CHAPTER 2

EXPERIMENTAL PROCEDURE

2.1 chemical reagents and equipments

2.1.1 Chemical reagents

1) Potassium Titanium Oxalate Oxide 2-Hydrate, ($C_4K_2O_9Ti{\bullet}2H_2O$) Assay 90% Riedel-de Haen, Germany.

2) Zinc Nitrate Hexahydrate, ($Zn(NO_3)_2{\bullet}6H_2O$) Assay min. 99% Carlo Erba, Italy.

3) Ammonium Hydroxide, NH_4OH min37%, Carlo Erba, Italy.

4) Lanthanum Nitrate Hexahydrate ($La(NO_3)_3{\bullet}6H_2O$) Assay min. 99% Carlo Erba, Italy.

5) Ethanol, C_2H_5OH, 95%, Qrec, New Zealand

6) Absolute ethanol, C_2H_5OH, 99.9%, Qrec, New Zealand

7) Deionized water

2.1.2 Equipments

1) Hotplate & magnetic stirrer, model 502P-2, PMC Industries, Inc., San Diego, America.

2) Analytical balance, model BP-210S, Sartorius AG. Goettingen, Germany

3) pH meter, model 691, Metrom

4) X-ray Diffraction, XRD, Philips X’ Pert MPD, PANalytical B.V., Netherlands

5) Field Emission scanning electron microscope, SEM-FE, JSM-6335F, JEOL, Japan

6) Low vacuum scanning electron microscopy, LV-SEM, JEOL, JSM-5910LV, Japan

7) Transmission electron microscope, TEM, JEM-2010. JEOL, Japan

8) Fourier transforms infrared spectroscopy, FTIR, TENSER 27, BRUKER, USA

9) UV-Visible spectrometer, Varian Cary 50 Scan, Varian Inc., America

10) Ultrasonic bath, Beldelin Sonorex, Germany

11) Raman Spectrometer, TENSER 27, BRUKER, USA

2.2 Synthesized methods

2.2.1 Synthesized of ZnO-TiO_2 nanocomposites, $ZnTiO_3$, Zn_2TiO_4 and $Zn_2Ti_3O_8$

Basing on the chemical solution process, an analytical grade of 0.000, 0.100 and 0.200 mol zinc nitrate hexahydrate ($Zn(NO_3)_2 \cdot 6H_2O$) was dissolved in each of 100 ml de-ionized water to form solutions to which ammonium hydroxide (NH_4OH) was slowly dropped until the pH was 10 and the solutions were transparency. Then 0.100 mol potassium titanium oxalate dihydrate ($C_4K_2O_9Ti \cdot 2H_2O$) in 100 ml de-ionized water each was slowly mixed with the transparency solutions with keeping the pH at 10 throughout the process. These solutions were hydrothermally processed at different temperatures and lengths of time. Subsequently, the samples processed from different molar ratios were calcined at high temperatures and lengths of time, as summarized in Table 2.1

Table 2.1 The samples prepared by different conditions.

Samples	$Zn(NO_3)_2 \cdot 6H_2O$ (mole)	$C_4K_2O_9Ti \cdot 2H_2O$ (mole)	Hydrothermal process		Calcination	
			T (^oC)	t (h)	T (^oC)	t (h)
S1	–	0.100	120	12	–	–
S2	0.200	0.100	120	12	700	3
S3	0.200	0.100	160	24	–	–
S4	0.100	0.100	200	48	750	3
S5	0.050 mole S2	0.100 mole S1	–	–	750	3

2.2.2 Template synthesis of Zn_2TiO_4 and $Zn_2Ti_3O_8$ nanorods by hydrothermal-calcination combined processes

Basing on the chemical solution process, an analytical grade of 0.200 mol zinc nitrate hexahydrate ($Zn(NO_3)_2 \cdot 6H_2O$) and 0.015 mol lanthanum nitrate hexahydrate were dissolved in 100 ml de-ionized water to form solutions to which ammonium hydroxide (NH_4OH) was slowly dropped until the pH was 10 and the solutions were transparency. Then 0.100 mol and 0.300 mol potassium titanium oxalate dihydrate ($C_4K_2O_9Ti \cdot 2H_2O$) in 100 ml de-ionized water each was slowly mixed with the transparency solutions with keeping the pH at 10 throughout the process. These solutions were hydrothermally processed at 120 ^oC 12h. Further, all of the samples were calcined at 750 ^oC 5h.

