



CHAPTER III EXPERIMENTAL

3.1 Materials:

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

- 3.1.1 Tetraisopropyl orthotitanate (TIPT, $\text{Ti}(\text{OCH}(\text{CH}_3)_2)_4$, synthesis grade, Merck)
- 3.1.2 Acetylacetone (ACA, $\text{CH}_3\text{COCH}_2\text{COCH}_3$, synthesis grade, Rasayan)
- 3.1.3 Magnesium nitrate hexahydrate ($\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, Ajax)
- 3.1.4 Calcium nitrate tetrahydrate ($\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, Ajax)
- 3.1.5 Strontium nitrate ($\text{Sr}(\text{NO}_3)_2$, Merck)
- 3.1.6 Anhydrous ethyl alcohol (EtOH, Carlo Erba)
- 3.1.7 Laurylamine hydrochloride (LAHC, $\text{CH}_3(\text{CH}_2)_{11}\text{NH}_2 \cdot \text{HCl}$, synthesis grade, Merck)
- 3.1.8 Hydrogen hexachloroplatinate (IV) hexahydrate ($\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$, analytical grade, Aldrich)
- 3.1.9 Commercial SrTiO_3 photocatalyst (Wako Pure Chemical Industries, Ltd.)
- 3.1.10 Commercial P-25 TiO_2 photocatalyst (J.J. Degussa Hüls Co., Ltd)
- 3.1.11 Eosin Y (E.Y., $\text{C}_{20}\text{H}_6\text{Br}_4\text{Na}_2\text{O}_5$, Aldrich)
- 3.1.12 Diethanolamine (DEA, $(\text{HOCH}_2\text{CH}_2)_2\text{NH}$, Ajax)
- 3.1.13 Triethanolamine (TEA, $\text{N}(\text{CH}_2\text{CH}_2\text{OH})_3$, Ajax)
- 3.1.14 Acetone (CH_3COCH_3)
- 3.1.15 Hydrochloric acid (HCl, Lab Scan)
- 3.1.16 Sodium hydroxide (NaOH, Lab Scan)
- 3.1.17 Distilled water

3.2 Equipments:

All equipments used in this research were as follows:

- 3.2.1 Thermogravimetric/differential thermal analyzer (TG-DTA, Perkin Elmer/Pyris Diamond)
- 3.2.2 X-ray diffractometer (XRD, Rigaku/Rint 2200 HV)
- 3.2.3 Surface area analyzer (SAA, Quantachrome/Autosorb 1)
- 3.2.4 Transmission electron microscope (TEM, JEOL 2000 CX)
- 3.2.5 Gas chromatograph (GC, Perkin Elmer/ARNEL)
- 3.2.6 UV-VIS spectrophotometer (Shimadzu UV-2550)
- 3.2.7 TG-DTA apparatus (Shimadzu DTG-50)
- 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

The mesoporous-assembled perovskite titanate nanocrystal photocatalyst synthesis by a sol-gel process with the aid of structure-directing surfactant

- a. A specified amount of analytical grade ACA was introduced into TIPT with the molar ratio of unity at room temperature to obtain the ACA-modified TIPT solution.
- b. A surfactant solution of LAHC was prepared by dissolving it in EtOH. Afterwards, an appropriate amount of alkaline earth nitrate ($\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, or $\text{Sr}(\text{NO}_3)_2$) dissolved in distilled water was added to the surfactant solution with continuously stirring at room temperature to obtain a clear solution.
- c. The surfactant-alkaline earth nitrate solution was then slowly dropped into the yellow mixture of the ACA-modified TIPT solution while stirring continuously at room temperature to obtain transparent yellow sol.

(d. and e. are the additional steps for the preparation of Pt-loaded mesoporous-assembled perovskite titanate photocatalysts by single-step sol-gel (SSSG) method.)

d. To the aged perovskite titanate sol solution, a necessary amount of hydrogen hexachloroplatinate(IV) hexahydrate for a desired optimum Pt loading of 0.5 wt.% was incorporated (Puangpetch, *et al.*, 2009).

e. The final mixture was further aged at room temperature for 2 h to acquire homogeneous solution.

f. Then, the sol-containing solution was placed into an oven at 80°C for 2 d in order to obtain complete gel formation.

g. The gel was dried at 80°C for 2 d to eliminate the solvents, which were mainly EtOH and distilled water used in the preparation of the surfactant-alkaline earth nitrate solution, and to obtain zero gel (dried gel).

h. The dried gel was finally calcined at various calcination temperatures (450-700°C) for 4 h to remove LAHC and consequently produce the desired perovskite titanate photocatalysts (MgTiO₃, CaTiO₃, and SrTiO₃).

