

## CHAPTER III

### EXPERIMENTAL PROCEDURES

This chapter consists of three major parts: preparation of  $\text{TiO}_2$  catalysts, characterization of  $\text{TiO}_2$  and photocatalytic efficiency determination. Details of each part are described below.

#### 3.1 Preparation of $\text{TiO}_2$ photocatalysts

##### 3.1.1 Pure $\text{TiO}_2$

A non-aqueous sol-gel method was employed for the preparation of  $\text{TiO}_2$  nanoparticle. Tetrabutyl orthotitanate ( $\text{Ti}(\text{OBu})_4$ , 97%, Fluka), anhydrous ethanol (99.9%, Mallinckrodt) and nitric (65%, Scharlau) /hydrochloric (37%, Merck) solutions were used as Ti source, solvent and reaction catalyst, respectively. Note that hydrochloric acid and nitric acid were used to study the effect of phase transformation at room temperature. Since the  $\text{Ti}(\text{OBu})_4$  is very sensitive to humidity, all the glassware were dried in the oven prior to each use. The sequence of preparation is divided into two routes using different hydrolysis catalysts.

##### A. Using HCl acid as a hydrolysis catalyst (Sol 1)

The preparation method of the  $\text{TiO}_2$  sol was modified from the previous work of Zhang. [53]. Various amounts of  $\text{Ti}(\text{OBu})_4$  were dissolved in anhydrous ethanol containing small amount of water and hydrochloric acid. The resulted solution was stirred at room temperature for 1 h. The concentration of  $\text{Ti}(\text{OBu})_4$  was varied between 0.07 - 0.7 M to study the effect of alkoxide concentration on kinetic of sol formation. The concentration of starting reagent and various compositions of  $\text{H}_2\text{O}$ : EtOH: HCl are listed in Table 3.1.

### B. Using HNO<sub>3</sub> as a hydrolysis catalyst (Sol\_2)

The preparation method for Ti precursor having nitric acid as catalyst was similar to the method described above except that various amounts of nitric acid were used in place of hydrochloric and the Ti concentration was fixed at 0.4 M. Then the resulted solution was stirred at room temperature for 3 hours. The amounts of all starting reagents are summarized in Table 3.2 [54].

The resulted precursors obtained from Sol\_1 and Sol\_2 were then kept in sealed containers for several weeks. To collect the TiO<sub>2</sub> powders, the volume of the TiO<sub>2</sub> suspension was reduced by rotor-evaporation and finally dried at 50°C for 1 day. Some of the TiO<sub>2</sub> powders were calcined in air at 300-700°C for 4 hours. The preparation procedure is shown schematically in Figure 3.1.

#### 3.1.2 V-doped TiO<sub>2</sub>

Vanadyl acetylacetonate (C<sub>10</sub>H<sub>14</sub>O<sub>5</sub>V, 97% Fluka) was the precursor used for V doping. The vanadium solution was prepared by dissolving C<sub>10</sub>H<sub>14</sub>O<sub>5</sub>V in anhydrous ethanol. The ultrasonication was applied until the green-transparent solution was obtained. The amount of V used in this work was varied as shown in Table 3.3 (0.01, 0.05, 0.10, 0.20, 0.50, 1.0, 2.0, 5.0 and 10.0 mole% relative to the amount of Ti in the precursor solution). The V-doped TiO<sub>2</sub> powders were obtained after finishing the evaporation, drying (45°C in air for 1 day) and calcination (300-800°C in air for 4 h). Flow chart of preparation method is shown in Figure 3.1, while heating profile of the powders is shown in Figure 3.3.

