measured and recorded as final pH. The PZC could be determined as the point, where the initial pH was equal to the final pH.
 - f. Total organic carbon of the solution was determined by a Shimadzu TOC analyzer. The degradation of dyes due to the decrease in organic carbon content in the solution was also followed by this technique.

3.3.3 Photocatalytic Activity Testing

Photocatalytic degradation of both single and mixed dyes (Acid Black 1 and Acid Yellow 23) was performed in an open system with UV light irradiation, as shown in Figure 3.2. The photocatalytic degradation of dyes was carried out according to the following procedure:

- a. A specified amount of the synthesized mesoporous-assembled TiO_2 photocatalyst was suspended in the aqueous solution of both single and mixed dyes under various reaction conditions by using magnetic stirrer within a reactor made of Pyrex glass.
- b. Prior to the photocatalytic activity testing, the continuously suspended mixture was left for 30 min in dark environment to establish the adsorption equilibrium.
- c. The reaction was started by exposing the mixture to UV light irradiation from a set of 11 W mercury lamps.

- d. The suspension was withdrawn every 15 min and then centrifuged by a centrifugal machine to separate the photocatalyst powder out.
- e. The liquid samples were analyzed by UV-Visible spectrophotometer for the concentration of both dyes and by TOC analyzer for the total organic carbon present in the dye solution to follow the dye degradation. The degradation efficiency was calculated by the following equations:

$$\text{UV-Visible : Degradation efficiency (\%)} = \left(\frac{C_0 - C}{C_0} \right) \times 100$$

$$\text{TOC : Degradation efficiency (\%)} = \left(\frac{\text{TOC}_0 - \text{TOC}}{\text{TOC}_0} \right) \times 100$$

Moreover, the pseudo-first order rate constant (k , min^{-1}) for the photodegradation reaction of dyes was calculated by the following equations:

$$\ln\left(\frac{C_0}{C}\right) = kt \quad \text{or} \quad \ln\left(\frac{\text{TOC}_0}{\text{TOC}}\right) = kt$$

The k value was calculated from the plot between $\ln(C_0/C)$ or $\ln(\text{TOC}_0/\text{TOC})$ and time (t),

where C_0 and C denote the concentration of both dyes from UV-Visible analysis at $t = 0$ and $t = t$, respectively,

and TOC_0 and TOC denote the total organic carbon from TOC analysis at $t = 0$ and $t = t$, respectively.

The degradation efficiency and pseudo-first order rate constant were used as the indicators for evaluating the photocatalytic activity of the synthesized mesoporous-assembled TiO_2 photocatalyst.

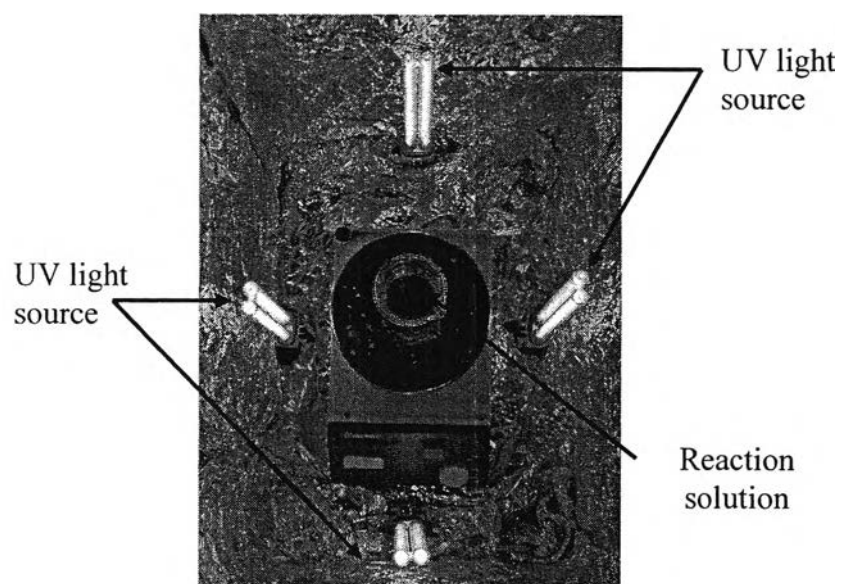


Figure 3.2 UV light irradiation system for photocatalytic activity testing.