



## CHAPTER III EXPERIMENTAL

### 3.1 Materials and Equipment

#### 3.1.1 Chemicals

- Tetraisopropyl orthotitanate (TIPT,  $\text{Ti}(\text{OCH}(\text{CH}_3)_2)_4$ )
- Zirconium (IV) butoxide, 80 wt% in 1-butanol  
(ZRB,  $\text{Zr}(\text{O}(\text{CH}_2)_3\text{CH}_3)_4$ )
- Tetraethyl orthosilicate (TEOS,  $\text{C}_8\text{H}_{20}\text{O}_4\text{Si}$ )
- Strontium nitrate ( $\text{Sr}(\text{NO}_3)_2$ )
- Laurylamine hydrochloride (LAHC,  $\text{CH}_3(\text{CH}_2)_{11}\text{NH}_2 \cdot \text{HCl}$ )
- Acetylacetone (ACA,  $\text{CH}_3\text{COCH}_2\text{COCH}_3$ )
- Copper nitrate ( $\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$ )
- Methanol ( $\text{CH}_3\text{OH}$ )
- Ethanol ( $\text{C}_2\text{H}_5\text{OH}$ )
- Distilled water

#### 3.1.2 Equipment

- Thermogravimetric/derivative thermogravimetric analyzer  
(TG-DTG, Perkin Elmer/Pyris Diamond)
- X-ray diffractometer (XRD, Rigaku/Rint2200 HV)
- Surface area analyzer (SAA, Quantachrome/Autosorb 1)
- Scanning electron microscope (SEM, JEOL 5200-2AE) equipped  
with energy dispersive X-ray (EDX) analyzer
- Transmission electron microscope (TEM, JEOL 2000 CX)  
equipped with energy dispersive X-ray (EDX) analyzer
- Gas chromatograph (GC, Perkin Elmer/ARNEL)
- UV-visible spectrophotometer (Shimadzu UV-2550)
- $\text{H}_2$  chemisorption apparatus
- Oven (CARBOLITE/CWE 1100)

- pH meter (HANAA/pH 211)
- Magnetic stirrer
- Centrifuge machine (HERMLE Z383)
- UV light source (11-W low-pressure mercury lamp, Philips)

## 3.2 Experimental Procedures

### 3.2.1 Mesoporous-Assembled SrTi<sub>x</sub>Zr<sub>1-x</sub>O<sub>3</sub> and SrTi<sub>x</sub>Si<sub>1-x</sub>O<sub>3</sub> Nanocrystal Photocatalyst Synthesis by a Sol-Gel Process with the Aid of a Structure-Directing Surfactant

The mesoporous-assembled SrTi<sub>x</sub>Zr<sub>1-x</sub>O<sub>3</sub> and SrTi<sub>x</sub>Si<sub>1-x</sub>O<sub>3</sub> nanocrystal photocatalysts were synthesized according to the following procedure:

- a. The TIPT and ZRB or TIPT and TEOS were firstly mixed together with various Ti-to-Zr or Ti-to-Si molar ratios (various x values in SrTi<sub>x</sub>Zr<sub>1-x</sub>O<sub>3</sub> or SrTi<sub>x</sub>Si<sub>1-x</sub>O<sub>3</sub> ranging from 0.89 to 1).
- b. A specified amount of analytical grade ACA was introduced into the TIPT/ZRB or TIPT/TEOS mixture with the [TIPT/ZRB]-to-ACA or [TIPT/TEOS]-to-ACA molar ratio equal to unity.
- c. A surfactant solution of LAHC was prepared by dissolving it in EtOH. Afterwards, an appropriate amount of Sr(NO<sub>3</sub>)<sub>2</sub> dissolved in distilled water was added to the surfactant solution with continuously stirring at room temperature to obtain a clear solution.
- d. The mixed solution was then 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/ZRB or ACA-modified mixed TIPT/TEOS solution, in which the [TIPT/ZRB]-to-LAHC or [TIPT/TEOS]-to-LAHC molar ratio were tailored to a value of 4.
- e. The mixture was kept continuously stirring at 40 °C for 8 h to obtain transparent sol.
- f. Then, the sol-containing solution was placed into an oven at 80 °C for 4 d in order to obtain complete gel formation.

