



CHAPTER III EXPERIMENTAL

3.1 Materials

- 3.1.1 Tetraisopropyl orthotitanate (TIPT, $\text{Ti}(\text{OCH}(\text{CH}_3)_2)_4$)
- 3.1.2 Indium nitrate trihydrate (INT, $\text{In}(\text{NO}_3)_3 \cdot 3\text{H}_2\text{O}$)
- 3.1.3 Acetylacetone (ACA, $\text{CH}_3\text{COCH}_2\text{COCH}_3$)
- 3.1.4 Laurylamine hydrochloride (LAHC, $\text{CH}_3(\text{CH}_2)_{11}\text{NH}_2 \cdot \text{HCl}$)
- 3.1.5 Silver nitrate (AgNO_3)
- 3.1.6 Congo Red (CR, $\text{C}_{32}\text{H}_{22}\text{N}_6\text{Na}_2\text{O}_6\text{S}_2$)
- 3.1.7 Hydrochloric acid (HCl)
- 3.1.8 Distilled water

3.2 Equipment

- 3.2.1 X-ray diffractometer (XRD, Bruker/AXS, D8 Advance)
- 3.2.2 Surface area analyzer (SAA, Quantachrom/Autosorb 1)
- 3.2.3 Scanning electron microscope (SEM, Hitachi/S-4800)
- 3.2.4 Transmission electron microscope (TEM, JEOL/JEM-2100)
- 3.2.5 UV-visible spectrophotometer (Shimadzu/UV-2550)
- 3.2.6 UV-visible spectrophotometer (Shimadzu/UV-1800)
- 3.2.7 H_2 chemisorption apparatus
- 3.2.8 Thermogravimetric-differential thermal analyzer (TG-DTG, Perkin Elmer/Pyris Diamond)
- 3.2.9 Oven (CARBOLITE/CWE 1100)
- 3.2.10 Magnetic stirrer
- 3.2.11 Centrifugal machine (HERMLE/Z383)
- 3.2.12 UV light source (11-Watt low-pressure mercury lamp, Philips)

3.3 Methodology

3.3.1 Synthesis of Mesoporous-Assembled In₂O₃-TiO₂ Mixed Oxide Nanocrystal Photocatalysts by a Sol-Gel Process with the Aid of Structure-Directing Surfactant

a. The TIPT and ACA were firstly mixed together and gently shaken until homogeneous mixing at room temperature to obtain the TIPT/ACA solution.

b. The LAHC/INT solution was separately prepared by adding an appropriate amount of INT to a 0.1 M LAHC aqueous solution with continuously stirring at room temperature.

c. The LAHC/INT solution was then slowly added to the ACA-modified TIPT solution while stirring continuously to obtain various In₂O₃ and TiO₂ molar concentrations (various x values in xIn₂O₃-(1-x)TiO₂), where the molar ratios of (TIPT+INT)-to-LAHC and (TIPT+INT)-to-ACA were controlled at 4:1 and 1:1, respectively.

d. The mixture was kept continuously stirring at 40 °C for 8 h to obtain transparent yellow sol.

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

f. The gel was dried at 80 °C to eliminate the solvent for 2 d, which was mainly distilled water used in the preparation of the LAHC/INT solution, to obtain zero gel (dried gel).

g. The dried gel was finally calcined at various temperatures (500–800 °C) for 4 h to remove the LAHC surfactant and consequently produce the desired In₂O₃-TiO₂ mixed oxide photocatalysts.

(h. - k. were the additional steps for the preparation of Ag-loaded mesoporous-assembled In₂O₃-TiO₂ mixed oxide photocatalysts by a photochemical deposition (PCD) method.)

h. An In₂O₃-TiO₂ mixed oxide photocatalyst, which was initially prepared by the sol-gel method, was firstly dispersed in the 50 vol.% aqueous methanol solution mixed with distilled water and ultrasonicated for 15 min.

- i. Then, the desired amount of AgNO_3 was added to the solution.
- j. The mixture was magnetically stirred and irradiated by a set of 11 W low-pressure Hg lamps (total light intensity of 44 W) for 3 h.
- k. After the irradiation, the Ag-deposited photocatalyst powders were recovered by filtration, repeatedly washed with hot distilled water, and dried at 80 °C.

