



CHAPTER III EXPERIMENTAL

3.1 Materials:

- 3.1.1 Tetraisopropyl orthotitanate (TIPT, $\text{Ti}(\text{OCH}(\text{CH}_3)_2)_4$)
- 3.1.2 Zirconium (IV) butoxide, 80 wt.% in 1-butanol (ZRB, $\text{Zr}(\text{O}(\text{CH}_2)_3\text{CH}_3)_4$)
- 3.1.3 Hydrogen hexachloroplatinate (IV) hexahydrate ($\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$, analytical grade)
- 3.1.4 Eosin Y (E.Y., $\text{C}_{20}\text{H}_6\text{Br}_4\text{Na}_2\text{O}_5$)
- 3.1.5 Laurylamine hydrochloride (LAHC, $\text{CH}_3(\text{CH}_2)_{11}\text{NH}_2 \cdot \text{HCl}$)
- 3.1.6 Acetylacetone (ACA, $\text{CH}_3\text{COCH}_2\text{COCH}_3$)
- 3.1.7 Diethanolamine (DEA, $(\text{HOCH}_2\text{CH}_2)_2\text{NH}$)
- 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:

- 3.2.1 Thermogravimetric/derivative thermogravimetric analyzer (TG-DTG, Perkin Elmer/Pyris Diamond)
- 3.2.2 X-ray diffractometer (XRD, Rigaku/Rint2200 HV)
- 3.2.3 Surface area analyzer (SAA, Quantachrome/Autosorb 1)
- 3.2.4 Scanning electron microscope (SEM, JEOL 5200-2AE) equipped with energy dispersive X-ray (EDX) analyzer
- 3.2.5 Transmission electron microscope (TEM, JEOL 2000 CX) equipped with energy dispersive X-ray (EDX) analyzer
- 3.2.6 Temperature-programmed reduction (TPR) apparatus
- 3.2.7 H_2 chemisorption apparatus

- 3.2.8 Gas chromatograph (GC, Perkin Elmer/ARNEL)
- 3.2.9 UV-visible spectrophotometer (Shimadzu UV-2550)
- 3.2.10 Visible light source (300-W Xenon arc lamp, KXL-300/WACOM Electric)
- 3.2.11 UV light source (11-W low-pressure mercury lamp, Philips)
- 3.2.12 Oven (CARBOLITE/CWE 1100)
- 3.2.13 pH meter (HANAA/pH 211)
- 3.2.14 Magnetic stirrer
- 3.2.15 Centrifuge machine (HERMLE Z383)
- 3.2.16 UV cut-off filter (B-48S/ATG)

3.3 Methodology

The mesoporous-assembled $\text{TiO}_2\text{-ZrO}_2$ nanocrystal photocatalysts were synthesized by a sol-gel process with the aid of structure-directing surfactant according to the following procedure:

- a. The TIPT and ZRB was firstly mixed together with various Ti and Zr concentrations (various x values in $x\text{TiO}_2\text{-(1-x)ZrO}_2$ ranging from 0 to 1).
- b. A specified amount of analytical grade ACA was introduced into the TIPT/ZRB mixture with the TIPT/ZRB-to-ACA molar ratio equal to unity.
- c. The mixed solution was gently shaken until homogeneous mixing. Afterwards, a 0.1 M LAHC aqueous solution with pH of 4.2 was added to the ACA-modified mixed TIPT and ZRB solution, in which the molar ratio of mixed TIPT and ZRB to LAHC was tailored to a value of 4.
- d. The mixture was kept continuously stirring at 40°C for 8 h to obtain transparent sol.
- (e. and f. are the additional steps for the preparation of Pt-loaded mesoporous-assembled $\text{TiO}_2\text{-ZrO}_2$ by a single-step sol-gel (SSSG) method.)
- e. To the aged $\text{TiO}_2\text{-ZrO}_2$ sol solution, a necessary amount of hydrogen hexachloroplatinate (IV) hexahydrate was incorporated.

f. The final mixture was further aged at 40°C for 1 h to acquire homogeneous solution.

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

h. 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 LACH aqueous solution.

i. The dried gel was finally calcined at various calcination temperatures (500-900°C) to remove the LAHC and consequently produce the desired TiO₂-ZrO₂ photocatalysts.

