

CHAPTER III

METHODOLOGY

3.1 Preparation of TiO₂ thin film by sol-gel method

3.1.1 Materials

All chemicals in this research were analytical grade and were used as received. Titanium tetraisopropoxide (Ti(OCH(CH₃)₂)₄) or TTiP obtained from Aldrich and absolute ethanol supplied by Merck were used as a Ti-precursor and a solvent, respectively. Polyethylene glycol with molecular weight 600 (PEG 600) from Acros organics and diethylene glycol (DEG) from Unilab were used as organic additives.

3.1.2 Preparation of stainless steel plate

The TiO₂ thin film was deposited on stainless steel 316L plates (purchased from Thainox Stainless Public Company Limited) with surface dimension of 2 x 5 cm. The surfaces were cleaned prior to use as follows. First, stainless plates were washed with 2% HF for 5 min, and then dipped in a mixed solution of water and anhydrous ethanol, and dried at room temperature (Liqiang et al., 2003). Before use, each plate was weighed and covered with adhesive tape in order to measure the amount of TiO₂ that was coated on one side.

3.1.3 Preparation of TiO₂ thin film

Precursor solution for TiO₂ coated film was prepared as follows. PEG 600 and DEG were dissolved in ethanol, and then TTiP was added quickly with stirring to obtain a transparent and colorless solution. The stainless plates were dipped in the solution and withdrawn at 1 mm/s. After coating, the coated films were dried at room temperature and then calcined at 500°C in a furnace for 30 min.

3.2 Experimental procedure

The experiment was divided into 3 parts as follows: effects of mole ratio of each chemical precursor, calcination temperature and coating cycle

Part 1: Mole ratio of TTIP: ethanol: PEG 600: DEG

First, a TiO₂ precursor solution was prepared by varying amounts of ethanol which was the first parameter as 20, 30, 40, 50 and 60 mole. After obtaining a suitable amount of ethanol, PEG600 was varied corresponding to TiO₂ amounts with the mole ratio of TTiP:PEG600 as 0.5,1 and 1.5 with the fixed concentration of ethanol. Next, DEG was varied corresponding to the amount of TTiP with the mole ratio of DEG in the fixed concentration of ethanol at 0.5, 1, and 1.5. In this part, the coated substrates were calcined at 500°C in a furnace for 30 min.

Table 3.1 Preparation conditions of TiO₂ thin film

Mole ratio			
TTiP	Ethanol	PEG600	DEG
1	20,30,40,50,60	0.5,1,1.5	0.5,1,1.5

Part 2: Calcination temperature

The optimum ratio of the precursors from part 1 was used so as to prepare TiO₂ precursor solution. To study the effect of calcination temperature and to obtain the optimum temperature, the coated gel films were calcined at 400, 500, 600, 700 and 800°C in a furnace for 30 min.

Part 3: Coating cycle

The optimum ratio of precursors from part 1 and optimum calcination temperature from part 2 were used. In addition, substrates were coated at different cycles at 1, 3, and 5. It should be noted that the sample should be done from heat-up to cool-down before beginning a new cycle.

3.3 Film characterizations

TiO₂ thin films were measured as follows:

- Amount of TiO₂ attached to substrate was weighed by scale.
- Adhesive test by adhesive tape (ASTM D3359-95a).
- Corrosive test by dipping the film into acid (1M, 5M and 10M of HNO₃) and alkali solutions (1M, 5M and 10M of NaOH).
- Film surface morphology and its smoothness analysis by Scanning Electron Microscope.
- Crystallinity analysis of the TiO₂ thin film by X-Ray Diffraction (XRD).

3.3.1 Weighing by scale

This method was the primary information demonstrating whether TiO₂ attached to substrate. A four-digit balance was used in this test which could obtain the results of only minute change in mass.

3.3.2 Adhesive test (ASTM D3359-95a)

This test method was used to establish whether the adhesion of a coating to a substrate is at a generally adequate level. First, the adhesive test was applied over the film with the tape running in the same direction. The tape was smoothed into place by finger. Second, removed the tape by seizing the free end and pulling it off rapidly back upon itself at as close to an angle of 180° as possible. Finally, the removal area of coating from the substrate was inspected as compared to the previous coating. The TiO₂ thin film should not be peeled off when the tape was removed.

3.3.3 Corrosive test

This test was employed in order to investigate whether the TiO₂ thin film can resist the aggressive condition of 1M, 5M and 10M of HNO₃ and NaOH. The sample should not be removed when dipping for 5 min.

3.3.4 Scanning electron microscope (SEM)

The morphology and smoothness of TiO₂ thin film were observed by SEM (JEOL JSM-5800 LV) using constant accelerating voltage of 15 kV.

The principal of SEM can be described as follows. A specimen was placed into a high vacuum chamber and an electron beam was forced onto the sample. The interaction of the electron beam from the filament and the sample atoms generates a variety of signals. The secondary or backscattered electrons were detected and converted to an image.