The schematic of the synthesis of mesoporous-assembled $\text{In}_2\text{O}_3\text{-TiO}_2$ mixed oxide nanocrystal photocatalysts without and with Ag loading by the PCD method is shown in Figure 3.1:

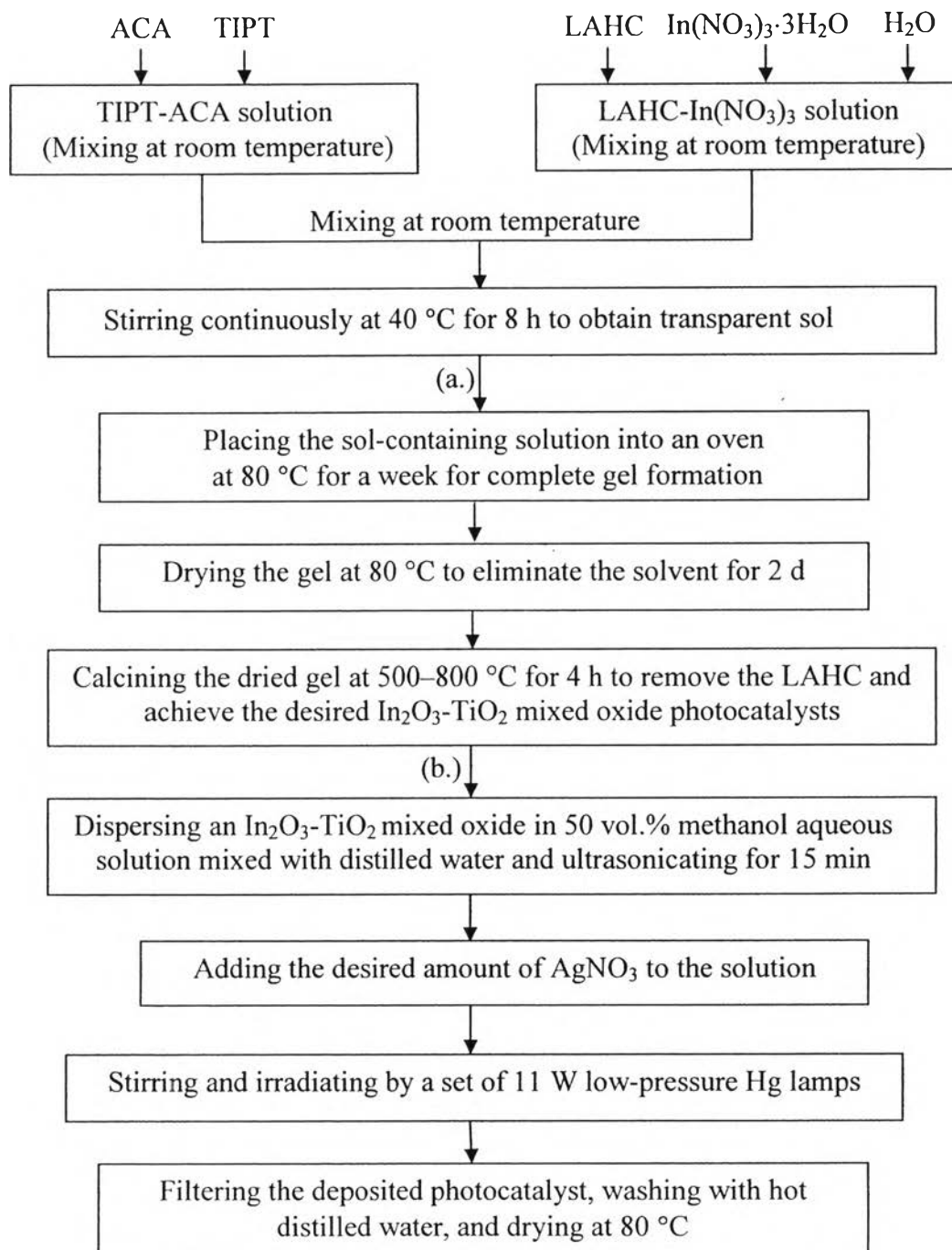


Figure 3.1 Synthesis procedure for mesoporous-assembled $\text{In}_2\text{O}_3\text{-TiO}_2$ mixed oxide photocatalysts: (a) $\text{In}_2\text{O}_3\text{-TiO}_2$ and (b) Ag-loaded $\text{In}_2\text{O}_3\text{-TiO}_2$ by PCD method.

