CHAPTER III

EXPERIMENTAL

3.1 Materials

Materials and reagents used in this research were as follows:

1. Tetraisopropyl orthotitanate (TIPT, $Ti(OCH(CH_3)_2)_4$) (analytical grade, Merck)

2. Zirconium (IV) butoxide, 80 wt.% solution in 1-butanol (ZRB, $Zr(O(CH_2)_3CH_3)_4$) (analytical grade, Sigma Aldrich)

3. Acetylacetone (ACA, $CH_3COCH_2COCH_3$) (analytical grade, Carlo Erba Reagents)

4. Laurylamine hydrochloride (LAHC, $CH_3(CH_2)_{11}NH_2 \cdot HCl$) (analytical grade, Merck)

5. Anhydrous ethyl alcohol (EtOH) (analytical grade, Carlo Erba Reagents)

6. Strontium nitrate ($Sr(NO_3)_2$) (analytical grade, Merck)

7. Hydrochloric acid (HCl) (analytical grade, Lab Scan)

8. Acid Black 1 (AB, $C_{22}H_{14}N_6Na_2O_9S_2$) (analytical grade, Nacalai Tesque)

9. Hydrogen hexachloroplatinate (IV) hexahydrate ($H_2PtCl_6 \cdot 6H_2O$) (analytical grade, Sigma Aldrich)

10. 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 (Quantachrome/Autosorb 1)

3. Scanning electron microscope (SEM, JEOL 5200-2AE) with energy dispersive X-ray (EDX) analyzer

4. Transmission electron microscope (TEM, JEOL 2000 CX) with energy dispersive X-ray (EDX) analyzer

5. UV-visible spectrophotometer (Shimadzu UV-2550)

6. Temperature-programmed reduction (TPR) analyzer

7. H_2 chemisorption apparatus

8. Thermogravimetric-differential thermal analyzer (TG-DTA, Shimadzu DTG-50)

9. Oven (CARBOLITE/CWE 1100)

10. pH meter (HANAA/pH 211)

11. Magnetic stirrer

12. Centrifuge machine (HERMLE Z383)

13. UV light source (11-Watt low-pressure mercury lamp, Philips)

3.3 Methodology

3.3.1 Mesoporous-Assembled $SrTi_xZr_{1-x}O_3$ Nanocrystal Photocatalyst Synthesis by a Sol-Gel Process with the Aid of Structure-Directing Surfactant and Pt-Loaded Mesoporous-Assembled $SrTi_xZr_{1-x}O_3$ Nanocrystal Photocatalyst Synthesis by a Single-Step Sol-Gel (SSSG) Method

The mesoporous-assembled $SrTi_xZr_{1-x}O_3$ and Pt-loaded mesoporous-assembled $SrTi_xZr_{1-x}O_3$ photocatalysts were synthesized according to the following procedure:

a. The TIPT and ZRB were firstly mixed together with various molar concentrations (various x values in $SrTi_xZr_{1-x}O_3$ ranging from 0 to 1). The mixed metal precursors were then immediately modified by adding ACA with the (TIPT+ZRB)-to-ACA molar ratio of unity at room temperature to obtain the TIPT-ZRB-ACA solution.

b. A surfactant solution of LAHC was prepared by dissolving it in EtOH. Afterwards, an appropriate amount of $Sr(NO_3)_2$ dissolved in distilled water was added to the surfactant solution with continuously stirring at room temperature to obtain a clear solution.

c. The LAHC-Sr(NO₃)₂ solution was then slowly dropped into the yellow mixture of the TIPT-ZRB-ACA solution while stirring continuously at room temperature to obtain transparent yellow sol.

(d. and e. were the additional steps for the preparation of Pt-loaded mesoporous-assembled SrTi$_x$Zr$_{1-x}$O$_3$ by a single-step sol-gel (SSSG) method)

d. A necessary amount of hydrogen hexachloroplatinate (IV) hexahydrate for desired Pt loadings of 0.5-1.5 wt.% was incorporated to the previously obtained yellow sol solution (Sreethawong and Yoshikawa, 2005).

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 4 d in order to obtain complete gel formation.

g. The gel was dried at 80°C for 4 d to eliminate the solvents, which were mainly EtOH and distilled water used in the preparation of the LAHC-Sr(NO₃)₂ solution, and to obtain zero gel (dried gel).

h. The dried gel was finally calcined at various calcination temperatures (600-800°C) to remove the LAHC surfactant and consequently produce the desired SrTi$_x$Zr$_{1-x}$O$_3$ photocatalysts.