(j. - m. are the additional steps for the preparation of Pt-loaded mesoporous-assembled TiO₂-ZrO₂ by a photochemical deposition (PCD) method.)

j. A TiO₂-ZrO₂ mixed oxide photocatalyst, which was initially prepared by the sol-gel method, was first dispersed in distilled water and ultrasonicated for 15 min.

k. Then, a desired amount of hydrogen hexachloroplatinate (IV) hexahydrate, methanol, and distilled water were added to obtain 50 vol.% aqueous methanol solution.

l. The mixture was magnetically stirred and irradiated with a set of 11 W low-pressure Hg lamps.

m. After the irradiation, the Pt-deposited photocatalyst powders were recovered by filtration, washed with hot distilled water, and dried at 80°C.

The flow chart for the synthesis of mesoporous-assembled $\text{TiO}_2\text{-ZrO}_2$ nanocrystal photocatalysts without and with Pt loading is shown in Figure 3.1:

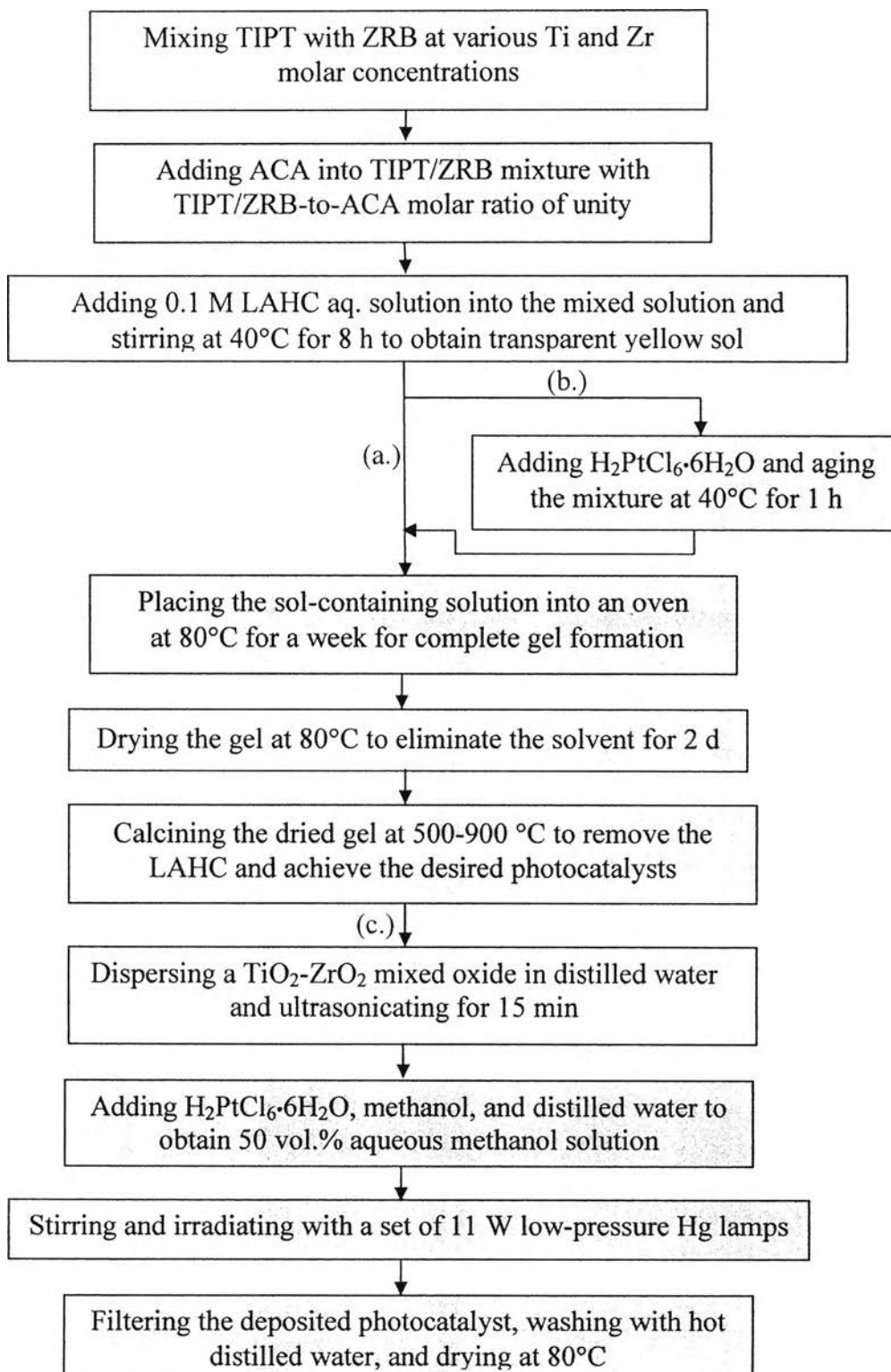


Figure 3.1 Synthesis procedure for mesoporous-assembled $\text{TiO}_2\text{-ZrO}_2$ photocatalysts: (a) $\text{TiO}_2\text{-ZrO}_2$, and Pt-loaded $\text{TiO}_2\text{-ZrO}_2$ by (b) SSSG and (c) PCD.