Table 3.1 Experimental conditions for the preparation of pure  $\text{TiO}_2$  (referred to as "Sol\_1", using HCl as a hydrolysis catalyst)

Samples code	Concentration of $\text{Ti}(\text{OBU})_4$ (Molar)	$\text{H}_2\text{O}$ : EtOH: HCl (Volume ratio)
Sol_1Aa	0.07	1:3:1
Sol_1Ab	0.20	
Sol_1Ac	0.30	
Sol_1Ad	0.50	
Sol_1Ae	0.70	
Sol_1Ba	0.07	1:2:2
Sol_1Bb	0.20	
Sol_1Bc	0.30	
Sol_1Bd	0.50	
Sol_1Be	0.70	
Sol_1Ca	0.07	1:1:3
Sol_1Cb	0.20	
Sol_1Cc	0.30	
Sol_1Cd	0.50	
Sol_1Ce	0.70	
Sol_1Da	0.07	1.5:1.5:2
Sol_1Db	0.20	
Sol_1Dc	0.30	
Sol_1Dd	0.50	
Sol_1De	0.70	
Sol_1Ea	0.07	2:2:1
Sol_1Eb	0.20	
Sol_1Ec	0.30	
Sol_1Ed	0.50	
Sol_1Ee	0.70	

Table 3.2 Experimental conditions for the preparation of pure TiO<sub>2</sub> (referred to as "Sol\_2", using HNO<sub>3</sub> as a hydrolysis catalyst)

Samples code	Concentration of Ti(OBu) <sub>4</sub> (Molar)	H <sub>2</sub> O: EtOH: HNO <sub>3</sub> (Volume ratio)
Sol_2A	0.4	10: 10: 2
Sol_2B		10: 10: 3
Sol_2C		10: 10: 4
Sol_2D		10: 10: 5
Sol_2E		10:10:2.6

Table 3.3 Experimental conditions for the preparation of V-doped TiO<sub>2</sub> (derived from Sol\_2C and Sol\_2D)

Samples code	H <sub>2</sub> O: EtOH: HNO <sub>3</sub>	%V-dopant
Sol_2C_0.01V	10: 10: 4	0.01
Sol_2C_0.05V		0.05
Sol_2C_0.10V		0.10
Sol_2C_0.20V		0.20
Sol_2D_0.01V	10: 10: 5	0.01
Sol_2D_0.05V		0.05
Sol_2D_0.10V		0.10
Sol_2D_0.20V		0.20
Sol_2D_0.50V		0.50
Sol_2D_1.00V		1.00
Sol_2D_2.00V		2.00
Sol_2D_5.00V		5.00
Sol_2D_10.0V		10.0