The schematic of the synthesis of mesoporous-assembled SrTi$_x$Zr$_{1-x}$O$_3$ nanocrystal photocatalysts is shown in Figure 3.1.
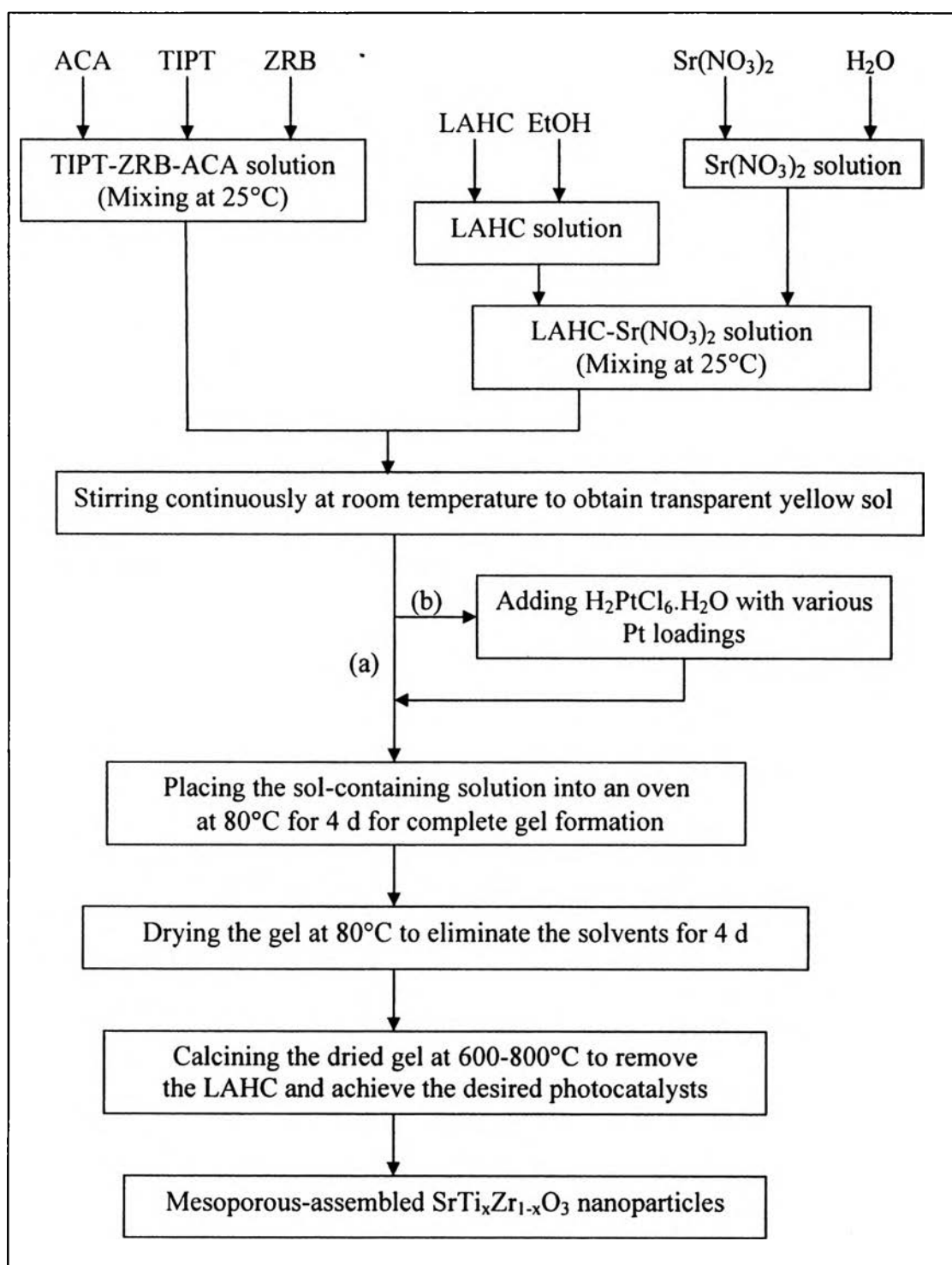
Figure 3.1 Synthesis procedure for mesoporous-assembled $SrTi_xZr_{1-x}O_3$ photocatalysts: (a) mesoporous-assembled $SrTi_xZr_{1-x}O_3$ and (b) Pt-loaded mesoporous-assembled $SrTi_xZr_{1-x}O_3$ by SSSG method.

