CHAPTER III
EXPERIMENTAL

3.1 Materials and Equipment

3.1.1 Chemicals

- Tetraisopropyl orthotitanate (TIPT, $Ti(OCH(CH_3)_2)_4$)
- Laurylamine hydrochloride (LAHC, $CH_3(CH_2)_{11}NH_2 \cdot HCl$)
- Acetylacetone (ACA, $CH_3COCH_2COCH_3$)
- Strontium nitrate ($Sr(NO_3)_2$)
- Zinc nitrate (ZN, $Zn(NO_3)_2 \cdot 6H_2O$)
- Copper nitrate ($Cu(NO_3)_2$)
- Silver nitrate ($AgNO_3$)
- Phenol (C_6H_6O)
- Hydrochloric acid (HCl)
- Ethanol (EtOH)
- Distilled water
- 4-aminoantipyrine ($C_{11}H_{13}N_3O$)
- Potassium ferricyanide ($K_3Fe(CN)_6$)

3.1.2 Equipment

- X-ray diffraction (XRD, Rigaku/Rint2200 HV)
- Surface area analyzer (SAA, Quantachrome/Autosorb 1)
- Thermogravimetric-differential thermal analyzer (TG-DTA,
- Perkin Elmer/Pyris Diamond)
- Scanning electron microscope (SEM, JOEL JSM-5200)
- equipped with energy dispersive X-ray (EDX) analyzer
- Transmission electron microscope (TEM, JEOL 2000 CX)
- equipped with energy dispersive X-ray (EDX) analyzer
- H_2 chemisorption apparatus
- UV-visible spectrophotometer (Shimadzu UV-2550)

- UV light source (11-Watt low-pressure mercury lamp. Philips)
- Oven (CARBOLITE/CWE 1100)
- Microcentrifuge (Spectrofuge 24D)
- Magnetic stirrer

3.2 Experimental Procedures

3.2.1 <u>Mesoporous-Assembled SrTi$_x$Zn$_{1-x}$O$_3$ Nanocrystal Photocatalyst Synthesis by a Sol-Gel Process with the Aid of a Structure-Directing Surfactant</u>

The mesoporous-assembled SrTi$_x$Zn$_{1-x}$O$_3$ nanocrystal photocatalysts will be synthesized according to the following procedure:

a. The TIPT and ACA will be firstly mixed together and gently shaken until homogeneous mixing at room temperature to obtain the TIPT-ACA solution A. Solution A must be prepare in various molar ratio of Ti-to-Zn to vary x value in the SrTi$_x$Zn$_{1-x}$O$_3$ solution (The value of x in SrTi$_x$Zn$_{1-x}$O$_3$ will be vary from 0 to 1).

b. Dissolve Sr(NO$_3$)$_2$ and ZN with distilled water. Afterward an appropriate amount of EtOH will be added into the solution (the ratio of EtOH:H$_2$O must be 3:2). When EtOH and Sr(NO$_3$)$_2$-ZN solution is mix together the surfactant solution of LAHC will be added to the solution. This final solution must continuously stirring at room temperature to obtain clear solution.(this solution is solution B)

c. The solution B will then be slowly added to the TIPT-ACA solution while stirring continuously, where the molar ratios of (TIPT/ZN)-to-LAHC and (TIPT/ZN)-to-ACA are 4:1 and 1:1, respectively.

d. The mixture will be kept continuously stirring at 40 °C for 4 h to obtain transparent sol.

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

f. The gel will be dried at 80 °C to eliminate the solvent for 2 d, which is mainly distilled water used in the preparation of the LAHC-ZN solution, to obtain zero gel (dried gel).

g. The dried gel will be finally calcined at various calcination temperatures for 4 h to remove the LAHC surfactant and consequently produce the desired $SrTi_xZn_{1-x}O_3$ photocatalysts.

(h.-k. are the additional steps for Ag, Cu, and Pt loading on the mesoporous-assembled $SrTi_xZn_{1-x}O_3$ by a photochemical deposition (PCD)).

h. A $SrTi_xZn_{1-x}O_3$ photocatalyst, which is initially prepared by the sol-gel method, will be firstly dispersed in distilled water and ultrasonicated for 15 min.

i. Then, a desired amount of $AgNO_3$, $Cu(NO_3)_2$, and $PtCl_6$ methanol, and distilled water will be added to obtain 50 vol.% aqueous methanol solution.

j. The mixture will be magnetically stirred and irradiated with a set of 11 W low-pressure Hg lamps.

k. After the irradiation, the metal-deposited photocatalyst powders will be recovered by filtration, washed with hot distilled water, and dried at 80 °C.

