CHAPTER 2

EXPERIMENTAL

2.1 Materials

Chemical	**Purity**	**Molecular formular**	**Molecular weight**	**Company**
Titanium tetraisopropoxide	97%	$C_{12}H_{28}O_4Ti$	284.2	Sigma-Aldrich
Titanium dioxide, P25 Degussa	99%	TiO_2	80	Degussa Germany
Ethanol absolute	100%	C_2H_5OH	46.08	Ajax
Ammonia	25%	NH_3	17	Merck
Percholric acid	70%	$HClO_4$	100.47	Ajax
Nitric acid	70%	HNO_3	63.01	Ajax
Ammonium metavanadate	98%	NH_4VO_3	116.99	Ajax
Iron (III) nitrate	98%	$Fe(NO_3)_3 \cdot 9H_2O$	353.18	Ajax
Copper (II) nitrate	98%	$Cu(NO_3)_2 \cdot H_2O$	232.59	Ajax
Sucrose	99%	$C_{12}H_{22}O_{11}$	342.3	Ajax
Phenol	88%	C_6H_5OH	54.1	Sigma-Aldrich
Oxalic acid	98%	$C_2H_2O_4 \cdot 2H_2O$	126.07	Aldrich
Formic acid	90%	$HCOOH$	46.02	Ajax
Methanol	99.8%	CH_3OH	32.04	Aldrich
Malonic acid	99%	$CH_2(COOH)_2$	104.06	Ajax
Magnesium oxide	99%	MgO	40.30	BDH

2.2 Instruments

1. UV-Vis diffuse reflectance spectroscope (UV-Vis DRS)-Varian Cary 5
2. X-ray diffractometer (XRD) – PW-3719, Philip Analytical and Bruker AXS D8
3. Transmission electron microscope (TEM) and energy dispersive X-ray spectroscope (EDS) – JEOL JEM-2010
4. Scanning electron microscope (SEM) and energy dispersive X-ray spectroscope (EDS) – JEOL JSM6335F
5. Brunauer-Emmett-Teller (BET) – Micromeritics Tristar 3000
6. X-ray photoelectron spectroscope (XPS) – Alpha 110 Hemispherical Analyzer, Model 8017 digital electronics and Twin Anode XR3E2 for X-ray source
7. Fourier transform infrared spectrophotometer (FT-IR) – Bruker, Model Tenser 27
8. Spiral photoreactor
9. UV-lamp – NEC 20 watt T10 black light blue
10. Solar light – Oceanlife, 50% natural daylight 6000K-50% actinic 03 blue, 18 watt
11. Visible light – Davis 33 cool white, 18 watt
12. Peristaltic pump - Masterflex Model 7553-79
13. Conductivity meter – JENWAY 4330 and EUTECH PC 5500

2.3 Sample preparations

2.3.1 The modified sol-gel method

2.3.1.1 Preparation of pure TiO_2

Pure titanium dioxide was directly prepared by hydrolysis and condensation of titanium tetraisopropoxide (TTIP) using 20 ml in absolute ethanol 250 ml and mixed these two solutions until a homogeneous solution was obtained. The solution was loaded into cellophane membrane pouch and placed in solution containing a 1:1 v/v ratio (350 ml) of absolute ethanol and Milli-Q water or deionized water with 0.5-1% concentrated (25%) ammonia. The solutions inside and outside the cellophane pouch were kept constant stirring with magnetic stirrer bar and heated temperature at 70-80 °C for 1h as shown in Figure 2.1. After the dialysis process was completed, the mixture solution in the pouch was then allowed to centrifuged (7500 rpm, 10 min) and rinsed with Milli-Q water or deionized water 3 times and then dries in an oven at 60 °C for 24h. The powder was calcined in a muffle furnace over the temperatures range of 400-700 °C for 3h.