3.4 Photocatalyst Characterizations

a. The simultaneous thermogravimetric and derivative thermogravimetric analyzer (TG-DTG) was used to study the thermal decomposition behavior of the as-synthesized dried TiO₂-ZrO₂ gels and obtain a suitable calcination temperature for removing the LAHC surfactant. 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 the BET surface area analyzer. The photocatalyst sample was firstly 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, and the quantity of gas adsorbed onto or desorbed from their solid surface at some equilibrium vapor pressure was measured 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 the X-ray diffractometer equipped with a Ni filter and a CuK α radiation source ($\lambda = 1.542 \text{ \AA}$) operating at 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 will be scanned in the 2θ range of 20 to 80° 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 UV-visible spectrophotometer was used to identify absorption ability of the photocatalysts. The analysis was operated under scanning wavelengths of 200-900 nm using BaSO₄ as the reference.

e. The sample morphology was observed by the scanning electron microscope (SEM) and a transmission electron microscope (TEM). For the SEM analysis, the sample was coated with Au before measurement for improving conductivity of sample. For TEM analysis, 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. 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 can be easily scattered by air molecules, and the TEM columns must be kept under high vacuum. Additionally, the electromagnetic lenses were used for focusing the electron beam.

f. The temperature-programmed reduction (TPR) apparatus was employed to investigate the reducibility of samples. Temperature-programmed reduction was performed on the fresh photocatalysts. For each run, the sample was weighed for 50 mg. TPR runs were conducted using a heating rate of 10°C/min in a flow of 5% H₂/Ar (30 ml/min) up to 900°C. The ice trap was used to eliminate water during the operation.

g. H₂ chemisorption was used to determine the Pt dispersion on the photocatalyst surface. It was performed in a conventionally made-up system connected to a thermal conductivity detector (TCD) using 50 mg of each photocatalyst sample at room temperature with 20-μl pulses of the purified H₂. The result was detected with the TCD connected online to a software to determine the irreversibly bound chemisorbed H₂, which should correspond to H₂ adsorbed on the Pt surface. To calculate the Pt dispersion, it was supposed that the adsorption stoichiometry is one H atom for one surface Pt atom.

3.5 Photocatalytic H₂ Production System

The photocatalytic H₂ production reaction was performed in a closed gas system, as shown in Figure 3.2.

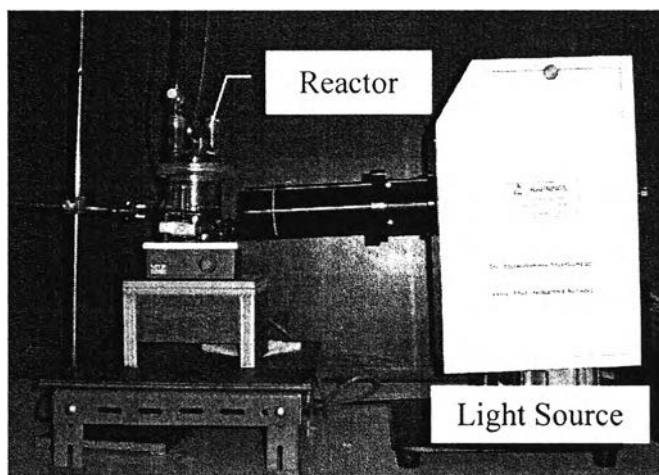


Figure 3.2 Setup of photocatalytic H₂ production system.

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

- a. A specified amount of all synthesized photocatalysts (0.2 g) 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 30 min in dark environment to establish adsorption equilibrium.
- c. The reaction was started by exposing the mixture with visible light irradiation from the 300 W Xe arc lamp emitting light with wavelength longer than 400 nm using the UV cut-off filter.
- d. The gaseous H₂ produced was periodically collected by a gas-tight syringe and analyzed by the 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