3.3.2 Photocatalyst Characterizations

a. The thermal decomposition behavior of the zero gels and their suitable calcination temperatures were investigated by using a TG-DTG apparatus (Shimadzu, Perkin Elmer/Pyris Diamond) with a heating rate of $10\text{ }^{\circ}\text{C min}^{-1}$ in a static air atmosphere and with $\alpha\text{-Al}_2\text{O}_3$ powder as the reference.

b. The surface area was measured by BET surface area analyzer. The photocatalyst sample was firstly outgassed to remove the humidity and volatile adsorbents adsorbed on surface under vacuum at $150\text{ }^{\circ}\text{C}$ for 4 h prior to the analysis. Then, N_2 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. 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 specific surface area.

c. X-ray diffraction (XRD) was used to identify phases present in the samples by using a X-ray diffractometer (XRD, Bruker/AXS, D8 Advance) diffractometer equipped with a Ni filtered $\text{CuK}\alpha$ radiation source ($\lambda = 1.542\text{ \AA}$) of 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 15° to 70° in the continuous mode with the rate of $1^{\circ}/\text{min}$. The XRD results show peak parameters, including the centroid 2θ , the full width at half the maximum of intensity (β), d-value, and intensity. The mean crystallite size was calculated using 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 TEM analysis, 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. 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 lenes. 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 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 Au before measurement for improving conductivity of sample.

e. UV-visible spectrophotometer was used to identify light absorption ability of the photocatalysts. The analysis was operated under scanning wavelength of 200–900 nm. And, it was also used to measure the quantity of dye by using absorbance mode and to follow the degradation of dye due to the cleavage of N=N bond.

f. H₂ chemisorption was used to determine the Ag 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- μ l 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 Ag surface. To calculate the Ag dispersion, it was supposed that the atomic ratio of H/Ag is equal to 1.

3.3.3 Photocatalytic Experiment

Photocatalytic degradation of CR dye was performed in an open system with UV light irradiation, as shown in Figure 3.2.

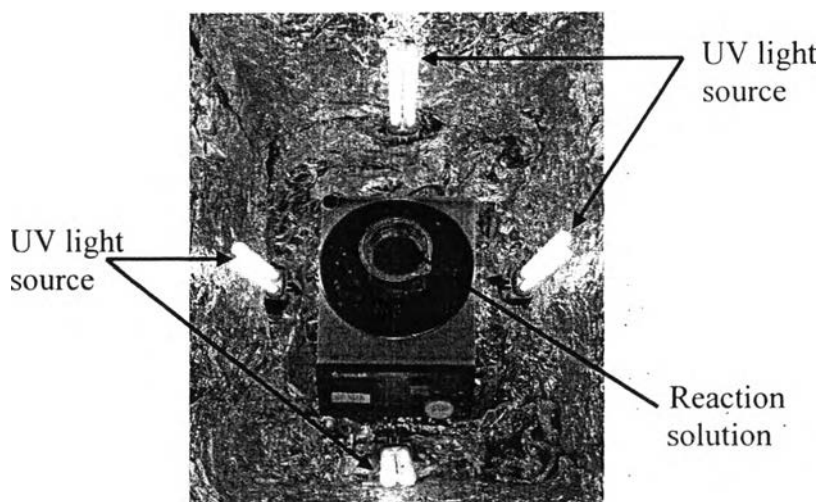


Figure 3.2 UV light irradiation system for photocatalytic activity test.

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

- a. A specified amount of each synthesized photocatalyst was suspended in the aqueous solution of CR dye under various reaction conditions 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 a set of 11 W mercury lamps.
- d. The suspension was withdrawn every 30 min and then centrifuged by a centrifugal machine to separate the photocatalyst powders out.
- e. The liquid samples were analyzed for the concentration of CR dye by the UV-visible spectrophotometer to follow its degradation. The pseudo-first order reaction kinetics, which was calculated by using Eq. (3.1), was used to obtain apparent reaction rate constant from the concentration data:

$$\ln \frac{C_0}{C} = kt \quad (3.1)$$

where C_0 is initial concentration of CR dye, C is concentration of CR dye at any time of t , and k is reaction rate constant.