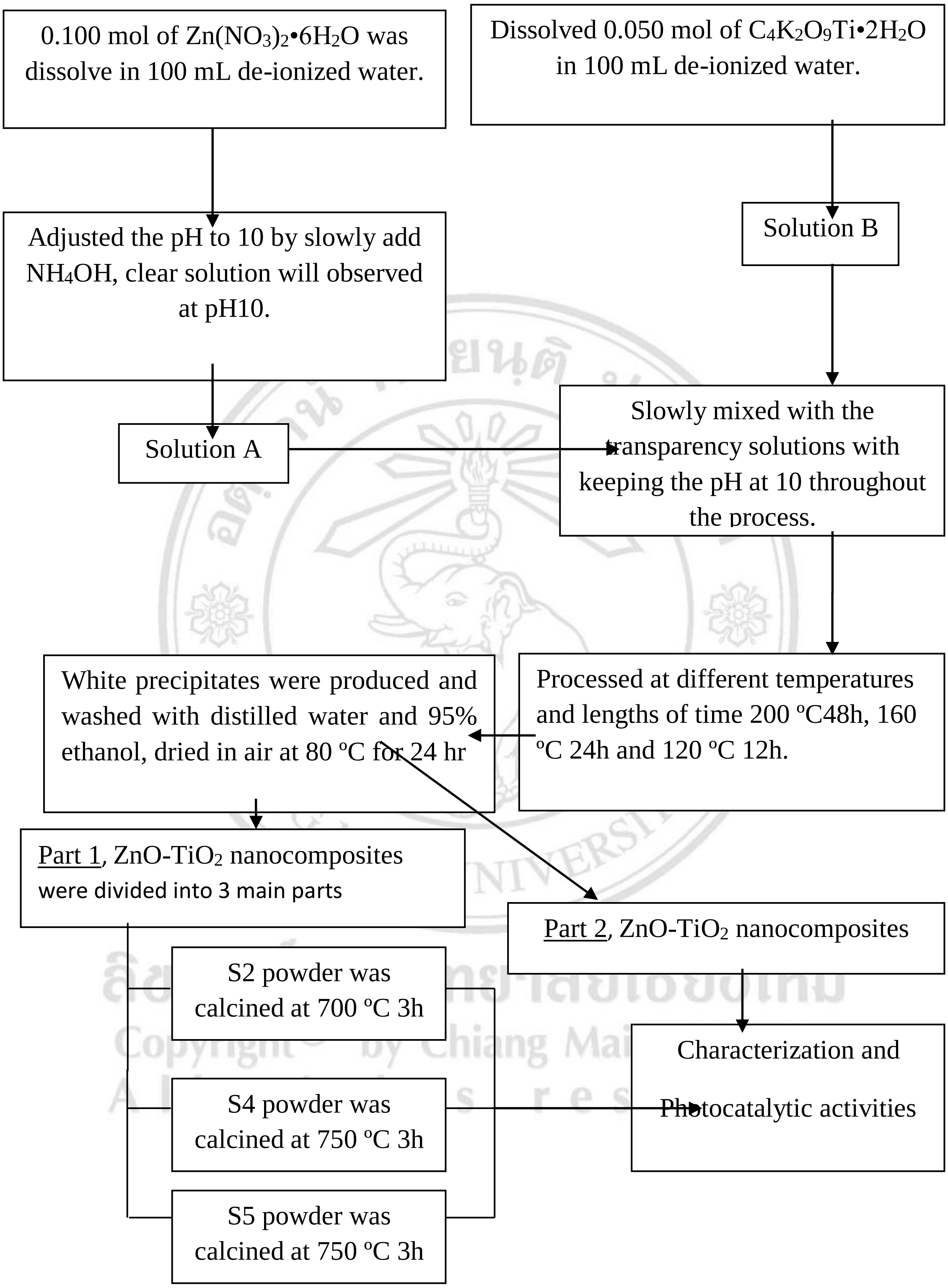

Fig. 2.1 Schematic diagram for the synthesis procedure of the $ZnO-TiO_2$ nanocomposites and Zinc Titanates using Hydrothermal and calcinations method.