The schematic of the synthesis of mesoporous-assembled perovskite titanate nanocrystal photocatalysts is shown in Figure 3.1.

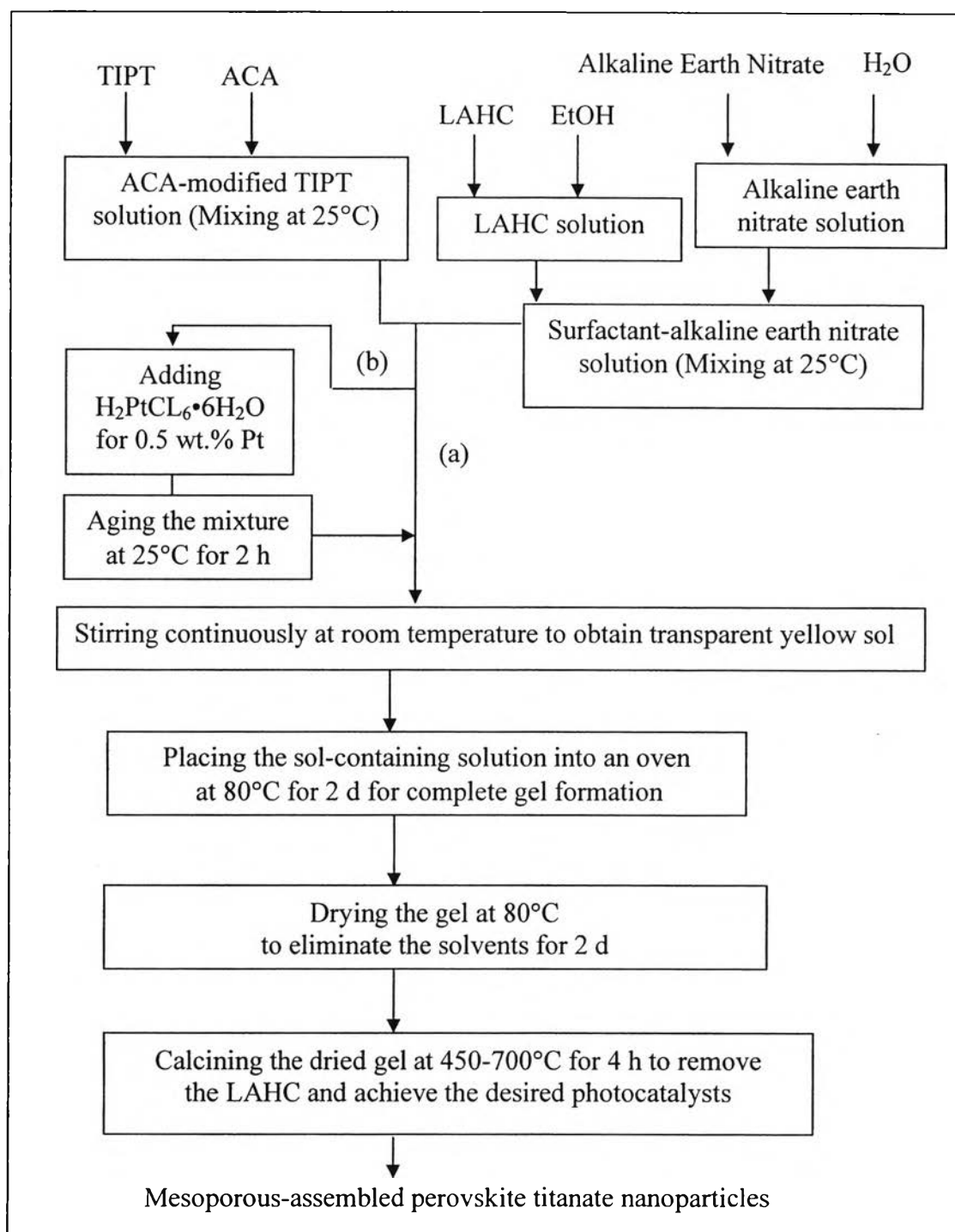


Figure 3.1 Preparation procedure for synthesized (a) mesoporous-assembled perovskite titanate photocatalysts and (b) 0.5 wt.% Pt-loaded mesoporous-assembled perovskite titanate photocatalyst.

