



CHAPTER III EXPERIMENTAL

3.1 Material

All chemicals/materials used in this research are as follows:

- 3.1.1 Tetraisopropyl orthotitanate (TIPT, $\text{Ti}(\text{OCH}(\text{CH}_3)_2)_4$, synthesis grade, Merck)
- 3.1.2 Hydrogen hexachloroplatinate (IV) hexahydrate ($\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$, analytical grade, Aldrich)
- 3.1.3 Eosin Y (E.Y., $\text{C}_{20}\text{H}_6\text{Br}_4\text{Na}_2\text{O}_5$, Aldrich)
- 3.1.4 Commercial TiO_2 photocatalysts (P-25 (J.J. Degussa Hüls Co., Ltd.), ST-01 (Ishihara Sangyo Co., Ltd.), JRC-01 (Ishihara Sangyo Co., Ltd.), and JRC-03 (Ishihara Sangyo Co., Ltd.))
- 3.1.5 Laurylamine hydrochloride (LAHC, $\text{CH}_3(\text{CH}_2)_{11}\text{NH}_2 \cdot \text{HCl}$, synthesis grade, Merck)
- 3.1.6 Acetylacetone (ACA, $\text{CH}_3\text{COCH}_2\text{COCH}_3$, synthesis grade, Rasayan)
- 3.1.7 Diethanolamine (DEA, $(\text{HOCH}_2\text{CH}_2)_2\text{NH}$, Lab Scan)
- 3.1.8 Acetone (CH_3COCH_3)
- 3.1.9 Hydrochloric acid (HCl)
- 3.1.10 Sodium hydroxide (NaOH)
- 3.1.11 Distilled water

3.2 Equipment

All equipments used in this research are as follows:

- 3.2.1 Thermogravimetric/differential thermal analyzer (TG-DTA, Perkin Elmer/Pyris Diamond)
- 3.2.2 X-ray diffractometer (XRD, Rigaku/Rint2200 HV)
- 3.2.3 Surface area analyzer (SSA, Quantachrome/Autosorb 1)
- 3.2.4 Scanning electron microscope (SEM, JEOL 5200-2AE)

- 3.2.5 Transmission electron microscope (TEM, JEOL 2000 CX)
- 3.2.6 Gas chromatograph (GC, Perkin Elmer/ARNEL)
- 3.2.7 UV-VIS spectrophotometer (Shimadzu UV-2550)
- 3.2.8 Xenon discharge lamp (Type KXL-300/WACOM electric)
- 3.2.9 Oven (CARBOLITE/CWE 1100)
- 3.2.10 pH meter (HANAA/pH 211)
- 3.2.11 Magnetic stirrer
- 3.2.12 Centrifugal machine
- 3.2.13 UV cut-off filter (B-48S/ATG)

3.3 Methodology

Mesoporous-Assembled TiO₂ Nanocrystal Photocatalyst Synthesis by Sol-Gel Process with the Aid of Structure-Directing Surfactant and Pt-Loaded Mesoporous-Assembled TiO₂ Synthesis by Single-Step Sol-Gel 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 then gently 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 is 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. and e. are 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 a desired optimum Pt loading of 0.6 wt.% was incorporated (Sreethawong and Yoshikawa, 2006).

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 is mainly the distilled water used in the preparation of surfactant aqueous solution.

h. The dried gel was finally calcined at various calcination temperatures (500-700°C) for 4 h to remove LAHC template and consequently produce the desired TiO₂ photocatalysts.

The flow chart for the mesoporous-assembled TiO₂ and Pt-loaded mesoporous-assembled TiO₂ photocatalyst preparation is shown in Figure 3.1.