2.3 Characterization

2.3.1 X-Ray Diffraction

The crystallinity and phase purity of the products were analyzed by using XRD with Cu $K\alpha$ radiation (λ = 1.5418 A^{o}) operating at 20kV-15 mA, atscanning rate of 5^{o}/min in the 2θ range of 10^{o} - 60^{o}. The identification samples were assisted by X'pert highscore computer software for search matching phase in JCPDS database. [48]

Fig. 2.2 X-ray diffractometer.

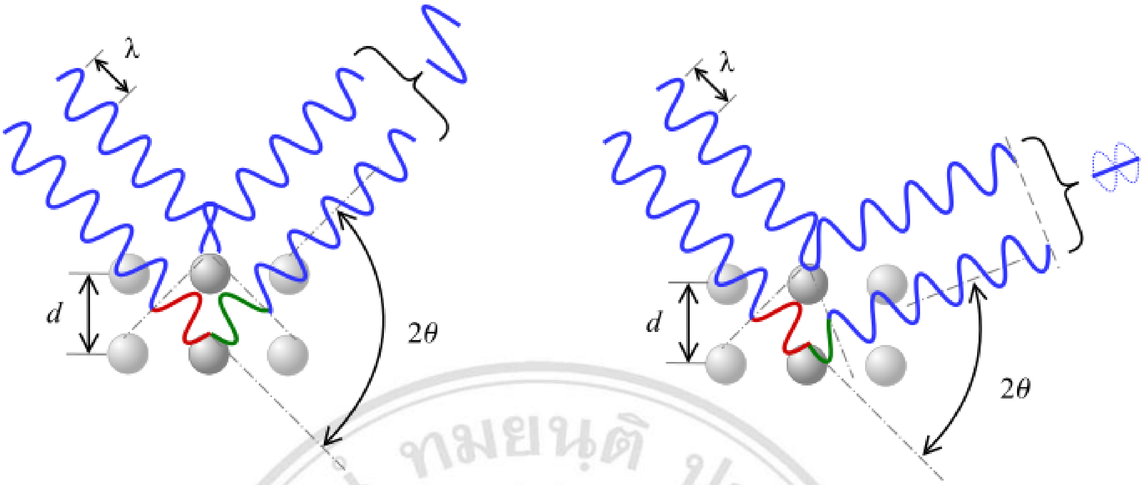

Fig. 2.3 Bragg's Law [48]

2.3.2 Scanning Electron Microscope (SEM)

The morphology and particle sizes of as-synthesized samples were determined by a scanning electron microscope operated at 15 kV accelerating voltage. The chemical composition was investigated by energy dispersive x-ray (EDX) analyzer equipped to SEM and controlled by Inca program used to determine the chemical composition. The morphology of the products were analyzed by Field Emission Scanning Electron Microscope, JEOL model SEM, JSM-6335F operating at 15 kV as an accelerating voltage. The products were dispersed in absolute ethanol using an ultrasonic bath. The dispersed samples were dropped on conductive gold tape which attached to the SEM stubs. The stubs were then coated with gold particles by plasma sputtering under argon atmosphere in order to increase conductivity.

Fig. 2.4 Field Emission Scanning Electron Microscope

2.3.3 Transmission electron microscopy

The morphology and structure of products were also characterized by transmission electron microscope, JEOL model JEM-2010 operating at 200 kV. The samples for TEM analysis were prepared by dispersing their small amount in absolute ethanol and put a drop of the solutions onto copper grids coated with holey carbon films and letting the ethanol evaporate slowly in ambient atmosphere.

Fig. 2.5 Transmission Electron Microscope.

2.3.4 Photoluminescence

The photoluminescence properties of products were investigated by Perkin Elmer Luminescence spectrometer LS50B at room temperature using an excitation wavelength of 200 nm. The appropriated amount of powder samples were dispersed in absolute ethanol using ultrasonic bath, and tested for emission.