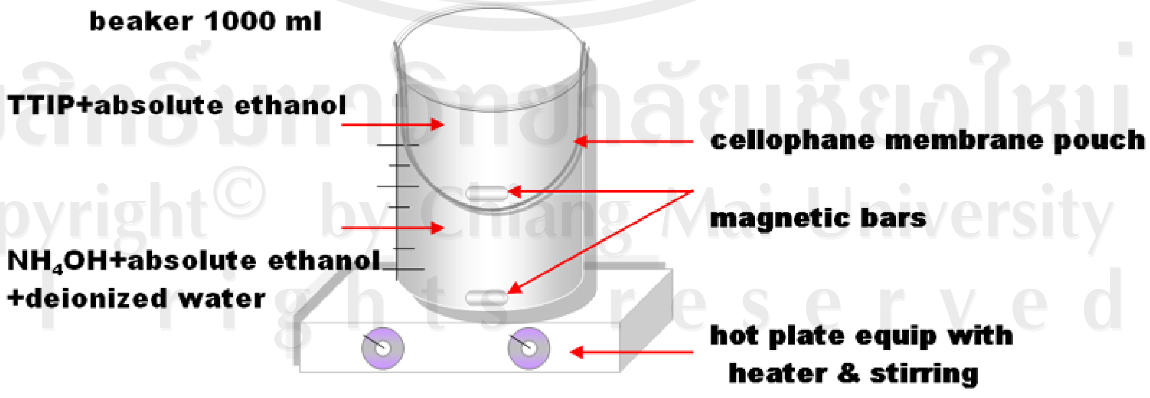

Figure 2.1 Schematic of the modified sol-gel synthesis method

2.3.1.2 Preparation of transition metal ions (V, Cu, and Fe) doped TiO_2

Transition metal ions (V, Cu, and Fe) doped TiO_2 were prepared by using titanium tetraisopropoxide as a Ti-precursor. Ammonium metavanadate (NH_4VO_3), copper (II) nitrate ($Cu(NO_3)_2 \cdot H_2O$), and iron (III) nitrate ($Fe(NO_3)_3 \cdot 9H_2O$) were used as the metal precursors. Titanium tetraisopropoxide 250 ml was dissolved in absolute ethanol 250 ml and mixed until a homogeneous solution was obtained. A solution containing the salt of the desirable metal dopant ion was added to the mixture. The amount of V, Cu, Fe ions added was calculated of 0.1, 0.5, 1, 2, 5, and 10 at.%. The mixture solution was loaded into a pouch type cellophane membrane and placed in a clear solution which contained a 1:1 (v/v) ratio of 350 ml absolute ethanol and Milli-Q water or deionized water with additional of 0.5-1 % concentrated ammonia solution (25 %) for 1h. After the dialysis process was completed, the mixture in the pouch was then centrifuged (7500 rpm, 10 min), washed with Milli-Q water or deionized water 3 times and then dried in an oven at 60 °C for 24h. The powder was finally calcined in a muffle furnace at a temperature of 400 °C for 3h. The condition of calcination temperature and the time (400 °C for 3h) gave high photocatalytic activity.

2.3.2 The impregnation method

2.3.2.1 Preparation of Fe-doped TiO_2

Pure titanium dioxide powder previously prepared an optimum condition calcined 400 °C for 3h from the modified sol-gel method was mixed with the solution of iron (III) nitrate ($Fe(NO_3)_3 \cdot 9H_2O$) in deionized water. Mixed the content well until it formed a smooth slurry and then dry in an oven at 80 °C for 2h. Grind the powder in an agate mortar and put to the crucible to calcined at 400 °C for 3h.

2.4 Sample characterization

In this study, the samples of pure TiO_2 and V, Cu, Fe-doped TiO_2 were obtained from the modified sol-gel method and the powder of Fe-doped TiO_2 were obtained from the impregnation method. The characterization of the powder were included X-ray diffraction spectroscopy (XRD), Scanning electron microscopy (SEM), Transmission electron microscopy (TEM), Energy dispersive X-ray spectroscopy (EDS), UV-Vis diffuse reflectance spectroscopy, X-ray photoelectron spectroscopy (XPS), and Fourier transform infrared spectrophotometry (FT-IR). The photocatalytic activity of all samples was examined by the studying the mineralization of sucrose, phenol, oxalic acid, formic acid, methanol, and malonic acid under UVA, solar light, and visible light irradiation.

2.4.1 UV-Vis diffuse reflectance spectroscopy (UV-Vis DRS)

UV–Vis diffuse reflectance spectra (DRS) data were obtained from the dry-pressed sample disks of pure TiO_2 and V, Cu, Fe-doped TiO_2 by using a scan UV–Vis spectroscopy (Varian Cary 5) equipped with an integrating sphere assembly, using MgO as reflectance sample. The absorption spectra were obtained and calculated by analyzing the reflectance measurement with Kubelka-Munk emission function. The spectra were recorded at room temperature in the range of 300-700 nm.

2.4.2 X-ray diffraction (XRD)

Phase compositions and crystallinity of pure TiO_2 and V, Cu, Fe-doped TiO_2 were examined by using XRD. XRD patterns obtained from the diffractometers of

PW-3719, Philip Analytical and Bruker AXS D8 using CuK_α radiation at a scan rate (2θ) of 0.5° s^{-1} were used to determine the identity of any phase present and their crystallite sizes. Rietveld refinement was carried out to determine the quantitative composition of the phases formed during the calcination process.

2.4.3 Transmission electron microscopy (TEM)

The morphology and particle sizes of pure TiO_2, V, Cu, Fe-doped TiO_2 were examined by using TEM, model JEOL JEM-2010 at an acceleration voltage of 200 kV. The element compositions of all samples were investigated by using energy dispersive X-ray spectroscopy (EDS). TEM imaging and EDS analysis of all samples were dispersed in absolute ethanol with 20 min sonication and one drop of the suspension was placed onto a carbon-coated copper grid. The deposit was dried in air prior to imaging.