h. The dried gel was finally calcined at 700 °C of  $\text{SrTi}_x\text{Zr}_{1-x}\text{O}_3$  or calcined at 650 °C to 800 °C of  $\text{SrTi}_x\text{Si}_{1-x}\text{O}_3$  for 4 h to remove the LAHC and consequently produced the desired  $\text{SrTi}_x\text{Zr}_{1-x}\text{O}_3$  or  $\text{SrTi}_x\text{Si}_{1-x}\text{O}_3$  photocatalysts.

(i. - l. are the additional steps for the Cu loading on the mesoporous-assembled  $\text{SrTi}_x\text{Zr}_{1-x}\text{O}_3$  or  $\text{SrTi}_x\text{Si}_{1-x}\text{O}_3$  by a photochemical deposition (PCD) method.)

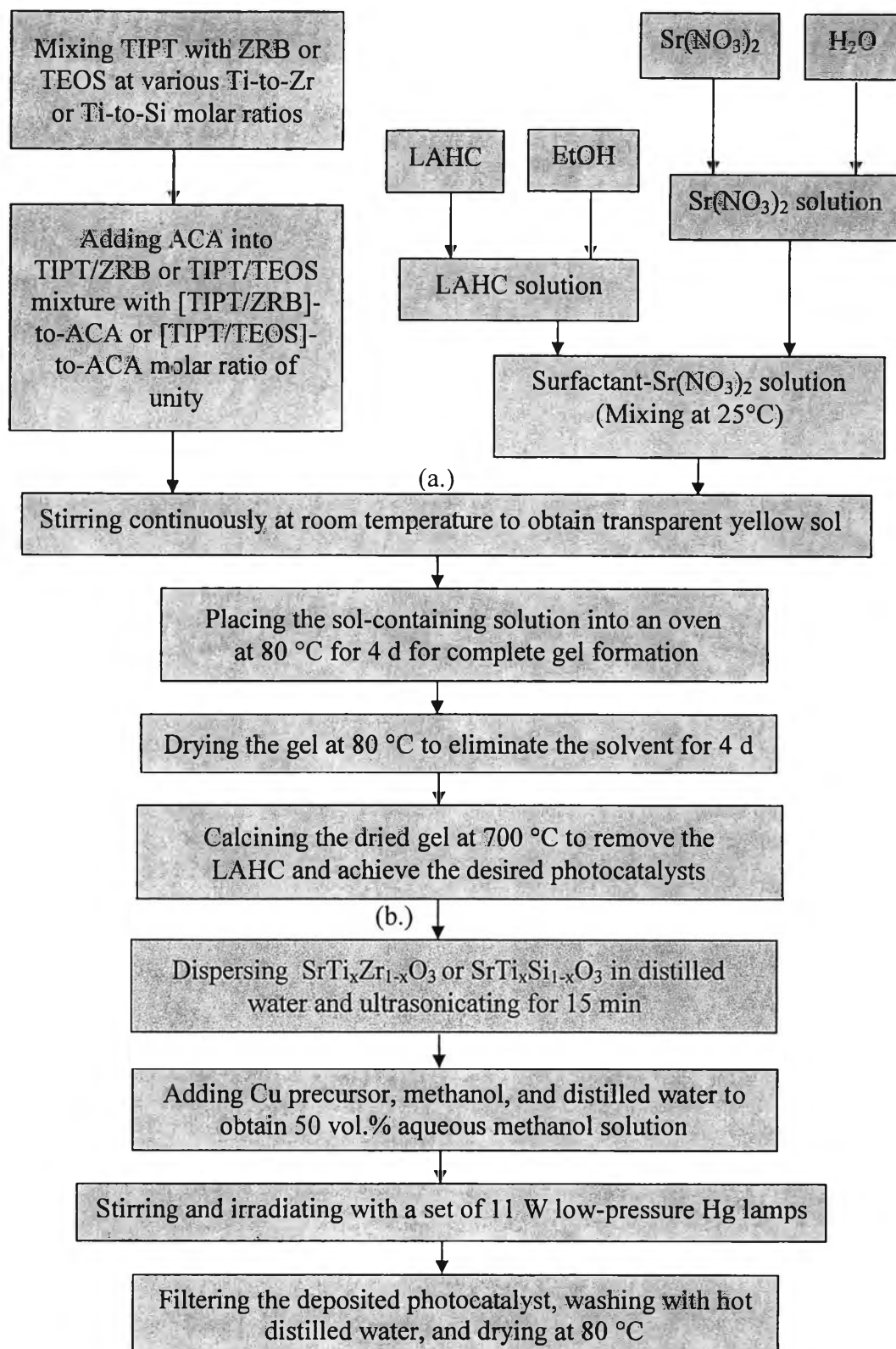
i. A  $\text{SrTi}_x\text{Zr}_{1-x}\text{O}_3$  or  $\text{SrTi}_x\text{Si}_{1-x}\text{O}_3$  photocatalyst, which was initially prepared by the sol-gel method, was first dispersed in distilled water and ultrasonicated for 15 min.

