



## CHAPTER III METHODOLOGY

### 3.1 Materials and Equipment

#### 3.1.1 Chemicals

- Tetraisopropyl orthotitanate (TIPT,  $\text{Ti}(\text{OCH}(\text{CH}_3)_2)_4$ )
- Tetraethyl orthosilicate (TEOS,  $\text{C}_8\text{H}_{20}\text{O}_4\text{Si}$ )
- Zirconium (IV) butoxide, 80 wt.% in 1-butanol  
(ZRB,  $\text{Zr}(\text{O}(\text{CH}_2)_3\text{CH}_3)_4$ )
- Strontium nitrate ( $\text{Sr}(\text{NO}_3)_2$ )
- Eosin Y (E. Y.,  $\text{C}_{20}\text{H}_6\text{Br}_4\text{Na}_2\text{O}_5$ )
- Laurylamine hydrochloride (LAHC,  $\text{CH}_3(\text{CH}_2)_{11}\text{NH}_2 \cdot \text{HCl}$ )
- Acetylacetone (ACA,  $\text{CH}_3\text{COCH}_2\text{COCH}_3$ )
- Diethanolamine (DEA,  $(\text{HOCH}_2\text{CH}_2)_2\text{NH}$ )
- Acetone ( $\text{CH}_3\text{COCH}_3$ )
- Methanol ( $\text{CH}_3\text{OH}$ )
- Anhydrous ethanol (EtOH,  $(\text{CH}_3\text{CH}_2\text{OH})$ )
- Hydrochloric acid (HCl)
- Sodium hydroxide (NaOH)
- Distilled water
- Silver nitrate ( $\text{AgNO}_3$ )
- Hydrogen hexachloroplatinate (IV) hexahydrate ( $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$   
analytical grade)

#### 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)
- H<sub>2</sub> chemisorption apparatus
- Oven (CARBOLITE/CWE 1100)
- pH meter (HANAA/pH 211)
- Magnetic stirrer
- Centrifuge machine (HERMLE Z383)
- Visible light source (300-W Xenon arc lamp, KXL-300/WACOM Electric)
- UV light source (11-W low-pressure mercury lamp, Philips)
- UV cut-off filter (B-48S/ATG)

## 3.2 Experimental Procedures

### 3.2.1 Mesoporous-Assembled TiO<sub>2</sub>-SiO<sub>2</sub> Nanocrystal Photocatalyst Synthesis by a Sol-Gel Process with the Aid of a Structure-Directing Surfactant

The mesoporous-assembled 0.97TiO<sub>2</sub>-0.03SiO<sub>2</sub> nanocrystal photocatalyst, which exhibited the highest photocatalytic activity (Rungjaroentawon, 2011) is synthesized according to the following procedure:

- a. The TIPT and TEOS were firstly mixed together with a Ti-to-Si molar ratio 97:3.
- b. A specified amount of analytical grade ACA was introduced into the TIPT/TEOS mixture with the [TIPT/TEOS]-to-ACA molar ratio equal to unity.
- c. 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/TEOS solution, in which the [TIPT/TEOS] to LAHC molar ratio 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. 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 the distilled water used in the preparation of LACH aqueous solution.

g. The dried gel was finally calcined at 500 °C to remove the LAHC and consequently produce the desired  $0.97\text{TiO}_2\text{-}0.03\text{SiO}_2$  nanocrystal photocatalyst.

(h. - k. are the additional steps for the Pt and/or Ag loading on the mesoporous-assembled  $0.97\text{TiO}_2\text{-}0.03\text{SiO}_2$  by a photochemical deposition (PCD) method.)