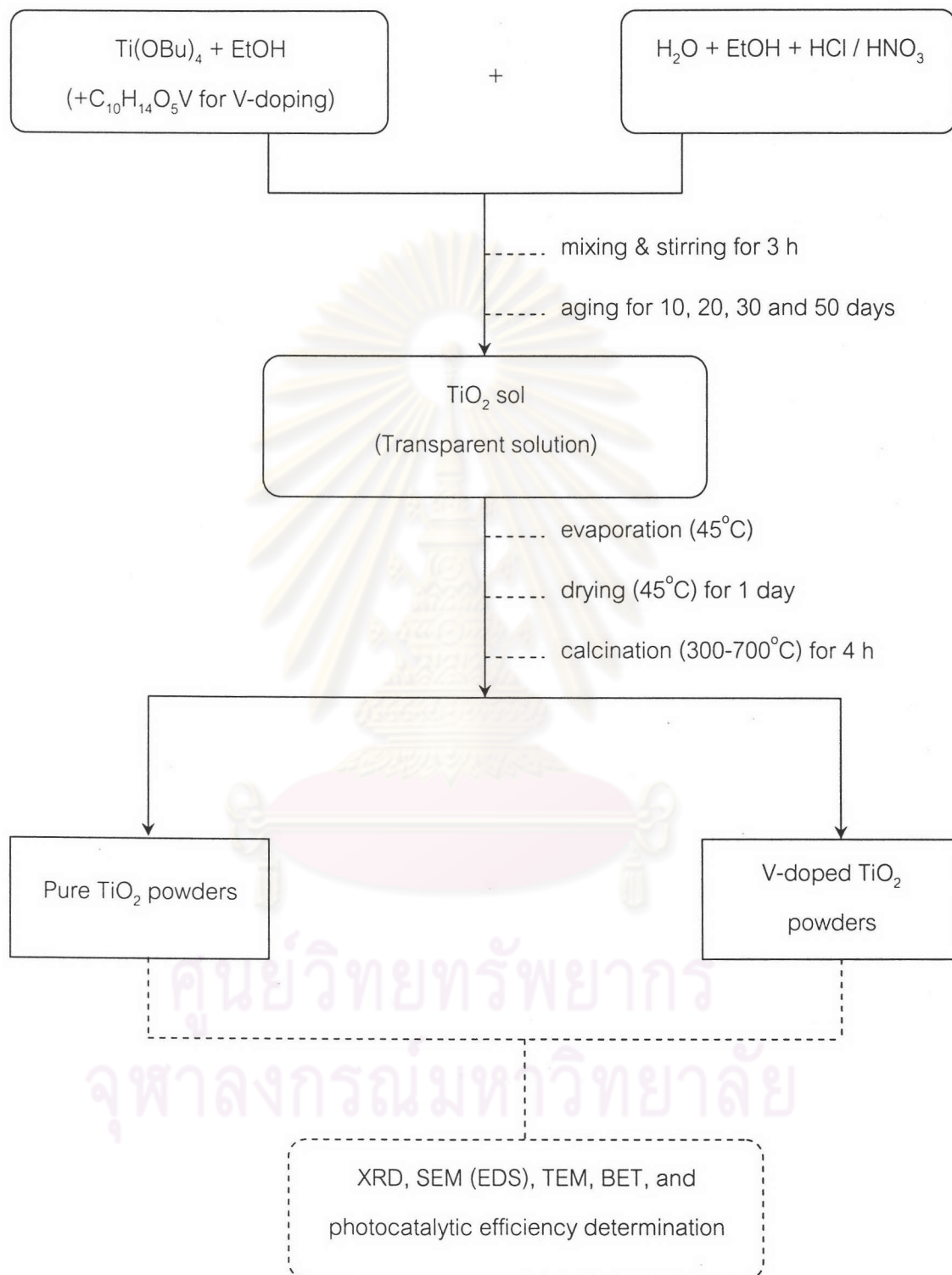


Figure 3.1 Flow chart of preparation procedure for pure and V-doped TiO<sub>2</sub>

### 3.2 TiO<sub>2</sub> coating on substrate

The TiO<sub>2</sub> sol was coated onto various substrates such as Al<sub>2</sub>O<sub>3</sub> beads (~ 600 μm) and glass-tubes (diameter = 0.75 in, Length = 2.94 in). Before each coating, substrates were cleaned with strong oxidizing solution, which is a mixture of H<sub>2</sub>O, HCl and H<sub>2</sub>O<sub>2</sub> (volume ratio = 6:1:1). The oxidizing solution was prepared by adding HCl into the distilled water (H<sub>2</sub>O) and heated to 70°C. Then the H<sub>2</sub>O<sub>2</sub> was slowly added into the previous solution. The substrates were soaked in this solution for 30 minute. Then, the cleaned substrates were washed with a large amount of distilled water, acetone, and rinsed with anhydrous ethanol. Finally, the substrates were dried at 100°C for 2 hours.

A dip and sprayed coating were employed for TiO<sub>2</sub> coating on the Al<sub>2</sub>O<sub>3</sub> beads and the glass-tubes, respectively. For dip coating, the Al<sub>2</sub>O<sub>3</sub> beads were soaked in the TiO<sub>2</sub> sol at room temperature for 1, 3, and 5 times, and soaking for 1 week. Each coating time consisted of soaking and dried process. First, the cleaned Al<sub>2</sub>O<sub>3</sub> beads were soaked into a fresh prepared TiO<sub>2</sub> sol for 1 h. Then, the TiO<sub>2</sub> coated Al<sub>2</sub>O<sub>3</sub> was separated and dried at 45°C for 1 h (coating for 1 time). The same procedure was repeated for 3 and 5 times, respectively. On the other hand, at soaking time for 1 week, the Al<sub>2</sub>O<sub>3</sub> beads were continuously soaked in the sol without any separation until 1 week. After that the coating products were dried at 45°C for 2 days.