j. Then, a desired amount of copper nitrate, methanol, and distilled water were added to obtain 50 vol.% aqueous methanol solution.

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

l. After the irradiation, the Cu-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  $\text{SrTi}_x\text{Zr}_{1-x}\text{O}_3$  and  $\text{SrTi}_x\text{Si}_{1-x}\text{O}_3$  nanocrystal photocatalysts without and with Cu loading is shown in Figure 3.1:



**Figure 3.1** Synthesis procedure for mesoporous-assembled  $\text{SrTi}_x\text{Zr}_{1-x}\text{O}_3$  and  $\text{SrTi}_x\text{Si}_{1-x}\text{O}_3$  photocatalysts: (a) without and (b) with Cu loading by PCD method.

### 3.2.2 Photocatalyst Characterizations

a. Simultaneous thermogravimetry and differential thermal analysis (TG-DTA) was used to study the thermal decomposition behavior of the as-synthesized dried  $\text{SrTi}_x\text{Zr}_{1-x}\text{O}_3$  and  $\text{SrTi}_x\text{Si}_{1-x}\text{O}_3$  gels and obtained 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  $\alpha\text{-Al}_2\text{O}_3$  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 °C for 4 h prior to the analysis. Then,  $\text{N}_2$  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 would be used to calculate the BET surface area.

c. X-ray diffraction (XRD) was used to identify crystalline phases present in the samples by using a Bruker AXS system (D8 Advance) with a copper tube for generating  $\text{Cu K}\alpha$  radiation ( $\lambda = 0.1542 \text{ nm}$ ) at 40 kV and 30 mV and a nickel filter. A photocatalyst sample was pressed into a hollow of glass holder and held in place by glass window. Then, it was scanned in the  $2\theta$  range of 10 to 80° in the continuous mode with the rate of 5°/min. The XRD results showed peak parameters, including the centroid  $2\theta$ , the full line width at half the maximum of intensity ( $\beta$ ), d-value, and intensity. The mean crystallite size will be calculated from the XRD data from X-ray line broadening.

d. UV-visible spectrophotometer is used to identify absorption ability of the photocatalysts. The analysis was operated under scanning wavelength at 200-900 nm using  $\text{BaSO}_4$  as the reference.

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

fine powder and ultrasonically dispersed in ethanol. A small droplet of the suspension was deposited on a nickel grid with polyvinyl desiccate, and the solvent was evaporated prior to loading the sample into the microscope. TEM was carried out in a JEOL 2000 CX operating 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 is 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 TEM columns must be kept under high vacuum. Additionally, the electromagnetic lenses are used for focusing the electron beam.

