CHAPTER 2

Experimental

2.1 Chemical reagents, equipments and instruments

2.1.1 Chemical reagents (All chemical reagent were analytical grade)

1) Zinc acetate dihydrate, $Zn(CH_3COO)_2 \cdot 2H_2O$, MW = 219.50, assay 99%, Guangdong Guanghua Chemical, China
2) Tin chloride dihydrate, $SnCl_4 \cdot 2H_2O$, MW = 225.63, assay 98%, Merck, Germany
3) Sodium hydroxide, NaOH, MW = 40.00, assay 97.0%, RCI Lab–scan, Thailand
4) Ethanol, C_2H_5OH, MW = 46.07, assay 95%, QRec, New Zealand
5) Absolute ethanol, C_2H_5OH, assay 99.9%, QRec, New Zealand
6) Methyl orange, $C_{14}H_{14}N_3NaO_3S$, MW = 327.33, Riedel–de Haen AG, China
7) Deionized water

2.1.2 Equipments

1) Analytical balance, Model PA–SERIES, Pioneer, Ohaus, USA
2) Oven, Model UE–400, Memmert, Germany
3) Hotplate and magnetic stirrer, Model C–MAG HS 7, IKA, Germany
4) pH meter, Model S20–K, Mettler Toledo, U.S.A.
5) Ultrasonic bath, Model Sonorex RK102H, Bandelin Germany
6) Table top centrifuge, Model PLC–03, Germany
7) Ultraviolet Germicide Lamp, Model T8 15W, NARWAR, Germany
8) X–ray Diffractometer (XRD), Model MiniflexII, Rigaku, Japan
9) X–ray Photoelectron Spectrometer (XPS), Model Axis Ultra DLD, Kratos Analytical, UK
10) Fourier Transform Infrared (FTIR) Spectrometer, Model Bruker Tensor 27, Germany
11) Scanning Electron Microscope (SEM), Model JEM–6335F, JEOL, Japan
12) Transmission Electron Microscope (TEM), Model JEM–2010, JEOL, Japan
13) Surface area analyzer, Model Autosorb 1 MP, Quantachrome, U.S.A.
14) Photoluminescence (PL) Spectrometer, Model LS50B, Perkin Elmer, UK
15) UV–visible (UV) Spectrometer, Model Lambda 25, PerkinElmer, UK

2.2 Synthesis of $ZnSn(OH)_6$

To synthesize cubic–like ZHS products, each 0.01 mol of tin chloride dihydrate ($SnCl_4 \cdot 2H_2O$) and zinc acetate dihydrate ($Zn(CH_3COO)_2 \cdot 2H_2O$) was separately dissolved in 40 ml de–ionized water with continuous stirring at room temperature. These solutions were mixed together. Then 3 M NaOH solution was added to the mixture solutions until the pH values of the solutions were 8–14, and the solutions were continuously stirred at room temperature for 30 min. Subsequently, the solutions were irradiated by 180 W microwave for 5–30 min. At this stage, the products formed and washed with de–ionized water and ethanol to remove some residual reactants for three times. The final products were dried in air at 70 ºC for 24 h before further characterization.