3.4 Photocatalyst Characterizations

a. The thermal decomposition behavior of the dried gels and the suitable calcination temperature for removing LAHC template were investigated by using a thermogravimetric and differential thermal analyzer (TG-DTA, Perkin Elmer/Pyris Diamond). Each dried gel of 5-15 mg was heated from 50 to 800°C with a heating rate of 10°C/min in a static air atmosphere and with α -Al₂O₃ powder used as the reference.

b. The surface area and N₂ adsorption-desorption isotherms were measured by the Brunauer-Emmett-Teller (BET) surface area analyzer (Quantachrome/Autosorb1). Each 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. The Dollimore-Heal (DH) approach using desorption data was used for calculation of mean pore size and pore size distribution.

c. X-ray diffraction (XRD, Rigaku/Rint 2200 HV) was used to identify phases present in the samples by using a diffractometer equipped with a Ni filtered Cu K α radiation source ($\lambda = 1.542 \text{ \AA}$) of 40 kV and 40 mA. Each 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 30 to 80° in the continuous mode with the rate of 2°/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 by Scherrer equation.

d. UV-VIS spectrophotometer (Shimadzu UV-2550) was used to determine light absorption ability of the photocatalysts. The analysis was performed under scanning wavelength of 200-900 nm by using BaSO₄ as the reference.

e. The sample morphology was observed by a transmission electron microscope (TEM, JEOL 2000 CX). Each 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 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 TEM.

3.5 Photocatalytic H₂ Production System

Photocatalytic H₂ production reaction is performed in a closed gas system, as shown in Figure 3.2.

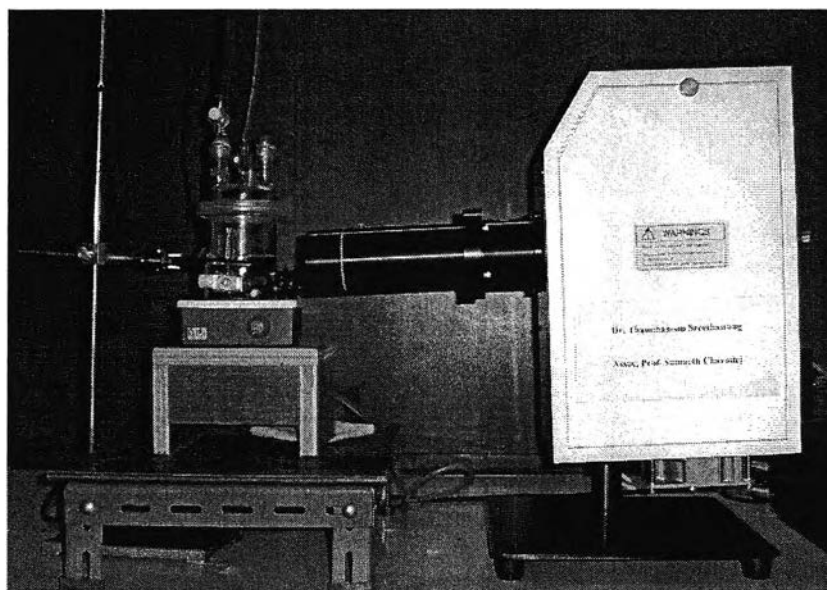


Figure 3.2 Setup of photocatalytic H₂ production system.

The photocatalytic H₂ production test was carried out according to the following procedure:

a. A specified amount of all prepared photocatalysts (0.2 g), namely synthesized mesoporous-assembled MgTiO₃, CaTiO₃, and SrTiO₃, 0.5 wt.% Pt-loaded mesoporous-assembled SrTiO₃, and commercial SrTiO₃, was suspended in 150 ml of aqueous diethanolamine (DEA) or triethanolamine (TEA) solution containing dissolved E.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.

c. The reaction was started by exposing the mixture with visible light irradiation from a 300 W Xe arc lamp (Type KXL-300/WACOM Electric, light intensity = 2.6 mW/cm²), emitting light with wavelength longer than 400 nm by using a UV cut-off filter (B-48S/ATG).

d. The gaseous H₂ produced was periodically collected from the reactor headspace by a gas-tight syringe and analyzed by a gas chromatograph (GC, Perkin Elmer/ARNEL, HayeSep D, Argon gas) 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