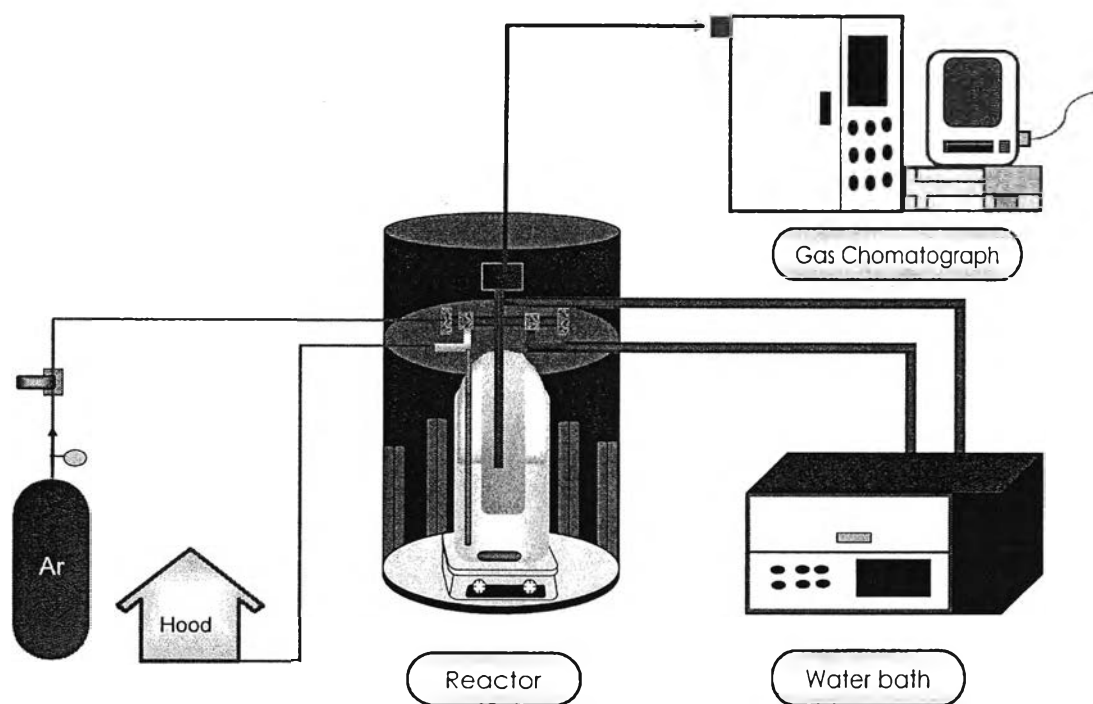
f.  $H_2$  chemisorption would be used to determine the Cu dispersion on the photocatalyst surface. It would be performed in a conventionally made-up system connected to a thermal conductivity detector (TCD) using 50 mg of each photocatalyst sample at room temperature with 20- $\mu$ l pulses of the purified  $H_2$ . The result would be detected with the TCD connected online to software to determine the irreversibly bound chemisorbed  $H_2$ , which should correspond to  $H_2$  adsorbed on the Cu surface. To calculate the Cu dispersion, it would be supposed that the adsorption stoichiometry was one H atom for one surface Cu atom.

### 3.2.3 Photocatalytic H<sub>2</sub> Production System

The photocatalytic H<sub>2</sub> production tests would be carried out according to the following procedure:

- a. A specified amount of all synthesized photocatalysts (0.2 g) were suspended in aqueous solution of methanol (50 vol.%) used the hole scavenger by using magnetic stirrer within a reactor made of Pyrex glass.
- b. The mixture was deaerated by purging with Ar gas for 30 min.
- c. The reaction was started by exposing the mixture with UV light irradiation from a set of Hg lamps (16 lamps, TUV11 WPL-S, Philips, total irradiance of 2.3 mWcm<sup>-2</sup>), which emitted light of more than 95% with a wavelength of 254 nm.
- d. The reaction temperature was controlled during the photocatalytic experiments by the cooling water circulated through a cylindrical jacket of the photoreactor.
- e. The produced hydrogen gas in the photoreactor headspace was periodically withdrawn every 1 h interval and analyzed by using a gas chromatograph (Hayesep D100/120, PERKIN ELMER) equipped with a thermal conductivity detector (TCD).

The photocatalytic H<sub>2</sub> production reaction would be performed in a closed gas system, as shown in Figure 3.2.



**Figure 3.2** Setup of photocatalytic H<sub>2</sub> production system.