3.3.5 X-ray diffraction (XRD)

The phase analysis of TiO₂ thin film was carried out by an x-ray diffractometer. X-ray diffraction patterns of the samples were recorded on a Philip diffractometer using Cu K α radiation and a step size of 0.02° in the range of 2 θ at 20-70°. The step time was 0.4 second. Peak positions were compared with the standard file to identify crystalline phases.

X-ray diffraction is a technique used to determine the existence of different material structures and phases in a sample, based on their characteristic diffraction behavior under X-ray irradiation of a known wavelength, i.e. each structure or phase will only diffract an incident X-ray at a specific set of incident angles, which can be measured. XRD can make a relatively quantitative analysis by comparing the intensity of the diffraction lines. When comparing the same crystalline substance of two different samples, the higher intensity shows the higher content.

X-ray diffraction patterns were used for the crystallite size estimation by line broadening measurements in the Debye-Scherrer equation:

$$L = K\lambda / \beta \cos\theta \quad (3.1)$$

where,

- L = the crystallite size (nm)
- K = the Debye-Scherrer constant (usually taken as 0.89)
- λ = the wavelength of the X-ray radiation (Cu K α = 0.15418 nm)
- β = the line width at half-maximum height of the broadened peak
- θ = the half diffraction angle of the centroid of the peak (degree)

3.4 Photocatalytic activity measurements

3.4.1 Materials

To prepare the Cr(VI) solutions for photocatalytic activity test, analytical grade of K_2CrO_4 (Merck) was mixed with deionized water. The pH of the solution was adjusted to the desired value by adding NaOH or H_2SO_4 . Both chemicals were products from Merck.

3.4.2 Experimental set-up

The photocatalytic activity of the thin films was evaluated from the reduction of chromium (VI) to chromium (III). A 1500 mL of glass container was used as a batch reactor in the study. The UV light source was 10-watt low pressure mercury lamp with a wavelength 254 nm. The UV lamp was placed over the reactor so that the light was projected directly to TiO_2 thin films. The reactor was covered by an opaque box to prevent the outer effects and for UV protection. The set-up of the photoreactor is shown in Figure 3.1.

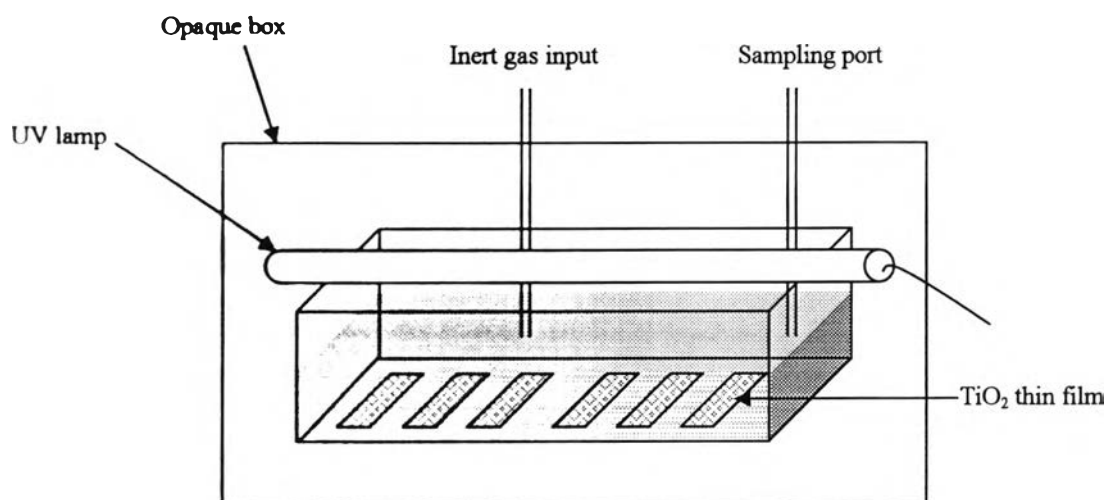


Figure 3.1 Photochemical reactor used in this study

3.4.3 Experimental procedure

The experimental procedure of chromium removal by TiO₂ thin film was carried out as the previous study (Watcharenwong, 2003). The details of experiments were as follows:

First, a 1000 mL solution containing 25 ppm of chromium (VI) with adjusted pH of 3, and 6 pieces of TiO₂ thin film deposited on stainless steel were placed in the reactor. Prior to irradiation, the solution was stirred well for 10 min to reach the adsorption equilibrium. The experiment started when the UV lamp was turned on. A sample was taken at 0, 5, 10, 15, 30, 60, 90, 120, 150 and 180 min.

3.4.4 Analytical method

The concentration of Chromium (VI) was analyzed by UV/Vis spectrophotometer (JASCO V-530) at 540 nm using diphenylcarbazide as the color reagent.