2.4.4 Scanning electron microscopy (SEM)

The element of copper on Cu-doped TiO_2 powder could not be found by using EDS in TEM instrument because the grid for TEM measurement composing carbon-coated copper. Therefore, the element of copper on Cu-doped TiO_2 was investigated on carbon tape substrate for EDS analysis in SEM instrument. The morphology and particle sizes of Cu-doped TiO_2 were examined by SEM, model JEOL JSM6335F. SEM imaging and EDS analysis, the powder of all samples were scattered on a carbon tape.

2.4.5 BET-Specific surface area (SSA)

The Brunauer–Emmett–Teller (BET) specific surface areas (SSA) of pure TiO_2 and V, Cu, Fe-doped TiO_2 samples were determined through nitrogen adsorption at 77 K (Micromeritics Tristar 3000). All samples were degassed at 150 °C for 1h before the measurement. The particle diameters of pure TiO_2 and V, Cu, Fe-doped TiO_2 were calculated from specific surface area and density of V, Cu, Fe-doped TiO_2 as $d_{\mathrm{BET}} = 6/[(\rho_{\mathrm{TiO2}}\times \mathrm{SSA}_{\mathrm{TiO2}}\times(\mathrm{wt.\%\ of\ TiO_2})) + (\rho_{\mathrm{V,\ Fe,\ Cu}}\times \mathrm{SSA}_{\mathrm{TiO2}}\times(\mathrm{wt.\%\ of\ V,\ Fe,\ Cu}))]$ equation, where $\rho_{\mathrm{anatase}} = 3.84\ \mathrm{g/cm^3}$, $\rho_{\mathrm{rutile}} = 4.26\ \mathrm{g/cm^3}$, $\rho_{\mathrm{V}} = 6.11\ \mathrm{g/cm^3}$, $\rho_{\mathrm{Fe}} = 7.87\ \mathrm{g/cm^3}$, $\rho_{\mathrm{Cu}} = 8.92\ \mathrm{g/cm^3}$.

2.4.6 X-ray photoelectron spectroscopy (XPS)

The elemental composition and oxidation state of elements were analyzed by X-ray photoelectron spectroscopy (XPS, Alpha 110 Hemispherical Analyzer using model 8017 digital electronics and Twin Anode XR3E2 for X-ray source). The samples of pure TiO_2, Fe, Cu-doped TiO_2 obtained from the modified sol-gel method were analyzed. The samples were scattered on carbon tape before measurement by using XPS equipment.

2.4.7 Fourier transform infrared spectrophotometry (FT-IR)

FT-IR spectra of pure TiO_2, Fe, Cu-doped TiO_2 were recorded by Bruker, Model Tenser 27 FT-IR instrument. Samples obtained from photooxidation of pure TiO_2, Fe, Cu-doped TiO_2 with oxalic acid and formic acid were analyzed. All powders were mixed with KBr and made to form a thin film before measurement.

2.4.8 Photocatalytic activity studies

2.4.8.1 Apparatus

In this work, V, Cu, Fe-doped TiO_2 prepared by the modified sol-gel method were tested for photocatalytic activity by using the setup of spiral photoreactor at ARC Centre of Excellence for Functional Nanomaterials, School of Chemical Sciences and Engineering, The University of New South Wale (UNSW), Sydney, Australia. The Fe-doped TiO_2 prepared by the impregnation method were measured the photoactivity by using the setup of spiral photoreactor reconstructed (similar to the one at UNSW's set up) at Nanoscience Research Laboratory, Faculty of Science, Chiang Mai University (CMU), Thailand. A schematic diagram of the spiral photoreactor at UNSW and CMU was given in Figure 2.2. The spiral photoreactor consisted of (i) 70 cm long spiral reactor. The spiral reactor was made out of borosilicate glass tube with an outside diameter of 5 mm and the wall thickness of 1 mm. Photocatalytic reaction was initiated by illuminating the suspension which suspended inside the tube with, UV-lamp (NEC 20 watt T10 black light blue), solar light (50% natural daylight 6000K-50% actinic 03 blue, 18 watt) a fluorescent lamp (Davis 33 cool white, 18 W) filtered with a double layer of Rosco® E-color UV filter to remove any UV component (ii) The glass spiral filtered with the lamp was covered with aluminum foil to prevent both the intrusions of ambient light and the emission of the harmful UV from the lamp. The attachment to the photoreactor were (iii) a peristaltic pump (Masterflex Model 7553-79) (iv) a conductivity meter (JENWAY 4330 (UNSW's setup) and EUTECH PC 5500 (CMU's setup)) and (v) a gas-liquid separator. All components were connected together using masterflex flexible tubing which was resistant to leaching of any organics.