3.3.2 Photocatalyst Characterizations

a. The thermal decomposition behavior of the zero gels and the suitable thermal treating conditions were investigated by using the thermo gravimetric-differential thermal analyzer with a heating rate of $10°C$ min^{-1} in a static air atmosphere and with $\alpha-Al_2O_3$ powder as the reference.

b. The surface area of the investigated photocatalysts 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, N_2 was purged to absorb on surface, and the quantity of gas adsorbed onto or desorbed from their solid surface at some equilibrium vapor pressures 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 was 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 $CuK\alpha$ radiation source (λ = 1.542 Å) 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 was scanned in the 2θ range of 10 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 of 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 light absorption ability of the photocatalysts. The analysis was operated 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.

e. The sample morphology was observed by the transmission electron microscope (TEM) and the scanning electron microscope (SEM). For the 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 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. For SEM analysis, the sample was coated with Pt before measurement for improving conductivity of sample.

f. Temperature-programmed reduction (TPR) was applied to study the reducibility of the loaded Pt species, as well as the interaction between the support and loaded Pt. A studied photocatalyst was packed into a quartz reactor connected to a mass spectrometer for on-line gas analysis. Prior to the analysis, the photocatalyst sample was treated under an air flow at 150°C for 1 h to remove water and other contaminants from its surface. Then, the photocatalyst sample was heated from 30 to 800°C under H_2/Ar flow (30 ml/min) with a heating rate of 10°C/min. The TPR profiles were obtained from peaks of H_2 consumption at the reduction temperature of the photocatalyst sample.

g. H_2 chemisorption was employed to characterize the Pt dispersion on the photocatalyst surface. 50 mg of each of the photocatalyst samples was packed in a quartz reactor connected to a thermal conductivity detector (TCD). The H_2 uptake and degree of Pt dispersion were determined by using a pulse technique at room temperature with the 20 μl purified H_2 pulses. The result was detected with the TCD connected online to a software to determine the Pt dispersion from the amount of H atoms adsorbed on the Pt atoms. For the calculation of Pt dispersion, it was assumed that the atomic ratio of H/Pt is equal to 1.

3.3.3 Photocatalytic Activity Testing

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

a. A specified amount of all synthesized mesoporous-assembled SrTi$_x$Zr$_{1-x}$O$_3$ nanocrystal photocatalysts without and with Pt loading was suspended in an aqueous solution of AB dye by using magnetic stirrer within a reactor made of Pyrex glass.

b. Prior to the photocatalytic activity test, 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 with UV light irradiation from 11 W mercury lamps.

d. The suspension was withdrawn every 30 min and then centrifuged by a centrifugal machine to separate the photocatalyst powder out.

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 according to the following equation:

$$\ln\left(\frac{C_0}{C}\right) = kt$$

where C_0 is initial concentration of AB dye, C is concentration of AB dye at any irradiation time t, k is pseudu-first order reaction rate constant, and t is irradiation time.

The photocatalytic degradation of AB dye was performed in an open system with UV light irradiation, as shown in Figure 3.2.
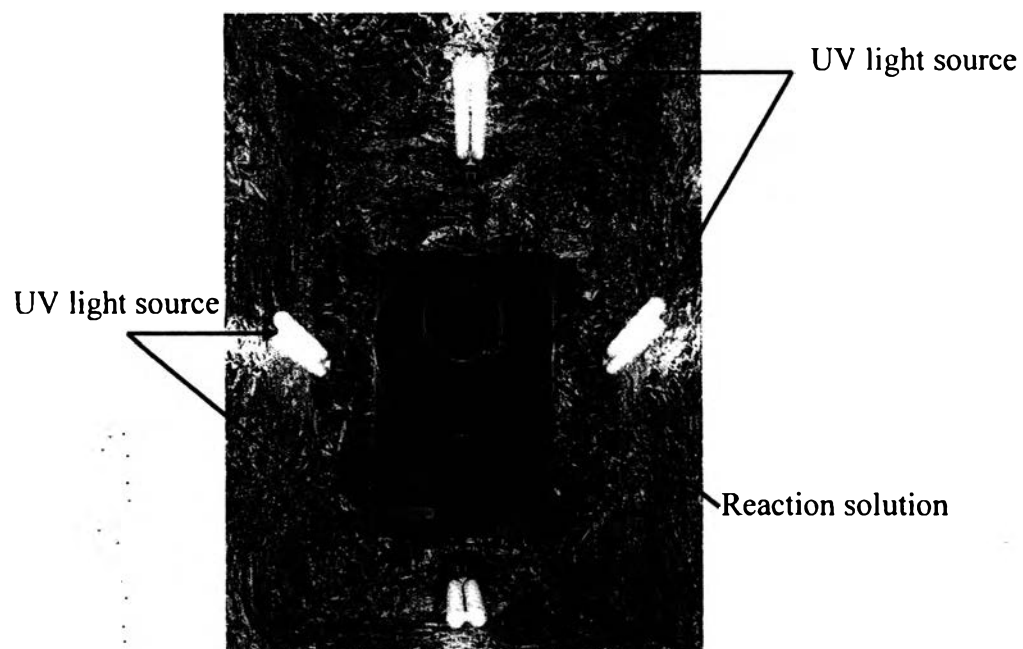
Figure 3.2 UV light irradiation system for photocatalytic activity test.