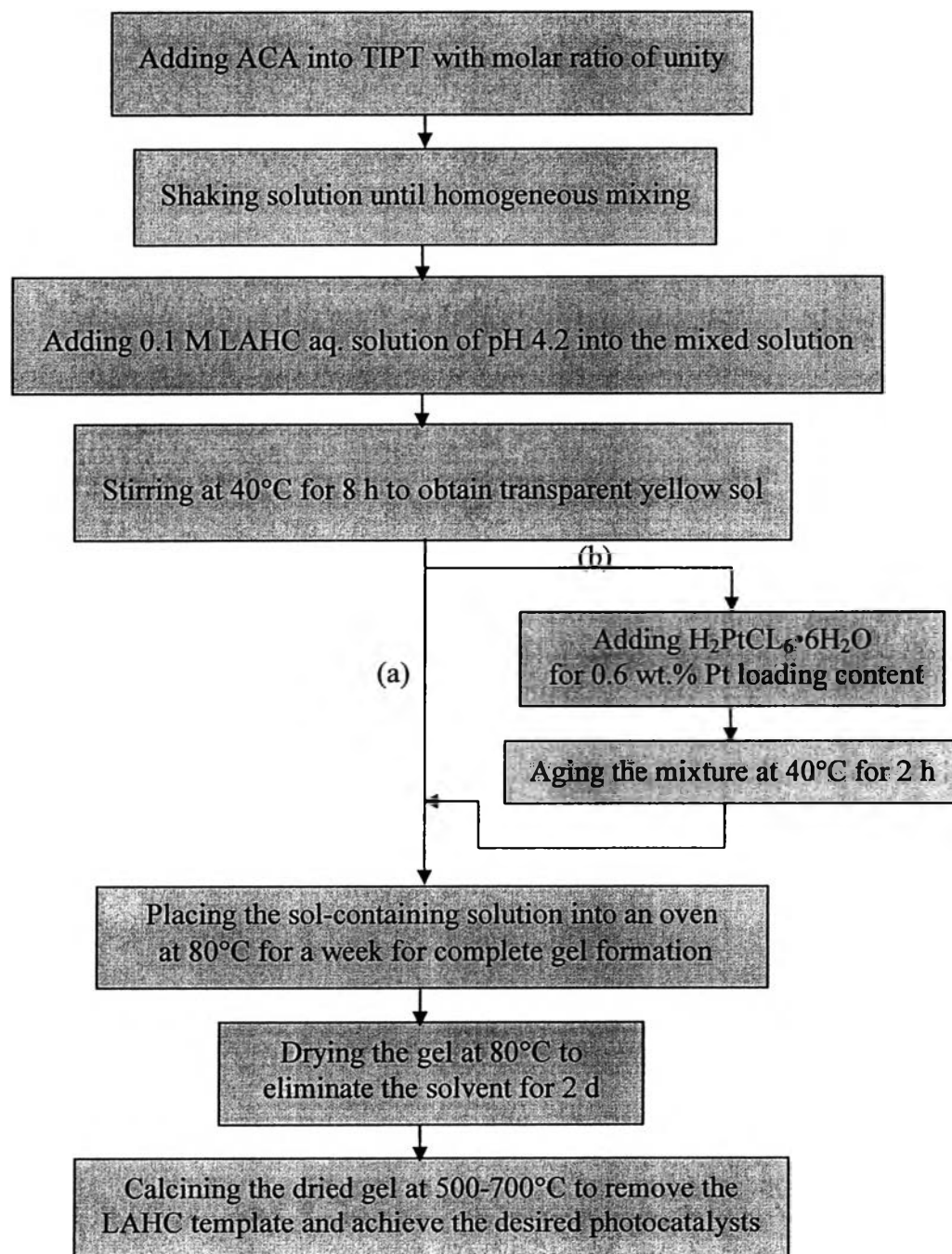


Figure 3.1 Synthesis procedure for mesoporous-assembled TiO₂ photocatalyst: (a) for mesoporous-assembled TiO₂ and (b) for Pt-loaded mesoporous-assembled TiO₂.

