

CHAPTER III

EXPERIMENT

3.1 Materials

All chemicals/materials used in this research are as follows:

- 3.1.1 Tetraisopropyl orthotitanate (TIPT, $\text{Ti}(\text{OCH}(\text{CH}_3)_2)_4$), (synthesis grade, MERCK)
- 3.1.2 Hydrogen hexachloroplatinate (IV) hexahydrate ($\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$), (analytical grade, ALDRICH)
- 3.1.3 Urea (NH_2CONH_2), (Laboratory Reagent, UNILAB)
- 3.1.4 Commercial TiO_2 (Degussa P-25)
- 3.1.5 Laurylamine hydrochloride (LAHC, $\text{CH}_3(\text{CH}_2)_{11}\text{NH}_2 \cdot \text{HCl}$), (synthesis grade, MERCK)
- 3.1.6 Acetylacetone (ACA, $\text{CH}_3\text{COCH}_2\text{COCH}_3$), (synthesis grade, Rasayan)
- 3.1.7 Methanol (CH_3OH), (Anhydroscan, LAB-SCAN Analytical Sciences)
- 3.1.8 Distilled water

3.2 Equipment

All equipments used in this research are as follows:

- 3.2.1 Thermogravimetric-differential thermal analyzer (TG-DTA, Perkin Elmer/Pyris Diamond)
- 3.2.2 X-ray diffraction (XRD, Rigaku/Rint2200 HV)
- 3.2.3 Surface area analyzer (SSA, Quantachrome/Autosorb 1)
- 3.2.4 Transmission electron microscope (TEM, JEOL 2000 CX)
- 3.2.5 Gas chromatography (GC, Perkin Elmer/ARNEL)
- 3.2.6 UV-VIS spectrophotometer (Shimadzu UV-2550)
- 3.2.7 X-ray Photoemission Spectroscopy (XPS, Alpha110 Hemispherical Analyser Model 8017 Digital Electronics)
- 3.2.9 Xenon discharge lamp (Type KXL-300/WACOM electric)

3.2.10 Oven (CARBOLITE/CWE 1100)

3.2.11 pH meter (HANAA/pH 211)

3.2.12 Magnetic stirrer

3.3 Methodology

3.3.1 Mesoporous TiO₂ Photocatalyst Synthesis by Surfactant-Assisted Templating Sol Gel Method

The mesoporous TiO₂ photocatalyst was synthesized by the following procedure:

a. A specified amount of analytical grade ACA was first introduced into TIPT with the molar ratio of unity.

b. The mixed solution was then gently shaken until homogenous mixing. Afterwards, 0.1 M LAHC aqueous solution of pH 4.2 was added into the ACA-modified TIPT solution, in which the molar ratio of TIPT to LAHC was tailored to a value of 4.

c. The mixture was kept continuously stirring at 40°C for a day to obtain transparent yellow sol.

d. Then, the gel was formed by placing the sol-containing solution into an oven kept at 80°C for a week.

e. The gel was dried at 80°C to eliminate the solvent, which was mainly the distilled water used in the preparation of surfactant aqueous solution.

f. The dried gel was finally calcined at 500°C to remove LAHC template and consequently produce the desired TiO₂ photocatalyst.

The flow chart for preparation of the mesoporous TiO₂ photocatalyst is shown in Figure 3.1