For the spray coating, an airbrush (Prospray-Mk-2) was used. The TiO<sub>2</sub> sol was sprayed inside of the glass tubes for 1, 4, 8 and 12 cycles. Each coating cycle was divided into three steps as shown in Figure 3.2 (a, b, c). In the first step, the 2 inch long glass tube was positioned then the sol was sprayed to an "area 1" as shown in Figure 3.2 (a). In the second step, a "2 inch" tube was replaced by a "1 inch", and the sol was sprayed to an "area 2" as shown in Figure 3.2 (b). Lastly, the same procedure in the first step was applied to the "area 3" as shown in Figure 3.2 (c).

After coating, all samples were dried at 45°C for 2 days and then calcined at 400°C for 4 hours. The flow chart of the cleaning and coating processes is shown in Figure 3.4. The heating profile of the coated sample is also shown in Figure 3.3.

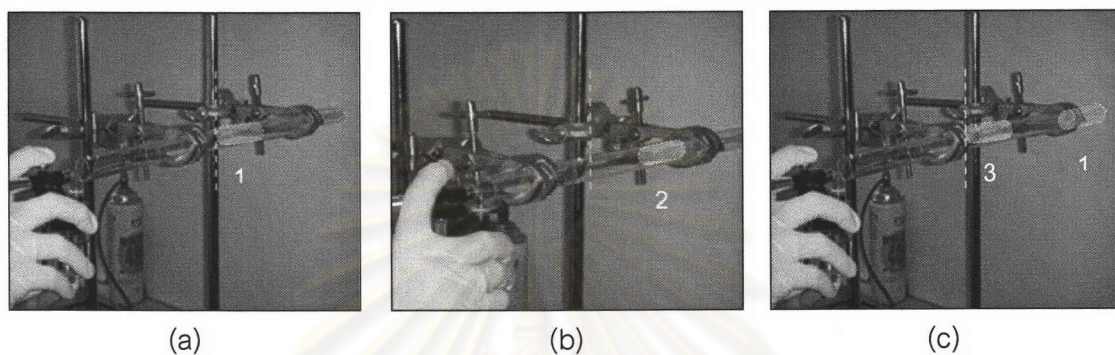


Figure 3.2 The model of spraying method; (a) area 1, (b) area 2 and (c) area 3

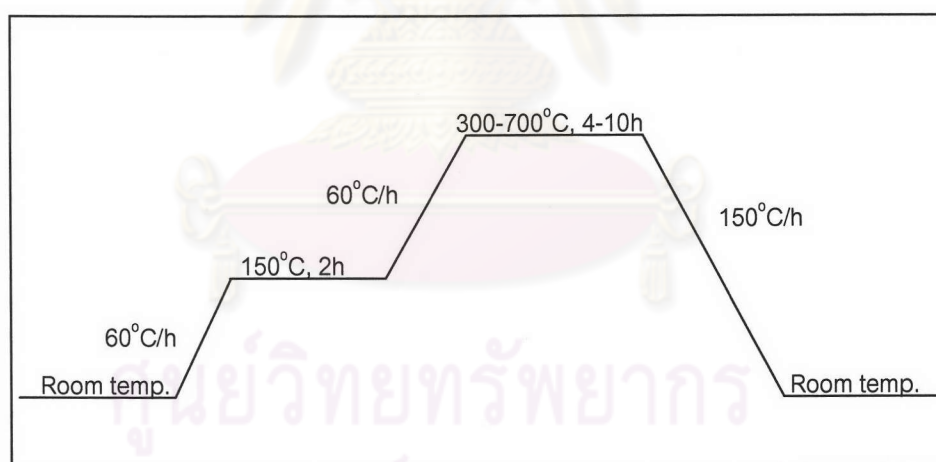
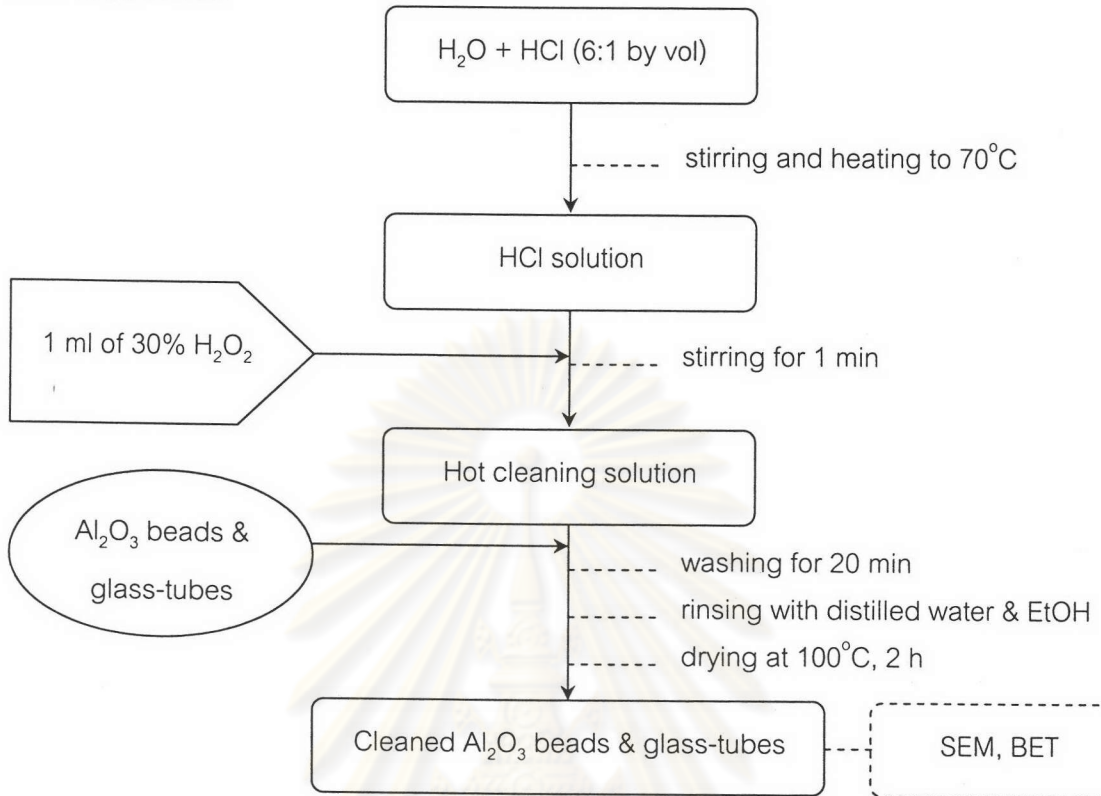


Figure 3.3 Heating profile of  $\text{TiO}_2$  powders and  $\text{TiO}_2$ -coated samples