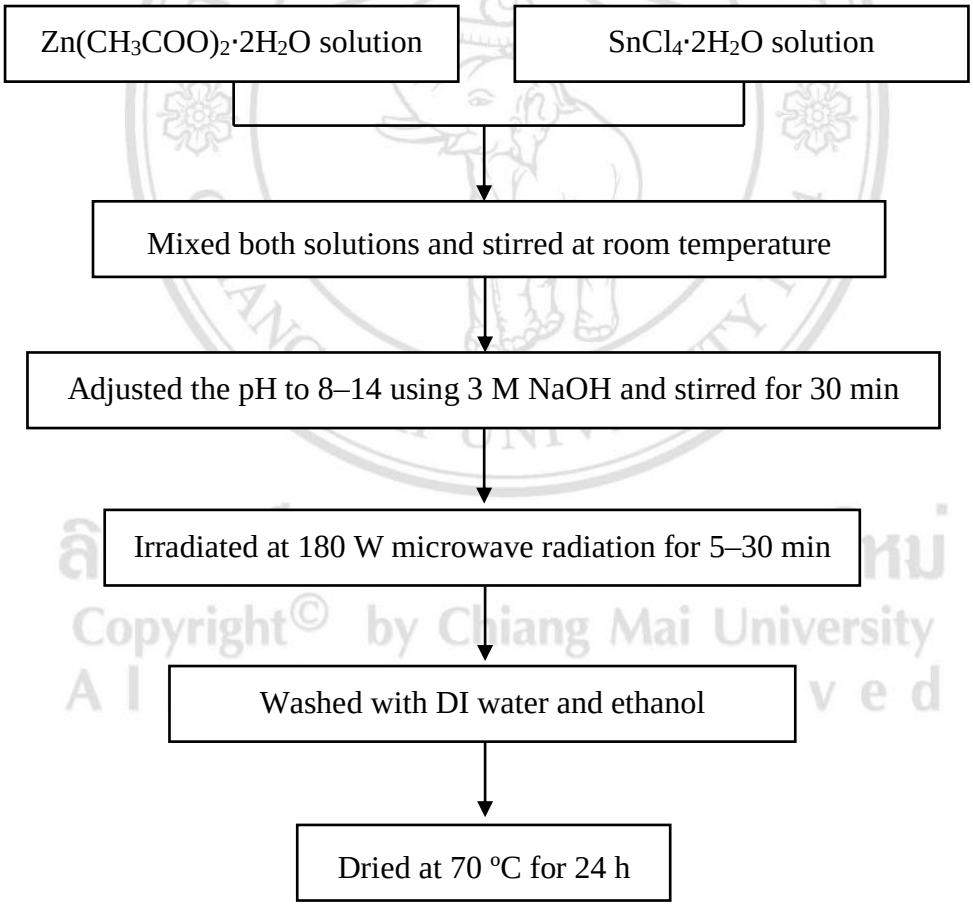

Figure 2.1 Schematic diagram used for synthesized $ZnSn(OH)_6$ in alkaline solutions under microwave radiation.

2.3 Characterizations

The crystallographic phase and purity information of the powder samples were characterized by an X–ray diffractometer (XRD, Rigaku MiniflexII) operating at 20 kV 15 mA with Cu Kα radiation (λ = 0.15405 nm) at a scanning rate of 0.02º/s in the 2θ range of 10–80º. The products were interpreted by Philips X'Pert Highscore Computer Software (search-match program) on database of JCPDS software. The chemical compositions were identified by X–ray photoelectron spectrometer (XPS, Kratos Axis Ultra DLD) with a monochromatic Al Kα (1486.6 eV) radiation as the excitation source at 15 kV with spectrum calibration using a C 1s electron peak at 285.1 eV. The functional groups were analyzed by a Fourier transform infrared spectroscopic analyzer (FTIR, Bruker Tensor 27) with potassium bromide (KBr) as a diluting agent operating in the wavelength range of 4000–400 cm^{-1}. The morphologies and sizes of the samples were examined by a field–emission scanning electron microscope (SEM, JEOL JSM–6335F) operating at 20 kV and a transmission electron microscope (TEM, JEOL JEM–2010) operating at 200 kV. The specific surface area was measured on an Autosorb 1 MP surface analyzer (Quantachrome Instruments) using the Brunauer Emmett Teller (BET) method. The photoluminescence (PL) emission spectra of all samples were analyzed using a Avantes (AvaSpec–2048TEC) spectrophotometer with an excitation wavelength of 280 nm. The appropriated amount of powder samples were dispersed in absolute ethanol using ultrasonic bath, and tested for emission. The visible ultraviolet spectra were recorded on a UV–visible spectrometer (Perkin Elmer Lambda 25) at room temperature.