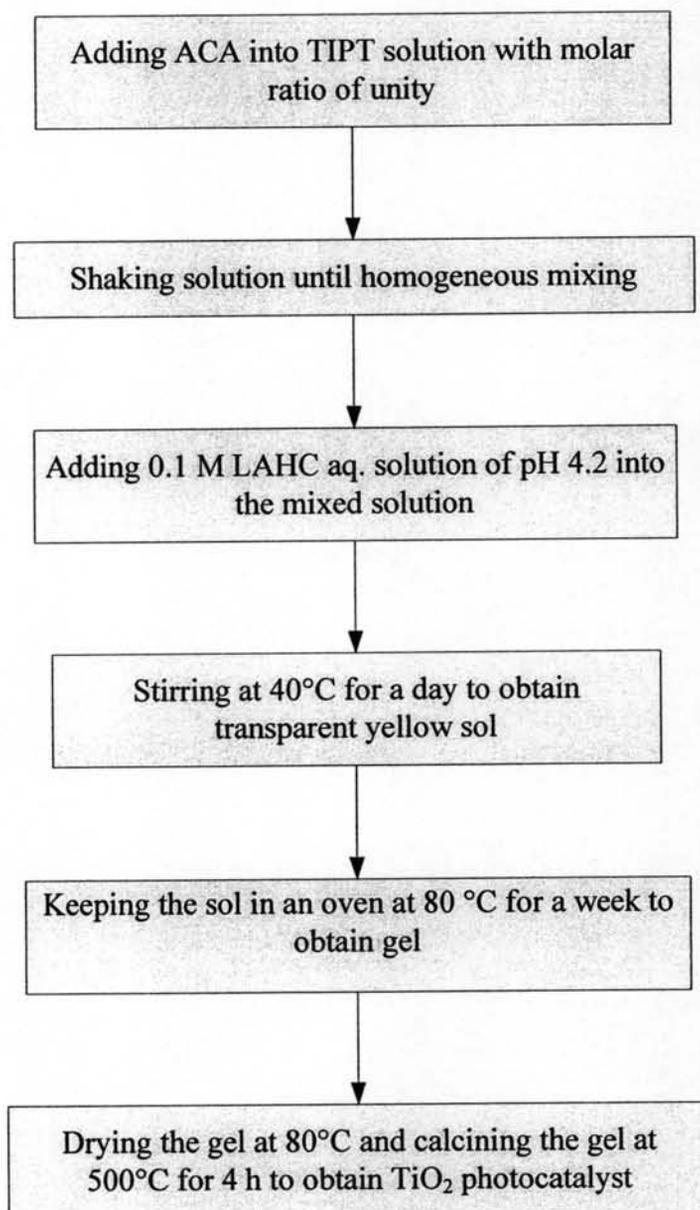


Figure 3.1 Preparation procedure for synthesized mesoporous TiO₂ photocatalyst.

3.3.2 Preparation of N-doped TiO₂ and Pt-loaded N-doped TiO₂

The N-doped and Pt-loaded N-doped TiO₂ photocatalysts was prepared by the following procedure:

a. Degussa P-25 TiO₂ powder (commercially available non-mesoporous TiO₂) was mixed with urea at various urea:TiO₂ molar ratios of 0.5:1, 1:1, and 3:1 by using agate mortar.

b. The ground powder was calcined at 200, 250, and 300°C for 2 h to obtain N-doped samples. The synthesized mesoporous TiO₂ photocatalyst was also N-doped by the same procedure.

c. According to the photocatalytic H₂ evolution activity test as shown in Chapter IV, the N-doped synthesized mesoporous TiO₂ prepared at appropriate condition exhibited comparatively high activity. Such the N-doped synthesized mesoporous TiO₂ powder was impregnated by appropriate amount of H₂PtCl₆.6H₂O aqueous solution to obtain various nominal Pt cocatalyst loading content at 0.4, 0.8, 1.0, 1.1, 1.3, 1.4, and 1.6 wt%.

d. The impregnated photocatalysts were dried at 110°C overnight and finally calcined at 200°C for 6 h.

e. The flow diagram for preparation of the N-doped TiO₂ and Pt-loaded N-doped TiO₂ preparations is shown in Figure 3.2

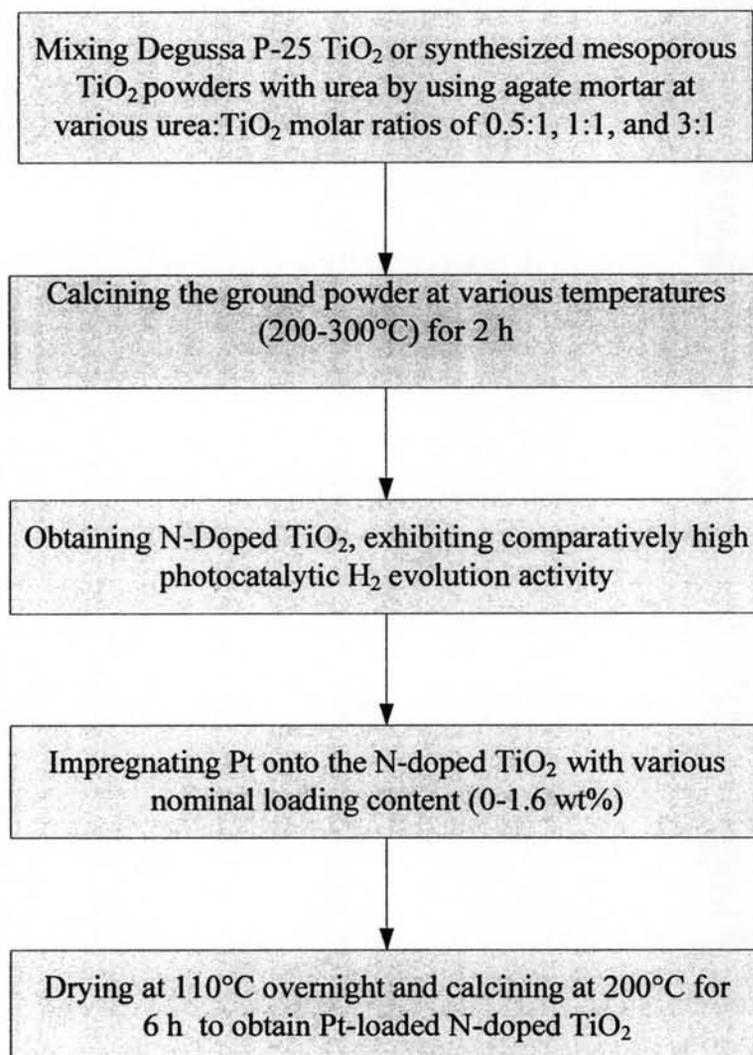


Figure 3.2 Preparation procedure for N-doped TiO₂ and Pt-loaded N-doped TiO₂ photocatalysts.