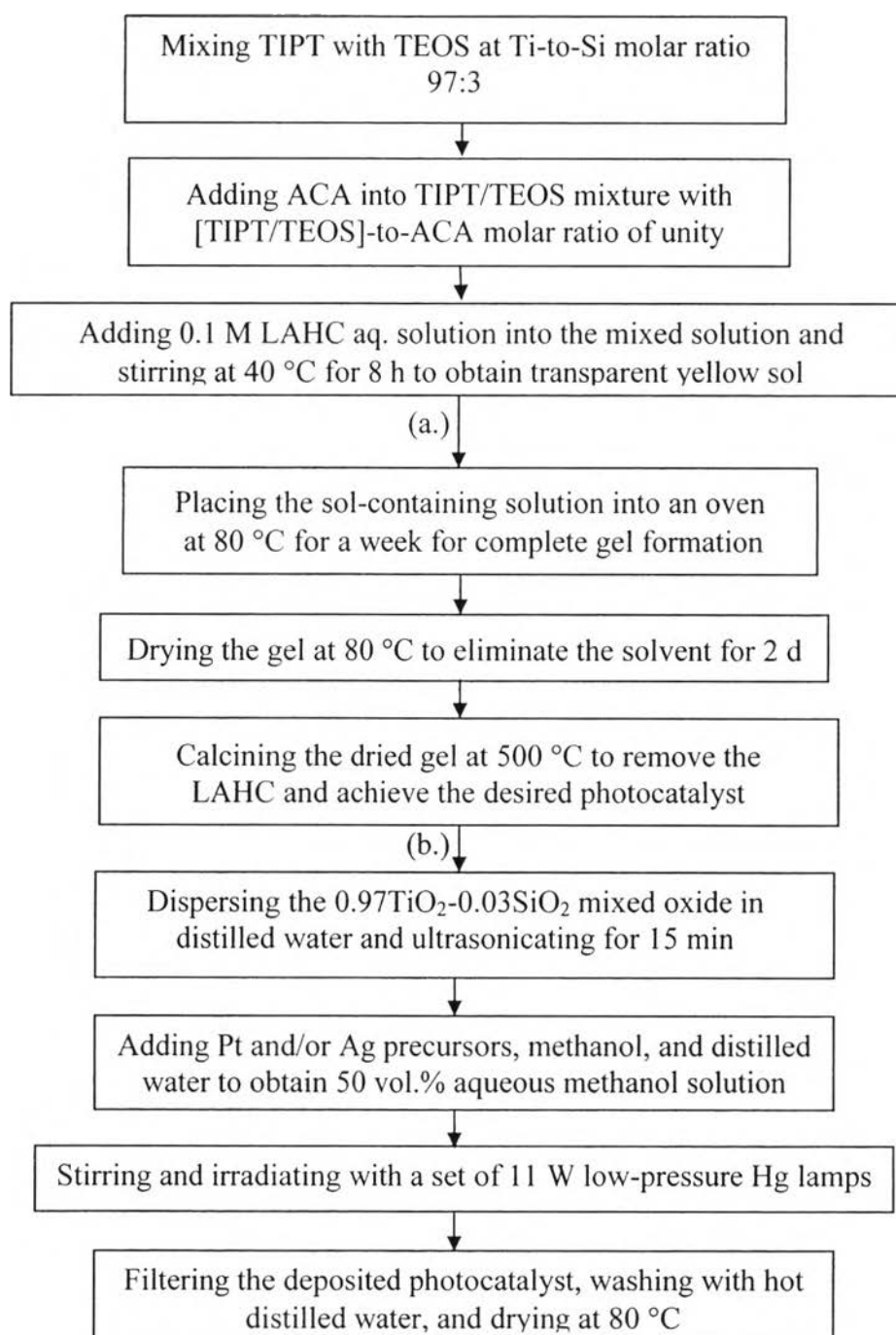
h. The synthesized  $0.97\text{TiO}_2\text{-}0.03\text{SiO}_2$  photocatalyst was first dispersed in distilled water and ultrasonicated for 15 min.

i. Then, a desired amount of hydrogen hexachloroplatinate (IV) hexahydrate and/or silver nitrate ( $\text{AgNO}_3$ ), methanol, and distilled water was added to obtain 50 vol.% aqueous methanol solution.

