



CHAPTER III EXPERIMENTAL

3.1 Materials

- Tetraisopropyl orthotitanate (TIPT, $\text{Ti}(\text{OCH}(\text{CH}_3)_2)_4$)
- Commercial TiO_2 (Degussa P-25)
- Laurylamine hydrochloride (LAHC, $\text{CH}_3(\text{CH}_2)_{11}\text{NH}_2\cdot\text{HCl}$)
- Acetylacetone (ACA, $\text{CH}_3\text{COCH}_2\text{COCH}_3$)
- Acid Black 1 (AB, $\text{C}_{22}\text{H}_{14}\text{N}_6\text{Na}_2\text{O}_9\text{S}_2$)
- Hydrochloric acid (HCl)
- Sodium hydroxide (NaOH)
- Triton X-100 ($\text{C}_{14}\text{H}_{22}\text{O}(\text{C}_2\text{H}_4\text{O})_n$) ($n = 9-10$)
- Ethanol ($\text{C}_2\text{H}_5\text{OH}$)
- Propanol ($\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$)
- Distilled water

3.2 Equipment

- X-ray diffractometer (XRD, Bruker/AXS, D8 Advance)
- Surface area analyzer (SAA, Quantachrome/Autosorb 1)
- Transmission electron microscope (TEM, JEOL/JEM-2100)
- Scanning electron microscope (SEM, Hitachi/S-4800)
- Thermogravimetric-differential thermal analyzer (TG-DTA, Perkin Elmer/Pyris Diamond)
- UV-visible spectrophotometer (Shimadzu/UV-2550)
- UV-visible spectrophotometer (Shimadzu/UV-1800)
- UV light source (11-Watt low-pressure mercury lamp, Philips)
- Atomic force microscope (AFM, Park Systems/XE-100)
- Oven (CARBOLITE/CWE 1100)
- pH meter (HANAA/pH 211)