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 TiO₂ gel and obtain suitable calcination temperature for removing LAHC template. The dried gel of 5-15 mg was heated from 30 to 700°C with a heating rate of 10°C/min in a static air atmosphere with α -Al₂O₃ as the reference.

b. X-ray diffraction (XRD) was used to identify phases present in the samples by using a Rigaku RINT 2000 diffractometer equipped with a Ni filter and CuK α radiation source ($\lambda = 1.542 \text{ \AA}$) and operated at 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 5°/min. The XRD results showed 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 was calculated from the XRD data from X-ray line broadening.

c. The sample morphology was observed by a transmission electron microscope (TEM). A 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. TEM was carried out in a JEOL 2000 CX operated 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. Since electron beams can be easily scattered by air molecules, TEM columns must be kept under high vacuum. Additionally, the electromagnetic lenses were used for focusing the electron beam.

d. The surface area of all photocatalyst samples was determined by BET surface area analyzer. The sample was first outgassed to remove the humidity and volatile molecules adsorbed on surface under vacuum at 150°C for 4 h prior to the analysis. Then, N₂ was purged to adsorb on surface, and the quantity of gas adsorbed

onto or desorbed from their solid surface was measured at some equilibrium vapor pressure 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 BET surface area, as well as pore size distribution and the total pore volume.

e. UV-VIS spectrophotometer was used to identify absorption of light in visible region. The sample was operated under scanning wavelength in the range of 200-600 nm.

f. The oxidation state and surface composition were analyzed by an X-ray photoelectron spectroscopy. A MgK α source emitting X-ray energy of 1253.6 eV was used as X-ray source. The sample powders were analyzed in a pellet form, mounted on a double-sided adhesive tape. The pressure in the analysis chamber was in the range of 10^{-8} Torr during data collection. The relative surface charging of the samples was removed by referencing all the energies to the C1s level as an internal standard at 285 eV, arising from the adventitious carbon. The invariance of the peak shapes and widths at the beginning and at end of the analyses ensured the absence of differential charging. Analysis of the peaks was performed with the software provided by Hemispherical Analyser, based on non-linear least squares fitting program using a properly weighted sum of Lorentzian and Gaussian component curves after background subtraction. Atomic concentrations were calculated from peak intensity using the correction factors provided with the software. The binding energy (BE) values were quoted with a precision of ± 0.15 eV.

3.5 Photocatalytic H₂ Evolution System

The photocatalytic H₂ evolution reaction was performed in a closed gas system, as shown in Figure 3.3

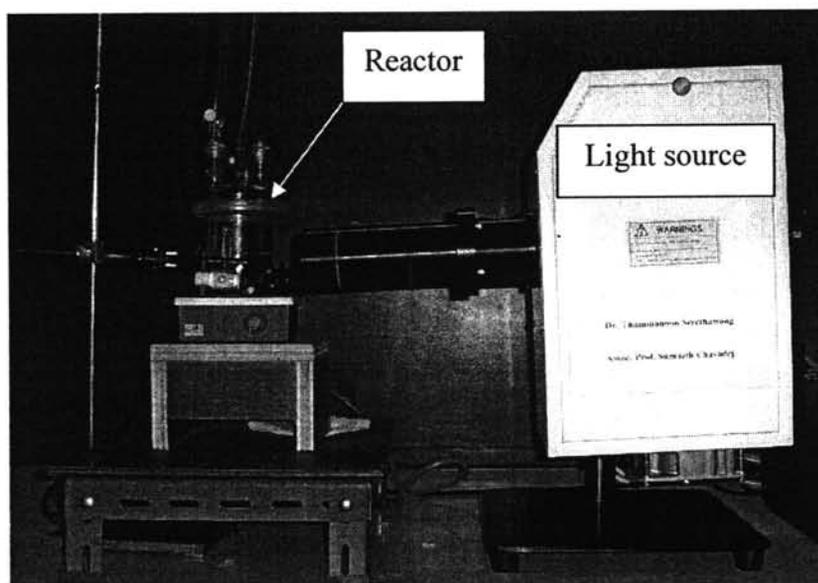


Figure 3.3 Setup of photocatalytic H₂ evolution system.

The photocatalytic H₂ evolution test was carried out according to the following procedure:

- a. A specified amount of all prepared photocatalysts (0.2 g), namely N-doped synthesized TiO₂, N-doped Degussa P-25, and Pt-loaded N-doped TiO₂, was suspended in an aqueous methanol solution (CH₃OH 50 ml and distilled water 150 ml) by means of magnetic stirrer within a reactor made of Pyrex glass.
- b. The mixture was deaerated by purging with Ar gas for 45 min in dark environment.
- 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.
- d. The gaseous H₂ evolved 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: 60°C
- Oven temperature: 33°C
- Detector temperature: 150°C
- Carrier gas: Ar
- Ar pressure: 50 psig