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

k. After the irradiation, the Pt and/or Ag-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  $0.97\text{TiO}_2$ - $0.03\text{SiO}_2$  nanocrystal photocatalysts without and with Pt and/or Au loading is shown in Figure 3.1 :



**Figure 3.1** Synthesis procedure for mesoporous-assembled  $0.97\text{TiO}_2$ - $0.03\text{SiO}_2$  photocatalysts: (a) without and (b) with Pt and/or Ag-loading by PCD method.

### 3.2.2 Mesoporous-Assembled TiO<sub>2</sub>-ZrO<sub>2</sub> Nanocrystal Photocatalyst

#### Synthesis by a Sol-Gel Process with the Aid of a Structure-Directing Surfactant

The mesoporous-assembled 0.93TiO<sub>2</sub>-0.07ZrO<sub>2</sub> nanocrystal photocatalyst which exhibited the highest photocatalytic activity (Onsuratoom *et al.*, 2011) is synthesized according to the following procedure:

a. The TIPT and ZRB were firstly mixed together with a Ti-to-Zr molar ratio 93:7.

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 then gently shaken until homogeneous mixing. Afterwards, a 0.1 M LAHC aqueous solution with pH of 4.2 is added to the ACA-modified mixed TIPT/ZRB solution, in which the [TIPT/ZRB]-to-LAHC molar ratio is tailored to a value of 4.

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

g. The dried gel was finally calcined at 500 °C to remove the LAHC and consequently produce the desired 0.93TiO<sub>2</sub>-0.07ZrO<sub>2</sub> nanocrystal photocatalyst.

(h. - k. are the additional steps for the Pt and/or Ag loading on the mesoporous-assembled 0.93TiO<sub>2</sub>-0.07ZrO<sub>2</sub> by the PCD.)

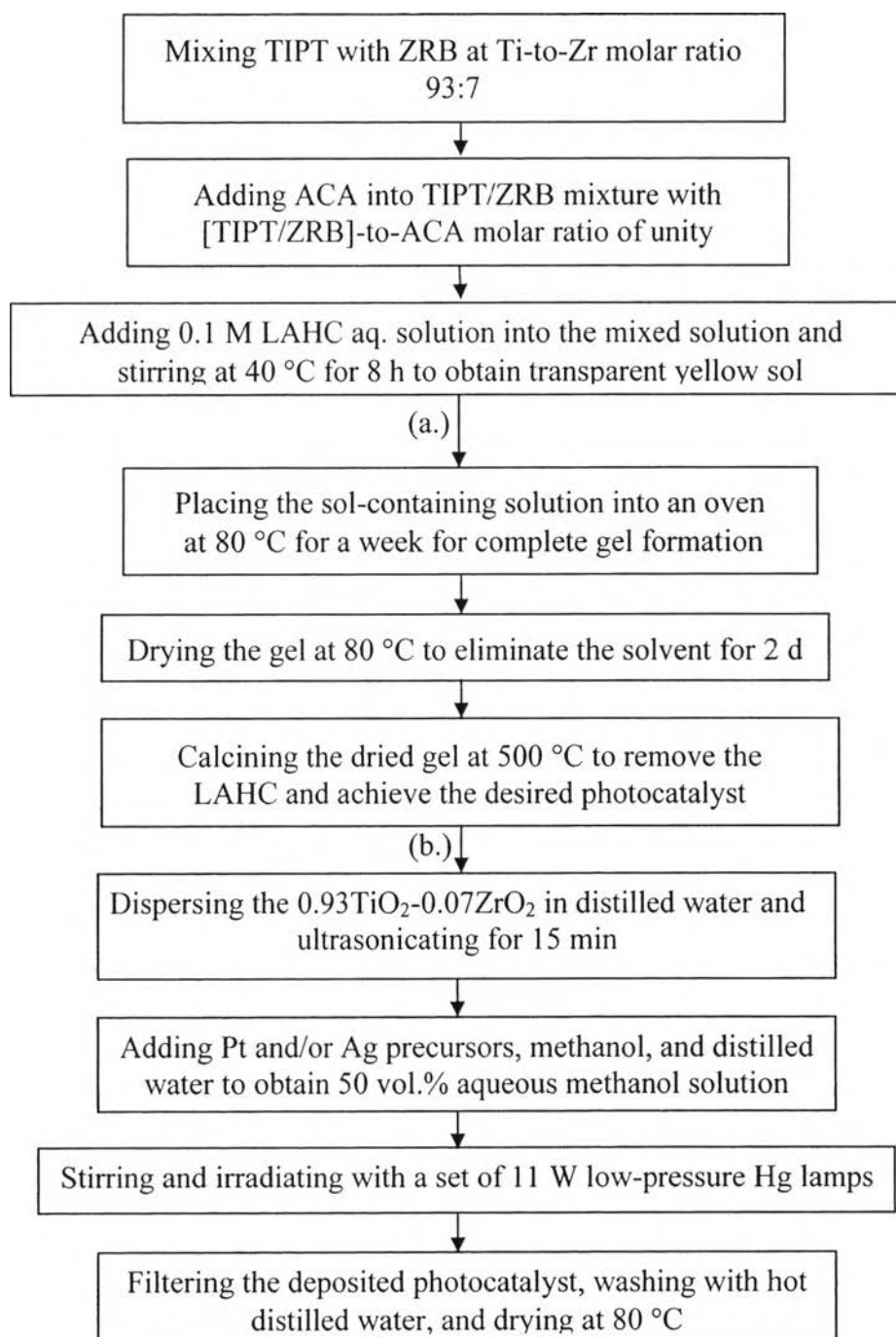
h. The synthesized 0.93TiO<sub>2</sub>-0.07ZrO<sub>2</sub> mixed oxide photocatalyst was first dispersed in distilled water and ultrasonicated for 15 min.

