

CHAPTER III

EXPERIMENTAL

3.1 Materials

- 3.1.1 Tetraisopropyl orthotitanate (TIPT, $\text{Ti}(\text{OCH}(\text{CH}_3)_2)_4$)
- 3.1.2 Tetraethyl orthosilicate (TEOS, $\text{C}_8\text{H}_{20}\text{O}_4\text{Si}$)
- 3.1.3 Eosin Y (E.Y., $\text{C}_{20}\text{H}_6\text{Br}_4\text{Na}_2\text{O}_5$)
- 3.1.4 Laurylamine hydrochloride (LAHC, $\text{CH}_3(\text{CH}_2)_{11}\text{NH}_2\cdot\text{HCl}$)
- 3.1.5 Acetylacetone (ACA, $\text{CH}_3\text{COCH}_2\text{COCH}_3$)
- 3.1.6 Diethanolamine (DEA, $(\text{HOCH}_2\text{CH}_2)_2\text{NH}$)
- 3.1.7 Acetone (CH_3COCH_3)
- 3.1.8 Hydrochloric acid (HCl)
- 3.1.9 Sodium hydroxide (NaOH)
- 3.1.10 Distilled water
- 3.1.11 Hydrogen hexachloroplatinate (IV) hexahydrate ($\text{H}_2\text{PtCl}_6\cdot 6\text{H}_2\text{O}$)
- 3.1.12 Hydrogen tetrachloroaurate (III) hydrate ($\text{HAuCl}_4\cdot 4\text{H}_2\text{O}$)

3.2 Equipment

- 3.2.1 Thermogravimetric/derivative thermogravimetric analyzer (TG-DTG, Perkin Elmer/Pyris Diamond)
- 3.2.2 X-ray diffractometer (Bruker AXS/D8 Advance)
- 3.2.3 Surface area analyzer (SAA, Quantachrom/Autosorb 1)
- 3.2.4 Scanning electron microscope (SEM, Hitachi/S-4800) equipped with energy dispersive X-ray (EDX) analyzer
- 3.2.5 Transmission electron microscope (TEM, JEOL/JEM 2100) equipped with energy dispersive X-ray (EDX) analyzer
- 3.2.6 Gas chromatograph (GC, Perkin Elmer/ARNEL)
- 3.2.7 UV-visible spectrophotometer (Shimadzu/UV-2550)
- 3.2.8 H_2 chemisorption apparatus

- 3.2.9 Oven (CARBOLITE/CWE 1100)
- 3.2.10 pH meter (HANAA/pH 211)
- 3.2.11 Magnetic stirrer
- 3.2.12 Centrifuge machine (HERMLE Z383)
- 3.2.13. Visible light source (300-W Xenon arc lamp, KXL-300/WACOM Electric)
- 3.2.14 UV light source (11-W low-pressure mercury lamp, Philips)
- 3.2.15 UV cut-off filter (B-48S/ATG)

3.3 Methodology

The mesoporous-assembled TiO₂-SiO₂-based nanocrystal photocatalysts were synthesized by a sol-gel process with the aid of a structure-directing surfactant according to the following procedure:

- a. The TIPT and TEOS were firstly mixed together with various TiO₂ and SiO₂ molar concentrations (various x values in xTiO₂-(1-x)SiO₂).
- 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 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 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 3 d, which was mainly the distilled water used in the preparation of LAHC aqueous solution.
- g. The dried gel was finally calcined at various temperatures (500-800 °C) for 4 h to remove the LAHC and consequently produce the desired TiO₂-SiO₂ mixed oxide photocatalysts.

(h. - k. are the additional steps for the preparation of Pt- and/or Au-loaded mesoporous-assembled $\text{TiO}_2\text{-SiO}_2$ mixed oxide photocatalysts by a photochemical deposition (PCD) method.)

h. A $\text{TiO}_2\text{-SiO}_2$ mixed oxide photocatalyst, which was initially prepared by the sol-gel method, was first dispersed in distilled water and ultrasonicated for 15 min.

i. Then, a desired amount of hydrogen hexachloroplatinate (IV) hexahydrate and/or hydrogen tetrachloroaurate (III) hydrate, methanol, and distilled water was added to obtain a 50 vol.% methanol aqueous 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 2 h.