- Microcentrifuge (Spectrofuge 24D)
- Magnetic stirrer
- Thermostat bath

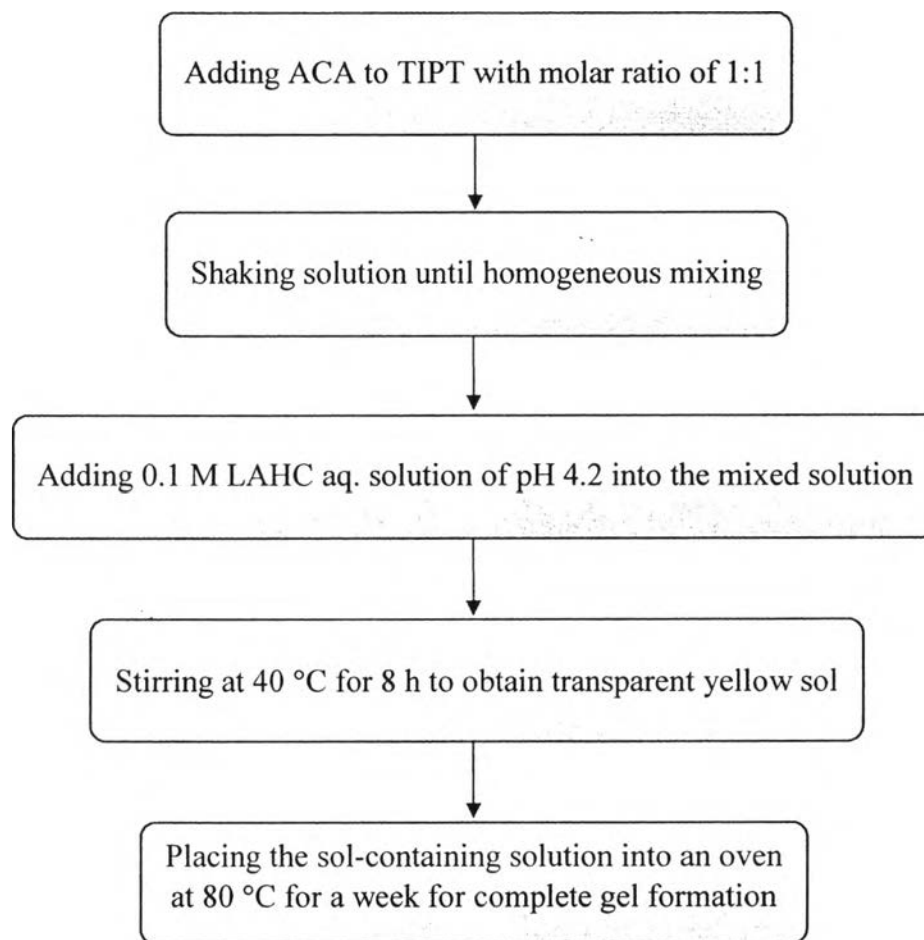
3.3 Methodology

3.3.1 Synthesis of Mesoporous-Assembled TiO₂ Gel by a Sol-Gel Process with the Aid of a Structure-Directing Surfactant

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

- a. A specified amount of analytical grade ACA was firstly added to TIPT with the molar ratio of unity.
- b. The mixed solution was then smoothly shaken until homogeneous mixing. Afterwards, a 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 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.

The preparation flow chart for the synthesis of mesoporous-assembled TiO₂ gel is shown below:



Flow diagram Synthesis procedure for mesoporous-assembled TiO₂ gel.

3.3.2 Immobilization of Mesoporous-Assembled TiO₂ Photocatalysts on Glass Plate Substrate

The immobilization of the synthesized mesoporous-assembled TiO₂ nanocrystal photocatalysts on glass plate was performed according to the following procedure:

- a. The as-synthesized TiO₂ gel was firstly mixed with propanol for washing and partly eliminating the LAHC surfactant. This mixture was continuously stirred at room temperature for 2 h. And then, the

mixture was centrifuged for separating gel from the mixture. Finally, the wet TiO₂ gel is obtained.

- b. To prepare TiO₂ pastes, a specified amount of the obtained wet TiO₂ gel was mixed with ethanol and triton x-100 used as a binder. This mixture was continuously stirred at room temperature for 1 d. The mixtures between the synthesized wet TiO₂ gel and Degussa P-25 TiO₂ were also comparatively used.
- c. To prepare glass a plate (2.4 cm × 7.6 cm), the glass plate was pretreated by soaking in a 10 M NaOH solution for 1 d. After that, it was sonicated in deionized water for removing NaOH. Then, it was rinsed with deionized water again and finally dried.
- d. The TiO₂ paste was coated on the pretreated glass plate by the simple doctor blading method, and the glass plate with TiO₂ film (1.9 cm × 6.6 cm) was placed in an oven at 80 °C for 1 d.
- e. The resulting TiO₂-immobilized glass plate was finally calcined at various temperatures for 2 h to remove the LAHC surfactant and to consequently produce the desired immobilized TiO₂ photocatalysts on glass plate.

3.3.3 Photocatalyst Characterizations

- a. The thermal decomposition behavior of the propanol-washed TiO₂ zero gel and its suitable calcination temperature were investigated by using a TG-DTA apparatus (Shimadzu, DTG-50) with a heating rate of 10 °C min⁻¹ in a static air atmosphere and with α-Al₂O₃ powder as the reference.
- b. The specific surface area of the TiO₂ samples was measured by BET surface area analyzer. A sample was first outgassed to remove the humidity and volatile adsorbents adsorbed on the surface under vacuum at 150 °C for 4 h prior to the analysis. Then, N₂ was purged to adsorb on the surface, and the quantity of gas adsorbed onto or desorbed from their solid surface at some equilibrium vapor

pressures by static volumetric method was measured. A sample was maintained at a constant temperature in the sample cell until the equilibrium was established. This volume-pressure data were used to calculate the specific surface area, as well as mean pore diameter and total pore volume.

- c. X-ray diffraction (XRD) was used to identify phases present in the TiO₂ samples by using a Bruker AXS D8 Advance diffractometer equipped with a Ni filtered CuK α radiation source ($\lambda = 1.542 \text{ \AA}$) operating at 40 kV and 30 mA. A sample was attached to 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 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.
- d. The sample morphology was observed by a transmission electron microscope (TEM) and a scanning electron microscope (SEM). For the TEM analysis, the TiO₂ 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. The TEM analysis was carried out 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 could be easily scattered by air molecules, and the TEM column must be kept under high vacuum. Additionally, the electromagnetic lens were used for focusing the electron beam. For the SEM analysis, the sample was coated with Au before measurement for improving conductivity of sample.