The schematic of the synthesis of mesoporous-assembled $SrTi_xZn_{1-x}O_3$ nanocrystal photocatalysts without and with metal loading by the PCD method is shown in Figure 3.1.

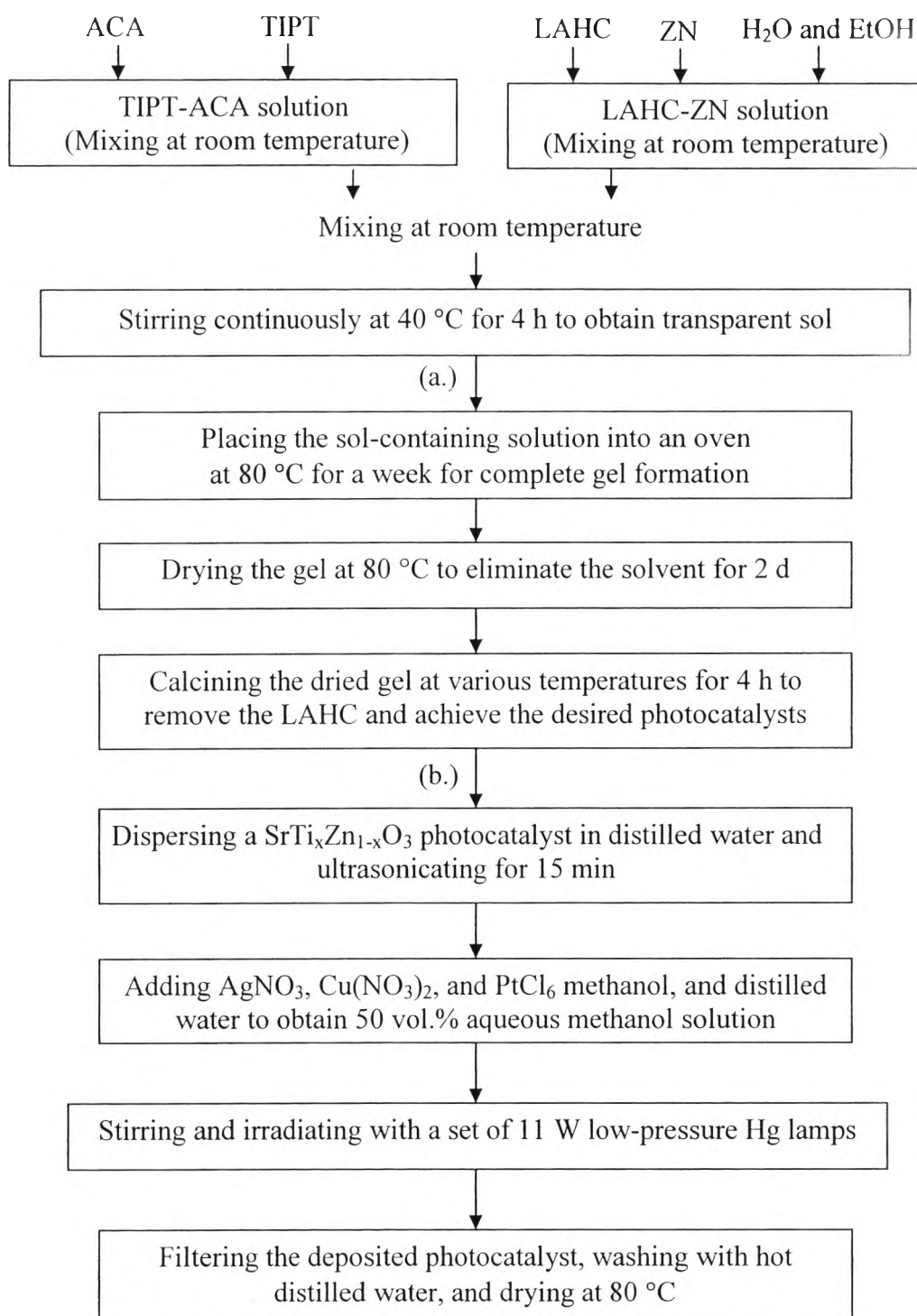**Figure 3.1** Synthesis procedure for mesoporous-assembled $SrTi_xZn_{1-x}O_3$ photocatalysts: (a) without metal loading and (b) with metal loading by PCD method.