i. Then, a desired amount of hydrogen hexachloroplatinate (IV) hexahydrate and/or silver nitrate (AgNO<sub>3</sub>), methanol, and distilled water was added to obtain 50 vol.% aqueous methanol solution.

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

k. After the irradiation, the Pt and/or Ag-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  $0.93\text{TiO}_2$ - $0.07\text{ZrO}_2$  nanocrystal photocatalysts without and with Pt and/or Ag loading is shown in Figure 3.2.



**Figure 3.2** Synthesis procedure for mesoporous-assembled  $0.93\text{TiO}_2$ - $0.07\text{ZrO}_2$  photocatalysts: (a) without and (b) with Pt and/or Ag-loading by PCD method.

### 3.2.3 Mesoporous-Assembled SrTi<sub>x</sub>Zr<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>0.93</sub>Zr<sub>0.07</sub>O<sub>3</sub> nanocrystal photocatalysts is synthesized according to the following procedure:

a. The TIPT and ZRB were firstly mixed together with a Ti-to-Zr molar ratio 93:7.

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. 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, in which the [TIPT/ZRB]-to-LAHC molar ratio was tailored to a value of 4. The mixture was kept continuously stirring at 40 °C for 8 h to obtain transparent 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 the distilled water used in the preparation of LAHC aqueous solution.

g. The dried gel was finally calcined at 700 °C to remove the LAHC and consequently produce the desired SrTi<sub>0.93</sub>Zr<sub>0.07</sub>O<sub>3</sub> photocatalyst.

(g. - k. are the additional steps for the Pt and/or Ag-loading on the mesoporous-assembled SrTi<sub>0.93</sub>Zr<sub>0.07</sub>O<sub>3</sub> by the PCD method.)

h. The synthesized SrTi<sub>0.93</sub>Zr<sub>0.07</sub>O<sub>3</sub> photocatalyst was first dispersed in distilled water and ultrasonicated for 15 min.