### Cleaning process



### Coating process

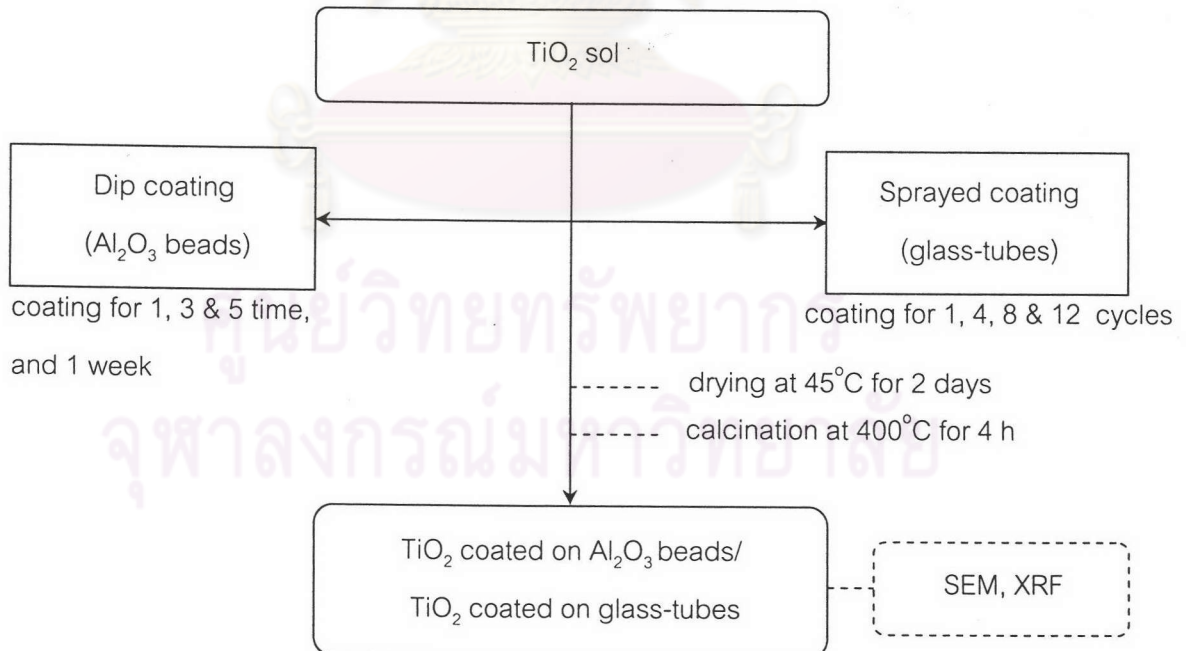


Figure 3.4 Flow chart of the substrates cleaning and coating processes



### 3.3 Material characterization

#### 3.3.1 Crystal structure and phase composition

Crystal structure of the TiO<sub>2</sub> catalysts obtained was determined using a JEOL JDX-3530 X-ray diffractometer. The X-ray source was Cu-K<sub>α</sub> (λ = 0.154 nm). It was operated at a voltage of 40 kV and a current of 25 mA with a scanning rate of 0.2 degree. s<sup>-1</sup>. The standard diffraction patterns of the Joint Committee Powder Diffraction Standard (JCPDS) were used to compare the peak positions obtained from the samples.

The phase composition was calculated from the peak intensity ratio in the XRD patterns according to Spurr and Meyers's equation: [20]

$$W_A = \frac{1}{1 + 0.8(I_A / I_R)} \times 100 \quad (3.1)$$

$$W_R = 100 - W_A \quad (3.2)$$

Where ;

$W_A$  = Weight fraction of anatase

$W_R$  = Weight fraction of rutile

$I_A$  = Integrated intensities of anatase (101)

$I_R$  = Integrated intensities of rutile (110)

The crystallite size was estimated from an XRD line broadening using the Debye-Scherrer equation: [20]

$$d = \frac{\kappa\lambda}{b \cos\theta} \quad (3.3)$$

Where;

- $d$  = X-ray crystallite size (nm)
- $\lambda$  = Wave length (0.154 nm.)
- $\kappa$  = Debye-Scherrer Constant (1.0)
- $b$  = Full width at half maximum (FWHM) of the broadening peak
- $\theta$  = Bragg angle of the reflection (degree)

### 3.3.2 Microstructure and morphology

The morphology of the TiO<sub>2</sub> powder, as well as dispersion of the TiO<sub>2</sub> particles on substrates were observed by a scanning electron microscope (SEM, JEOL JSM-5440) operated at a accelerating voltage of 20 KeV. Before the SEM observation, the samples were adhered on the aluminum stubs with a piece of double sided conducting tape and dried at 100°C for 15 min. The gold layer was sputtered onto the surface of the samples to avoid charging effect. Energy dispersive X-ray spectroscopy (EDS, Oxford, Inca 300) was used to determine the amount of V-doping.

The microstructure and crystallite size of the TiO<sub>2</sub> powders were determined by direct observation using a transmission electron microscope (TEM, JEOL JEM-2010). For the preparation of TEM samples, small amount of TiO<sub>2</sub> powders was suspended in ethanol. Then, carbon-coated copper grid was dipped into the TiO<sub>2</sub> suspension. Finally, the samples were dried in air.

### 3.3.3 Specific surface area

The Brunauer-Emmett-Teller (BET) method was employed to determine the specific surface area of the prepared catalysts. It was obtained by measuring the quantity of nitrogen ( $N_2$ ) gas adsorbed onto the  $TiO_2$  surface by using a Flow SorbII 2300. The  $TiO_2$  powder of about 0.15 gram was dried and outgassed at  $120^\circ C$ . Then the sample cell was moved to the analysis port and immersed into liquid nitrogen. Finally, the amount of  $N_2$  adsorbed was measured and the specific surface area of the samples was calculated from the adsorption data in the relative pressure ( $P/P_0$ ) range of 0.05-0.25.