2.4 Photocatalytic activity measurement

The photocatalytic activities of the ZHS were evaluated through the degradation of methyl orange (MO, $C_{14}H_{14}N_3NaO_3S$) dye under UV illumination. MO is chosen as the model pollutant because its photodegradation by the ZHS photocatalyst is mainly covered by the intrinsic photocatalytic process. In a typical experiment, each 150 mg photocatalyst was dispersed in 150 ml 1.0 x 10^{-5} M MO solutions. The suspension was magnetically stirred in the dark for 60 min to establish an adsorption–desorption equilibrium. Then, the suspension was irradiated under two 15 W UV lamps for different lengths of time until 240 min completion. For each appropriate time interval, 5 ml of the solution was sampled. The catalyst was separated from the sampled solutions by centrifugation to obtain a clear liquid. The solutions of both before and after testing were analyzed by Perkin Elmer Lamda 25 UV–visible spectrophotometer. The concentration and the photodegradation percentage of organic dye were measured by Lambert–Beer law at 463 nm wavelength. In this research, absorption intensities were assumed to be in linear proportion with the concentration of MO. The decolorization efficiency (%) was calculated by

$$\text{Decolorization efficiency (\%)} = \frac{C_0 - C}{C_0} \times 100 \qquad (2.1)$$

, where C_0 and C are the concentrations of MO before and after light irradiation.

The re–used ZHS was also investigated. For each reaction cycle, the photocatalyst was separated from the MO solution by filtration. Then, a new MO solution was tested by the re–used photocatalyst, and the photocatalysis was tested at the same condition for five cycles.

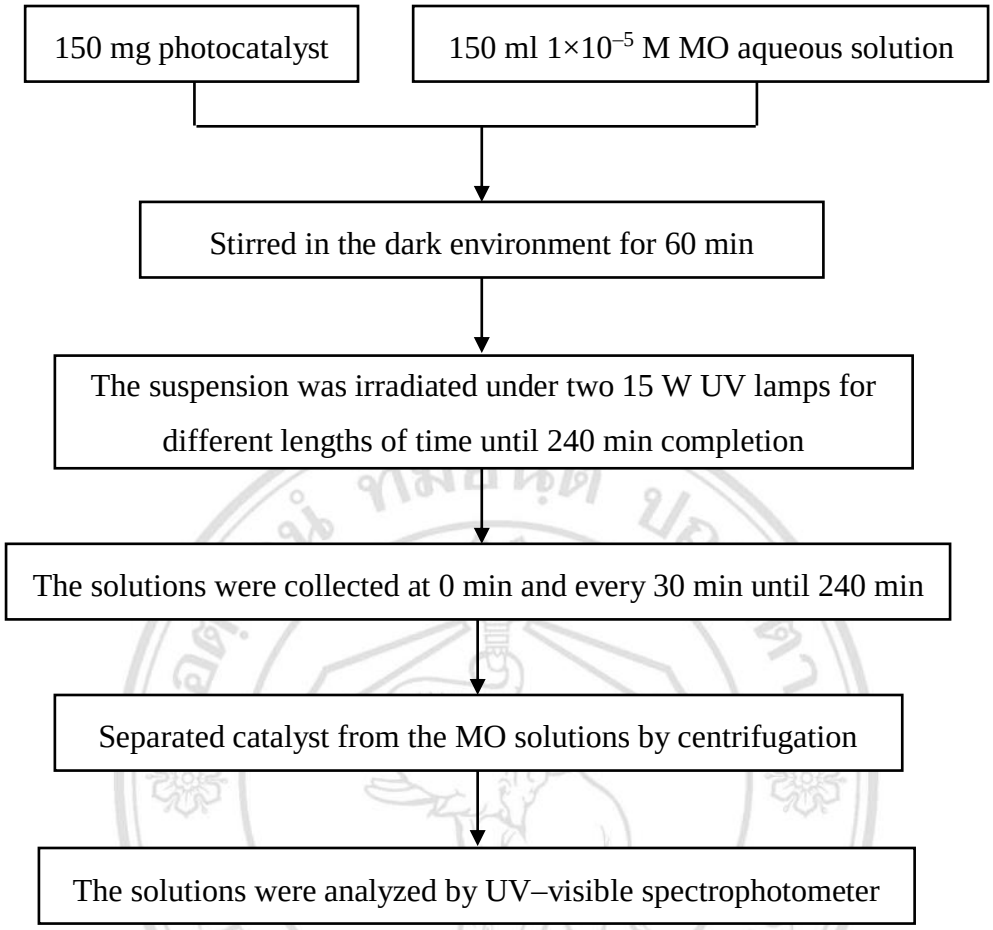

Figure 2.2 Schematic diagram used for photocatalytic testing.