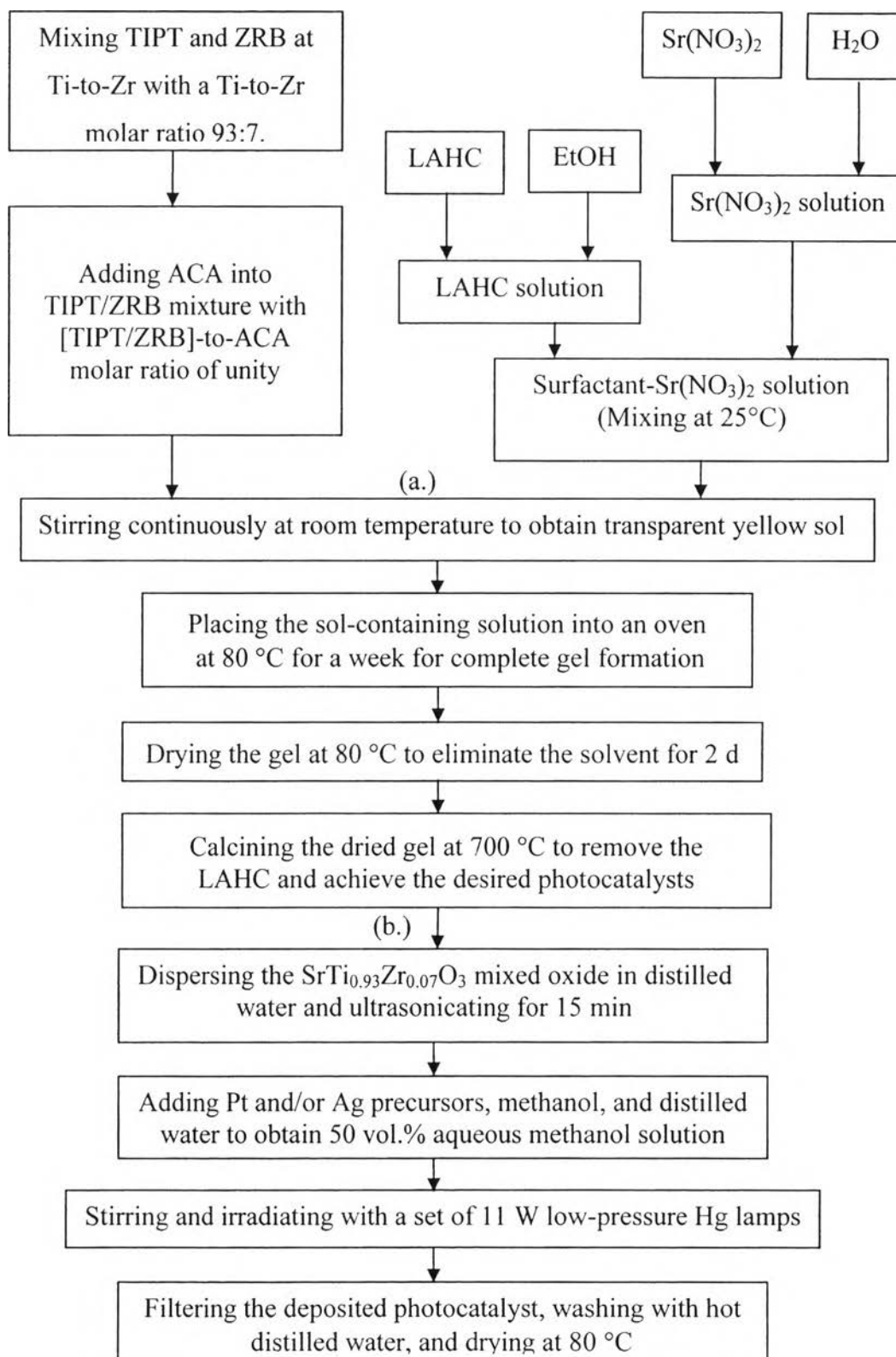
i. Then, a desired amount of hydrogen hexachloroplatinate (IV) hexahydrate and/or silver nitrate (AgNO<sub>3</sub>), methanol, and distilled water was added to obtain 50 vol.% aqueous methanol solution.