### 3.3.4 Chemical composition analysis

The X-Ray fluorescent (XRF, Philips PW-2404) analysis was performed to analyze the  $TiO_2$  content dispersing on the  $Al_2O_3$  beads. 0.5 gram of the samples was mixed with 0.4 gram of tableting aid or wax (Hoechst C micropowder). The weight ratio of the samples to the wax was about 5:1. The mixed powders were pressed under a pressure of 35 MPa to form a pellet of 30 mm in diameter.

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### 3.4 Photocatalytic efficiency determination

#### 3.4.1 Pure $\text{TiO}_2$ powders and $\text{TiO}_2$ coating on $\text{Al}_2\text{O}_3$ beads

The photocatalytic efficiency of the  $\text{TiO}_2$  products (pure  $\text{TiO}_2$ , V-doped  $\text{TiO}_2$  powders, and  $\text{TiO}_2$  coated on  $\text{Al}_2\text{O}_3$  beads) was determined by measuring a Cibracron Red (CR, Rama textile Co; 50 ppm) degradation under UV illumination. A 0.10 gram of  $\text{TiO}_2$  catalyst and a 1.72 g of  $\text{TiO}_2$  coating on  $\text{Al}_2\text{O}_3$  was dispersed in 10 ppm CR solution (200 ml). The pH was adjusted to 3 by adding sulfuric acid. Then the suspension was vigorously stirred by magnetic stirring to keep the  $\text{TiO}_2$  particles suspended. Air was supplied to the suspension through the distributor to make the suspension saturated with oxygen. The suspension was kept in the dark place to allow saturated adsorption of CR on the  $\text{TiO}_2$  surface. Then, the dispersion was continuously exposed to UV irradiation (20 W,  $\lambda = 350\text{-}400$  nm) for 6 hours. A 10 ml-aliquot was sampled at various time intervals. It was centrifuged and then filtered through a millipore membrane filter to separate the  $\text{TiO}_2$  particle prior to analysis. Variations in the concentration of CR in each aliquot were measured by using a UV-visible spectroscope (V-530, Jasco Corp.). A drawing of the apparatus set up is shown in Figure 3.5.

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### 3.4.2 TiO<sub>2</sub> coating on glass tubes

The photocatalytic efficiency of the TiO<sub>2</sub> coated on glass-tube was tested by measuring methanol (CH<sub>3</sub>OH) gas degradation under UV irradiation. It was equipped with a UV lamp and a quartz sleeve, which was made of diffused quartz to allow UV light, penetrates inside. A liquid phase of methanol was heated up to 60°C, in order to generate the gas phase of methanol. Then, a stream of O<sub>2</sub> gas was passed through a mass flow controller. It combined with the methanol gas to produce the desired gas mixture, which subsequently entered to the photoreactor. The retention times and inlet concentrations of both methanol and O<sub>2</sub> gases were adjusted using the mass flow controller and the rotameter, respectively. The reaction was started by exposed to UV irradiation (3,000 W,  $\lambda$  = 254 nm) for 8 hours. Finally, the exhaust CO<sub>2</sub> samples were taken from the outlet of the reactor and measured by using a gas chromatograph, as shown in Figure 3.6.