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

The flow chart for the synthesis of mesoporous-assembled TiO_2 - SiO_2 -based nanocrystal photocatalysts without and with Pt and/or Au loading is shown in Figure 3.1:

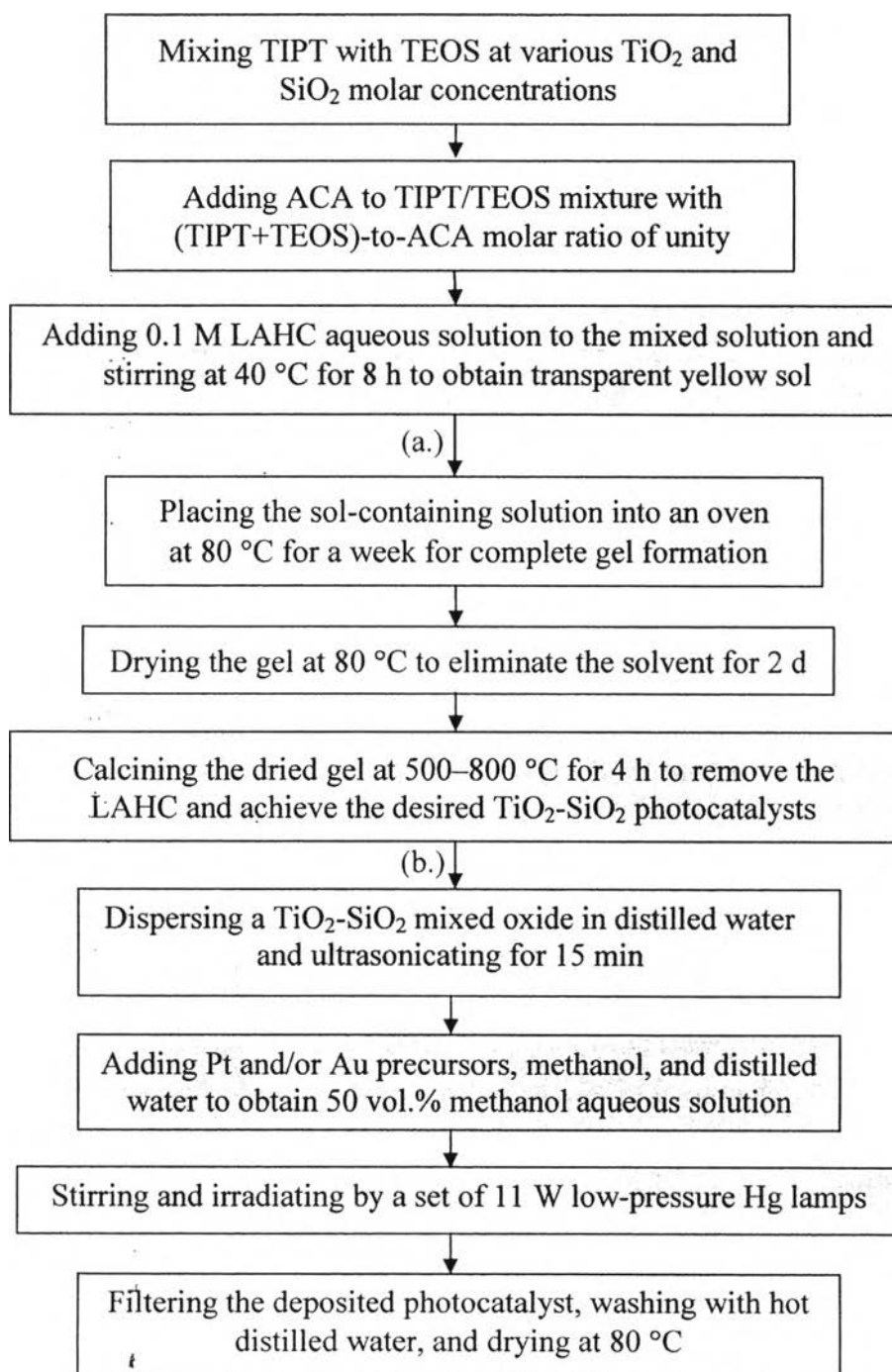


Figure 3.1 Synthesis procedure for mesoporous-assembled TiO_2 - SiO_2 -based photocatalysts: (a) TiO_2 - SiO_2 mixed oxides and (b) Pt- and/or Au-loaded TiO_2 - SiO_2 mixed oxides by PCD method.