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

k. After the irradiation, the Pt and/or Ag-deposited photocatalyst powders was recovered by filtration, washed with hot distilled water, and dried at 80 °C.

The flow chart for the synthesis of mesoporous-assembled  $\text{SrTi}_{0.93}\text{Zr}_{0.07}\text{O}_3$  nanocrystal photocatalysts without and with Pt and/or Ag loading is shown in Figure 3.3.



**Figure 3.3** Synthesis procedure for mesoporous-assembled SrTiZrO<sub>3</sub> photocatalysts: (a) without and (b) with Pt and/or Ag-loading by PCD method.

### 3.2.4 Photocatalyst Characterizations

a. Simultaneous thermogravimetry and differential thermal analysis (TG-DTA) was used to study the thermal decomposition behavior of the as-synthesized dried photocatalyst 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  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> 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, N<sub>2</sub> 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 was used to calculate the BET surface area.

c. X-ray diffraction (XRD) was used to identify phases present in the samples by using a Rigaku/Rint2200 diffractometer equipped with a Ni filtered 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  $2\theta$  range of 15 to 70° in the continuous mode with the rate of 5°/min. The XRD results show 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 was calculated from the XRD data from X-ray line broadening.

d. UV-visible spectrophotometer was used to identify absorption ability of the photocatalysts. The analysis was operated under scanning wavelength at 200-900 nm using BaSO<sub>4</sub> 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 Au before measurement for improving conductivity of sample. For TEM analysis, the photocatalyst samples were 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. 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 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 TEM columns must be kept under high vacuum. Additionally, the electromagnetic lenses are used for focusing the electron beam.

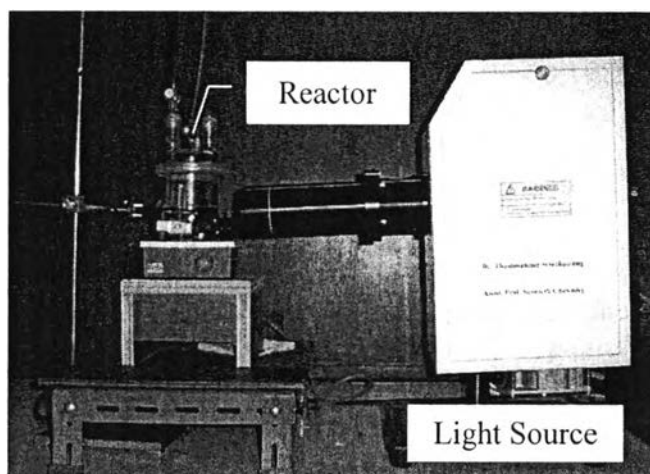
f. H<sub>2</sub> chemisorption was used to determine the Pt and/or Ag dispersion on the photocatalyst surface. It was performed in a conventionally made-up system connected to a thermal conductivity detector (TCD) using 50 mg of each photocatalyst sample at room temperature with 20- $\mu$ l pulses of the purified H<sub>2</sub>. The result was detected with the TCD connected online to software to determine the irreversibly bound chemisorbed H<sub>2</sub>, which should correspond to H<sub>2</sub> adsorbed on the Pt and/or Ag surface. To calculate the Pt and/or Ag dispersion, it was supposed that the adsorption stoichiometry was one H atom for one surface Pt and/or Ag atom.

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

The photocatalytic H<sub>2</sub> production test was 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 a 300 W Xe arc lamp emitting light with wavelength longer than 400 nm using a UV cut-off filter.
- d. The gaseous H<sub>2</sub> produced was periodically collected by a gas-tight syringe and analyzed by a gas chromatograph (GC) equipped with a thermal conductivity detector (TCD)

The photocatalytic H<sub>2</sub> production reaction was performed in a closed gas system, as shown in Figure 3.4.



**Figure 3.4** Setup of photocatalytic H<sub>2</sub> production system.