3.4 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 50 to 900°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 2 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 diffractometer equipped with a Ni filtered CuK α radiation source ($\lambda = 1.542 \text{ \AA}$) of 40 kV and 30 mA. 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 10 to 80° 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 (β), d-value, and intensity. The mean crystallite size was calculated from the XRD data from X-ray line broadening.
- d. UV-VIS spectrophotometer was used to identify light absorption ability of the photocatalysts and sensitizer. To obtain UV-Vis spectra of the photocatalysts, the analysis was operated under scanning wavelength at 200-900 nm using BaSO₄ as the reference.

- e. The sample morphology was observed by a scanning electron microscope (SEM). In addition, the sample morphology were observed by a transmission electron microscope (TEM). For SEM, the sample was coated with Au before measurement for improving conductivity of sample. SEM was operated at a voltage of 15 kv. For TEM, the photocatalyst samples 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 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 column must be kept under high vacuum. Additionally, the electromagnetic lenses were used for focusing the electron beam. The elemental analysis of photocatalyst was also investigated by an energy-dispersive X-ray (EDX) analyzer attached to both SEM and TEM.

3.5 Photocatalytic H₂ Production System

The photocatalytic H₂ evolution tests were carried out according to the following procedure:

- a. A specified amount of all prepared photocatalysts (0.2 g), namely synthesized mesoporous-assembled TiO₂, commercial TiO₂ (P-25, ST-01, JRC-01, and JRC-03), and 0.6 wt.% Pt-loaded mesoporous-assembled TiO₂, was suspended in 150 ml of aqueous diethanolamine solution containing dissolved Eosin Y sensitizer by means of magnetic stirrer within a reactor made of Pyrex glass.
- b. The mixture was deaerated by purging with Ar gas for 45 min in dark environment to establish adsorption equilibrium.
- c. The reaction was started by exposing the mixture with visible light irradiation from a 300 W Xe arc lamp emitting light with wavelength longer than 420 nm using a UV cut-off filler.

d. The gaseous H_2 evolved was periodically collected by a gas-tight syringe and analyzed by a gas chromatograph (GC) equipped with a thermal conductivity detector (TCD). The conditions used for operating GC are shown as follows:

- Injector temperature: 60°C
- Oven temperature: 33°C
- Detector temperature: 150°C
- Carrier gas: Ar
- Ar pressure: 50 psi

The photocatalytic H_2 evolution reaction was performed in a closed gas system, as shown in Figure 3.2.

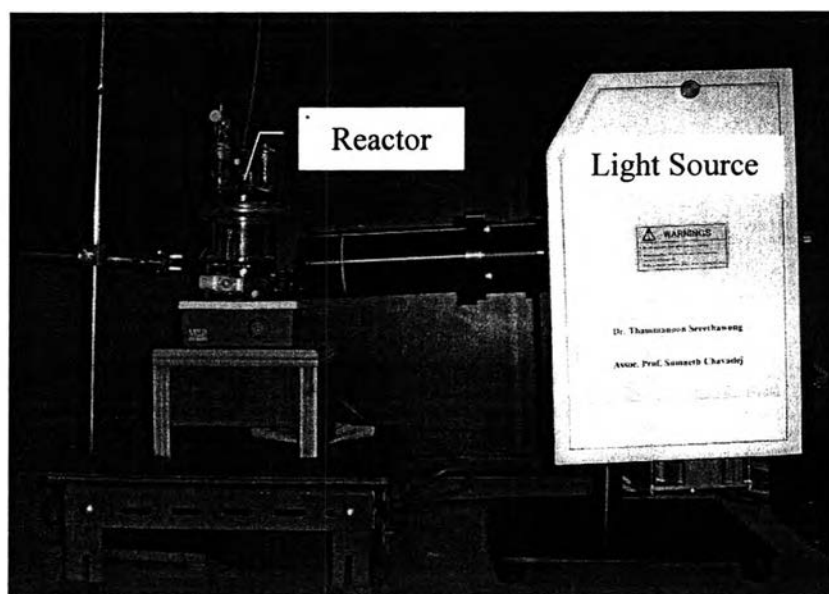


Figure 3.2 Setup of photocatalytic H_2 production system.