3.4 Photocatalyst Characterizations

- a. Simultaneous thermogravimetry and differential thermal analysis (TG-DTA) was used to study the thermal decomposition behavior of the as-synthesized dried $\text{TiO}_2\text{-SiO}_2$ gel and obtain a suitable calcination temperature for removing the LAHC surfactant. The dried gel of 5–15 mg was heated from 50 °C to 800 °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, 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 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 were used to calculate the specific 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 $\text{CuK}\alpha$ radiation (1.54056 Å) 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. The goniometer parameters were divergent slit = 1° (2 θ); scattering slit = 1° (2 θ); and receiving slit = 0.3 mm. Then, it was scanned in the 2 θ range of 20° to 60° in the continuous mode with the rate of 1 °/min with scan step of 0.02 (2 θ). The XRD results show peak parameters, including the centroid 2 θ , the full width at half the maximum of intensity (β), d-value, and intensity. The mean crystallite size was calculated from the XRD data using X-ray line broadening. The signal was sent to the online computer to record and analyze. The Scherrer equation as expressed in Equation 3.1 shows the relationship between the crystallite size (D) and the

broadening (β) of the diffraction line corresponding to the Bragg angle (θ) and X-ray wavelength (λ).

$$D_b = \frac{K \cdot \lambda}{\beta \cdot \cos\theta} \quad (3.1)$$

where:

D_b = Crystallite size (\AA)

K = Scherrer constant, 0.9

λ = X-ray wavelength (\AA)

β = Full width at half maximum of peak at 2θ (radian)

θ = Bragg angle of the reflection (radian)

- d. UV-visible spectrophotometer was used to identify absorption ability of the photocatalysts. The analysis was operated under scanning wavelength of 200–900 nm using 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 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. The TEM was carried out 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 column must be kept under high vacuum. Additionally, the electromagnetic lenses were used for focusing the electron beam. The energy dispersive X-ray (EDX) analyzer attached to both the SEM and TEM was used to obtain elemental mappings over a desired region of a photocatalyst.
- f. Hydrogen chemisorption was used to determine the Pt and/or Au 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 software to determine the irreversibly bound chemisorbed H₂, which should correspond to H₂ adsorbed on the Pt and/or Au surface. To calculate the Pt and/or Au dispersion, it was supposed that the adsorption stoichiometry was one H atom for one surface Pt and/or Au atom.

3.5 Photocatalytic H₂ Production System

The photocatalytic H₂ production reaction was performed in a closed gas system, as shown in Figure 3.2.

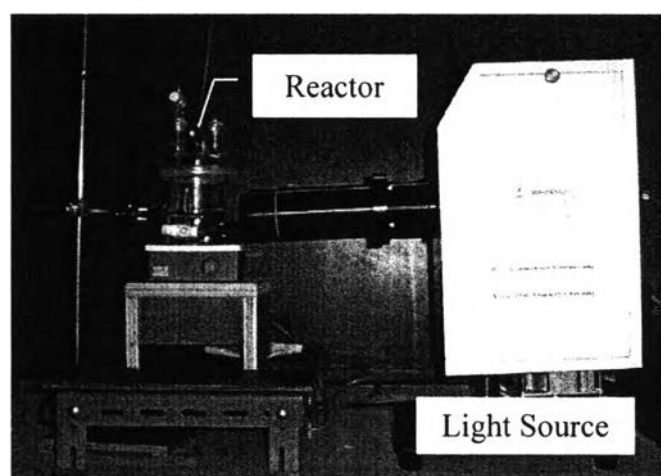


Figure 3.2 Setup of photocatalytic H₂ production system.

The photocatalytic H₂ production tests were carried out according to the following procedure:

- a. A specified amount of each synthesized photocatalyst (0.2 g) was suspended in 150 ml of diethanolamine aqueous 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 H₂ produced was periodically collected by a gas-tight syringe and analyzed by a gas chromatograph (GC) equipped with a thermal conductivity detector (TCD). The conditions used for operating GC are shown as follows:

- Injector temperature: 150 °C
- Oven temperature: 45 °C
- Detector temperature: 150 °C
- Carrier gas: Ar