3.3 Photocatalyst Characterizations

a. The thermal decomposition behavior of the zero gels and the suitable thermal treating conditions will be investigated by using a TG-DTA apparatus (Shimadzu, DTG-50) with a heating rate of 10 °C min^{-1} in a static air atmosphere and with α–Al_2O_3 powder as the reference.

b. The surface area will be meassured by BET surface area analyzer. The photocatalyst sample will be first 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 is purged to absorb 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 is maintained at a constant temperature of the sample cell until the equilibrium is established. This volume-pressure data will be used to calculate the BET surface area.

c. X-ray diffraction (XRD) will be used to identify phases present in the samples by using a Rigaku RINT 2000 diffractometer equipped with a Ni filtered CuKα radiation source (λ = 1.542 Å) of 40 kV and 30mV. A photocatalyst sample will be pressed into a hollow of glass holder and held in place by glass window. Then, it will be scanned in the 2θ range of 15 to 70° 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 will be calculated from the XRD data from X-ray line broadening.

d. The sample morphology will be observed by a transmission electron microscope (TEM) and a scanning electron microscope (SEM). For TEM, The photocatalyst samples will be ground into fine powder and ultrasonically dispersed in ethanol. A small droplet of the suspension will be deposited on a copper grid with polyvinyl desicate, and the solvent will be evaporated prior to loading the sample into the microscope. TEM

will be carried out in a JEOL 2000 CX operating at an accelerating voltage of 200 kV in bright field mode. A beam is passed through a series of lenses to form a magnified image of a sample that is inserted in the area of the objective lens. The image from selected area is 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 lens is used for focusing the electron beam. For SEM the sample will be coated with Pt before measurement for improving conductivity of sample.

e. UV-visible spectrophotometer will be used to identify light absorption ability of the photocatalysts. The analysis will be operated under scanning wavelength at 200-900 nm. And, it will also be used to measure the quantity of phenol by using absorbance mode and to follow degradation of phenol due to the cleavage of aromatic ring.

f. H_2 chemisorption will be used to determine the metal dispersion on the photocatalyst surface. It will be 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 H_2. The result will be detected with the TCD connected online to a software to determine the irreversibly bound chemisorbed H_2, which should correspond to H_2 adsorbed on the metal surface. To calculate the metal dispersion, it will be supposed that the adsorption stoichiometry is one H atom for one surface metal atom.

3.4 Photocatalytic Experiment

Photocatalytic degradation of phenol will be performed in an open system with UV light irradiation, as shown in Figure 3.2.
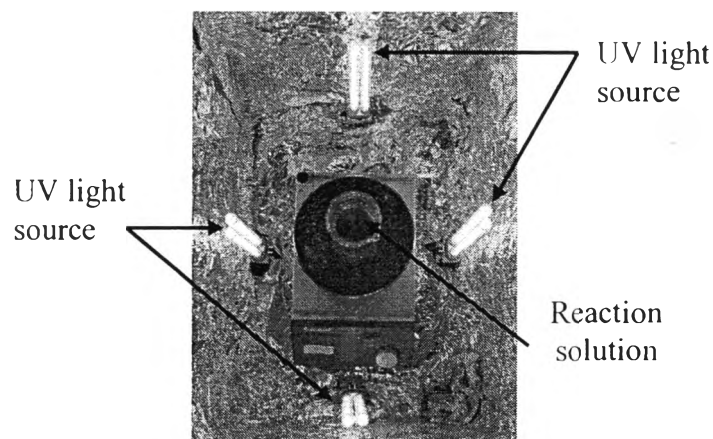

Figure 3.2 UV light irradiation system for photocatalytic activity test.

The photocatalytic degradation of phenol will be carried out according to the following procedure:

a. A specified amount of the synthesized $SrTi_xZn_{1-x}O_3$ photocatalyst will be suspended in the aqueous solution of phenol 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 will be left for 30 min in dark environment to establish the adsorption equilibrium.

c. The reaction will be started by exposing the mixture with UV light irradiation from 11 W mercury lamps.

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

e. The liquid samples will be analyzed for the concentration of phenol by UV-visible spectrophotometer and TOC analyser. The pseudo-first

order reaction kinetics will be used to obtain apparent reaction rate constant from the concentration data.