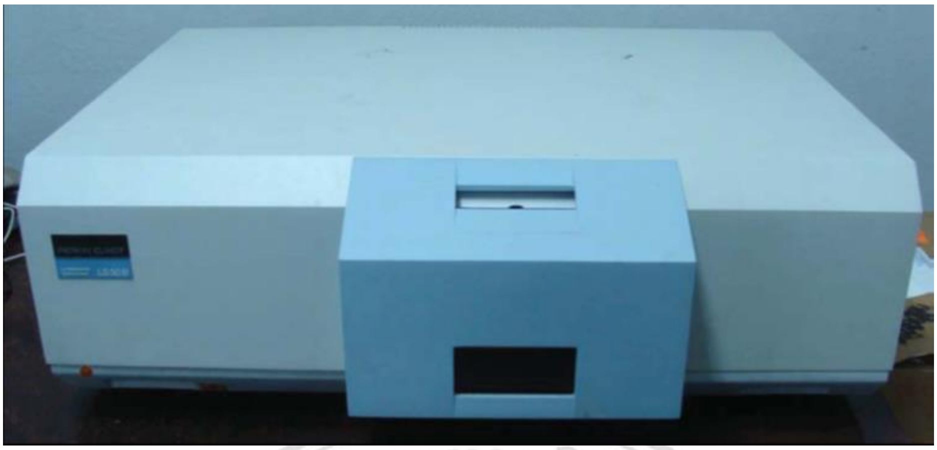

Fig. 2.6 Luminescence spectrometer

2.3.5 BET theory [45]

To determination of the surface area of the material, BET Theory those use to describe the adsorption in the powder products show including the range of following rules:

1. Infinity layers absorption in gas molecules;
2. Each adsorption layer should not have bonding and interaction
3. Each layer must apply in Langmuir isotherm.

The amount of gas were absorbed can measure the amount of surface area in the product in m^2/g. [46]

2.3.6 Fourier transforms infared (FTIR) spectroscopy

The vibration modes of products were analyzed by Fourier transform infared. The samples were diluted 40 times by KBr and operated in the wavelength range 400-4000 cm^{-1} for FTIR analysis (Bruker Tensor27)

Fig 2.7 Fourier transform inferred spectrometer

2.3.7 Raman Spectroscopy

The vibration modes of products were analyzed by Fourier transforms inferred (FTIR) and Raman spectroscopy. The samples were diluted 40 times by KBr and operated in the wavelength range 400-4000 cm^{-1} for FTIR analysis (BRUKER TENSOR27). Raman spectroscopy was operated on HORIBA JOBIN YVON T64000 Raman spectrometer with 50 mW and 514.5 nm wavelength Ar laser.

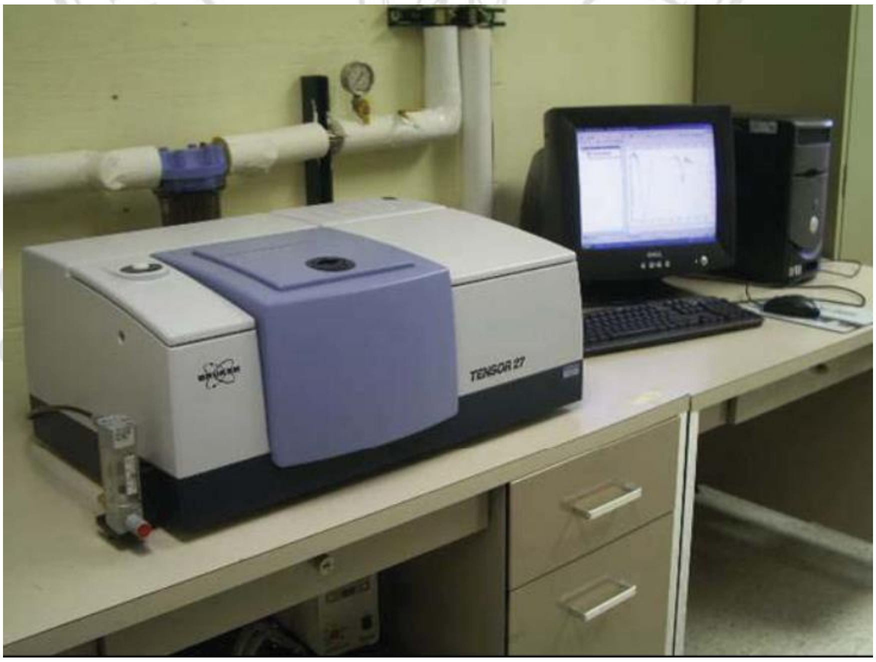

Fig. 2.8 Raman spectrometer