- e. UV-visible spectrophotometer was used to identify light absorption ability of the TiO_2 photocatalysts. The analysis was performed under scanning wavelength of 200 to 900 nm by using BaSO_4 as the reference. And, it was also used to measure the quantity of dye by using absorbance mode and to follow the degradation of AB dye due to the cleavage of N=N bond.
- f. Atomic force microscope (AFM) was used to identify roughness and surface topology of the TiO_2 photocatalyst film and glass plate. A sample was attached on a sample dish. Then, the cantilever (non-contact mode, ACTA-silicon probes) was adjusted to move close to the surface sample. The analysis was performed under scan size = $5 \times 5 \mu\text{m}$. The AFM results showed two-three dimensional image and roughness.

3.4 Photocatalytic Experiment

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

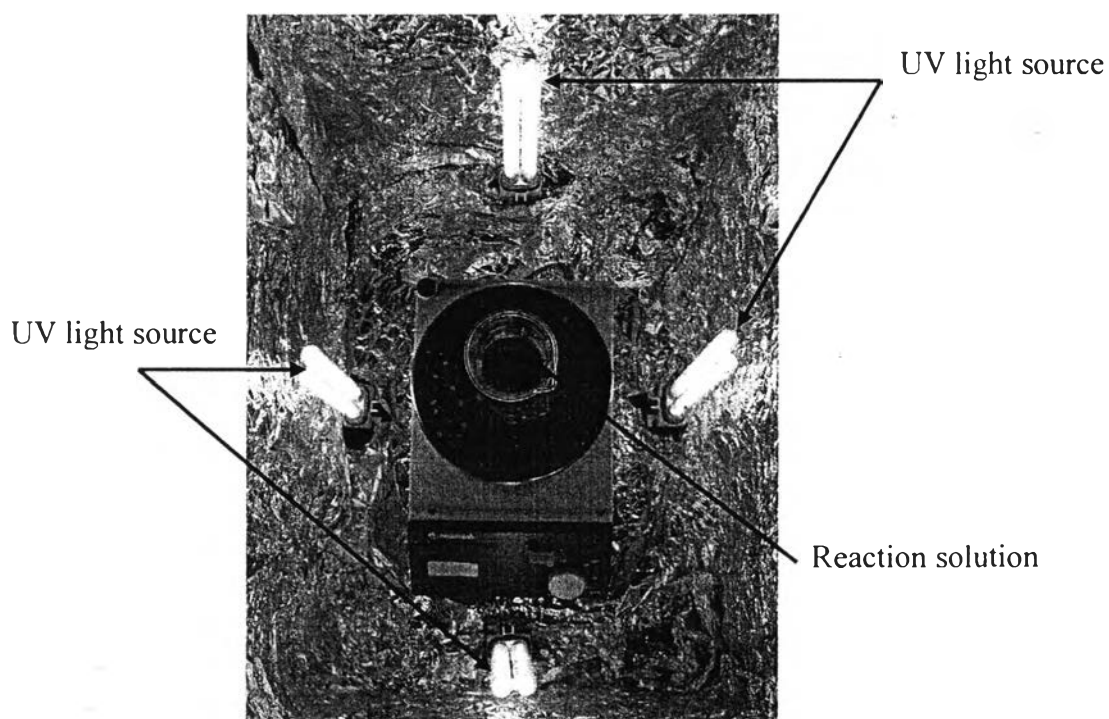


Figure 3.1 UV light irradiation system for photocatalytic activity test.

The photocatalytic degradation was carried out according to the following procedure:

- The prepared TiO_2 film-coated glass plates (8 plates) were placed in the Pyrex glass photocatalytic reactor containing an aqueous solution of AB dye agitated by using a magnetic stirrer.
- Prior to the photocatalytic activity test, the continuously agitated AB dye solution was left for 0.5 h in dark environment to establish the adsorption equilibrium of the AB dye on the TiO_2 film.
- The reaction was started by exposing the solution with UV light irradiation from 11 W mercury lamps.

- d. The dye solution was withdrawn every 30 min and then centrifuged by a centrifugal machine to separate the photocatalyst powders out if detached from the glass plates.
- e. The liquid samples were analyzed for the concentration of AB dye by the UV-visible spectrophotometer to follow its degradation. The pseudo-first order reaction kinetics was used to obtain apparent reaction rate constant from the concentration data.