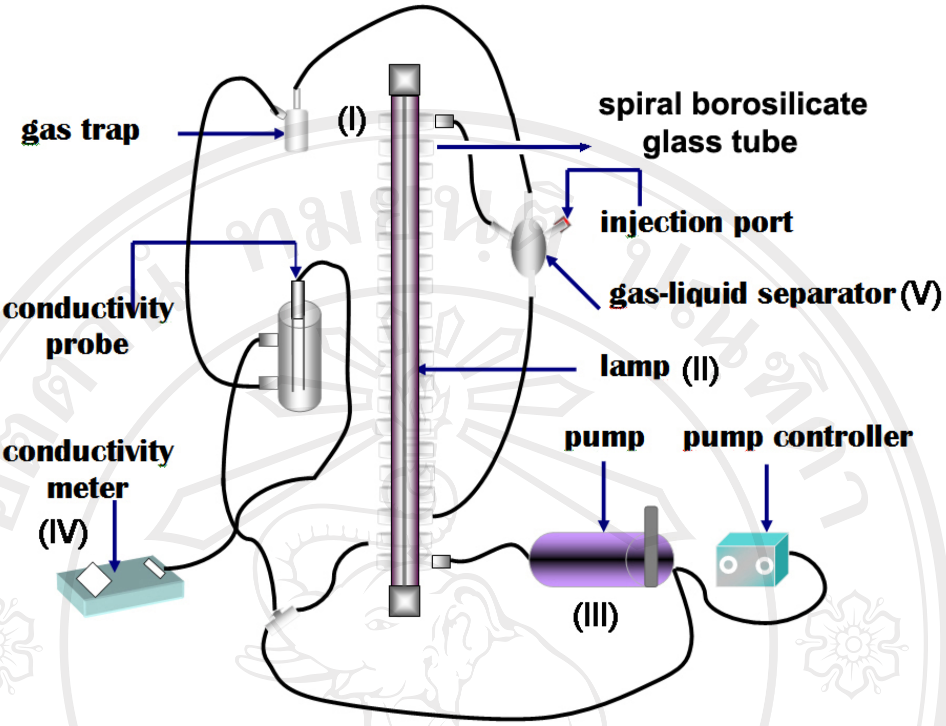

Figure 2.2 Scheme of spiral photoreactor

2.4.8.2 Preparation of photocatalyst suspension and operation

A 50 mL suspension of TiO_2 or V, Cu, Fe-doped TiO_2 having a loading of 1 g/L was prepared and its pH was adjusted to 3.0 by using 0.1 M perchloric acid. Acidification removes the possibility of CO_2 adsorption onto the catalyst surface and ensures maximum release into the solution of the carbon dioxide generated as the organic photodegrades. Perchloric acid was used since the presence of perchlorate anion has been found to provide the least interference in the operation of the equipment. The suspension was dispersed in an ultrasonic bath for 20 min before it was discharged into the spiral photoreactor. The suspension was circulated through out the spiral photoreactor. The suspension was subjected to a “carbon burn off” period, when it was illuminated to remove any contaminants adsorbed on the photocatalyst surface. The carbon dioxide generation was monitored using the conductivity meter (iv) in unit µSiemens/cm. During carbon burn off, the conductivity reading increased to a constant value which was an indicating or that all impurities were removed. The system was then slowed to equilibrate at ambient atmospheric conditions by opening a valve at an exit port (v).

Various organic carbon load (500 µg of carbon (500 µg C)), as sucrose, phenol, oxalic acid, formic acid, methanol, and malonic acid were injected into photocatalyst suspension through the inlet port (v). The catalyst-organic substrate mixture was circulated for 5 minutes without light illumination to ensure dispersion of the organic compound throughout the slurry. The lamp was then switched on. Subsequently, the increase in conductivity value was recorded every 15 seconds at UNSW and 1 second at CMU until the reaction ended. At the end of the photoreaction, the lamp was switched off and the system flushed several times with Milli-Q water. All runs were repeated at least twice.

2.4.8.3 Calibration curve measurement

The spiral photoreactor was calibrated to obtain a relationship between the conductivity value and the amount of organic degraded. A suspension of Degussa P25 as a catalyst loading (1 g/L) was used during the calibration. The photocatalyst was circulated through the reactor and subjected to carbon burn off. After carbon burn-off, a known amount of carbon was added as sucrose (100-2000 µg of carbon) to the system and the lamp switched on. The conductivity value increased and the final conductivity reading was recorded as previous section which, corresponding to the known amount of carbon added. Calibration was relied on the establishing of the relation between carbon mass in the sample and the conductivity measurement values.

For calculation, at the end of each run the recorded data which consisted of the increased in conductivity value was converted to the amount of carbon interpolated from the expression obtained from the calibration curve.