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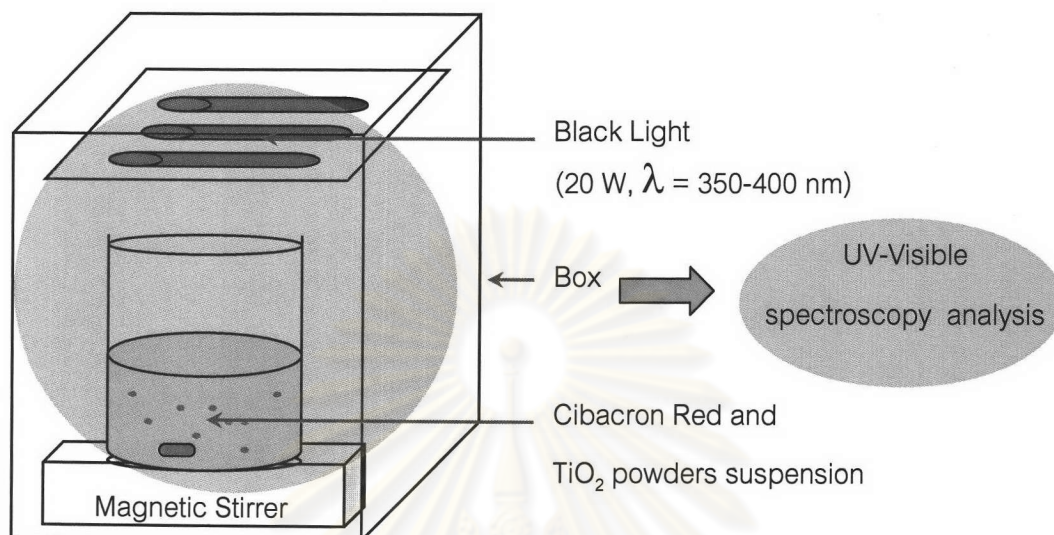


Figure 3.5 Schematic illustration of the photocatalytic efficiency determination in water system

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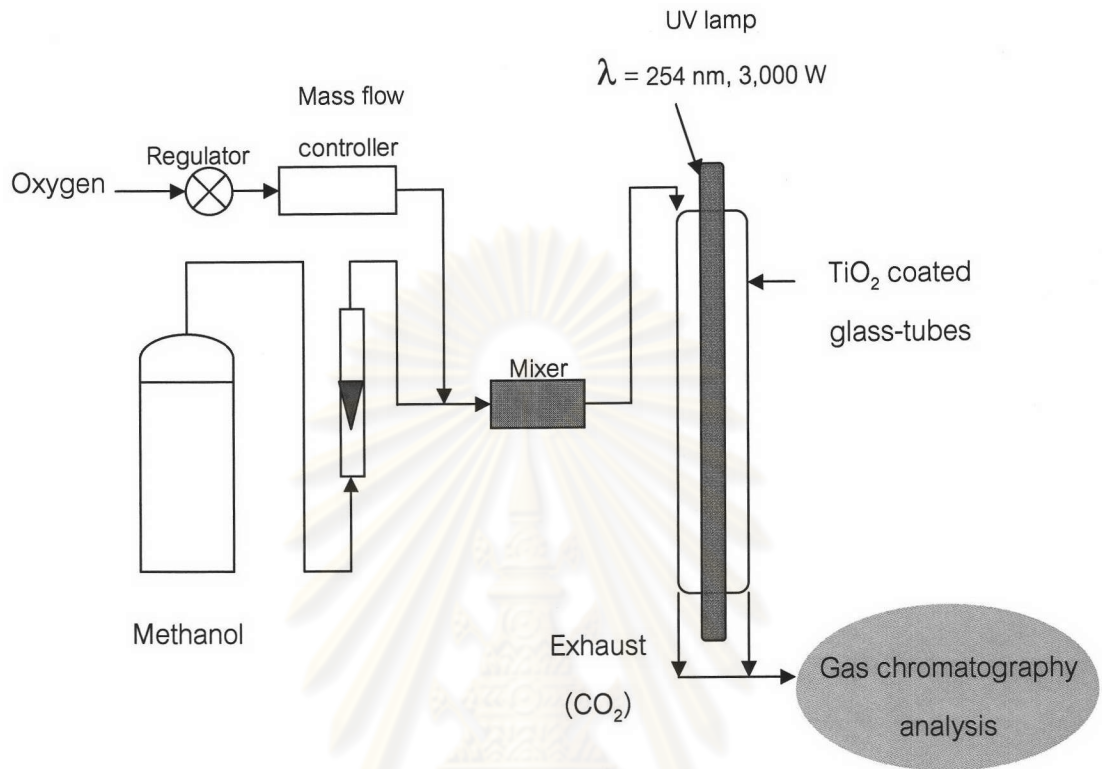


Figure 3.6 Schematic illustration of the photocatalytic efficiency determination in gas system

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