CHAPTER 2

Experimental procedure

2.1 Chemical reagents and equipments

2.1.1 Chemical reagents

1) Zinc nitrate hexahydrate, $Zn(NO_3)_2.6H_2O$, MW = 297.47, ≥ 99%, Carlo Erba, Italy

2) Cerium nitrate hexahydrate, $Ce(NO_3)_3.6H_2O$, MW = 434.22, ≥ 99.0%, Fluka

3) Neodymium nitrate hexahydrate, $Nd(NO_3)_3\cdot 6H_2O$, MW = 438.35, 99%, Aldrich

4) Dysprosium nitrate hexahydrate, $Dy(NO_3)_3.6H_2O$, MW = 456.61, 99.9%, Aldrich

5) Gadolinium nitrate hexahydrate, $Gd(NO_3)_3\cdot 6H_2O$, MW = 451.37, 99%, Aldrich

6) Ammonium hydroxide, NH_4OH, MW = 17.03, 25%, QRec, New Zealand

7) Methylene blue, $C_{16}H_{18}N_3SCl$, MW = 319.85, BDH, England

8) Ethanol, C_2H_5OH, 95%, QRec, New Zealand

9) Absolute ethanol, C_2H_5OH, 99.9%, QRec, New Zealand

10) Deionized water

2.1.2 Equipments

1) Hotplate and magnetic stirrer, model 502P-2, PMC Industries, Inc., San Diego, U.S.A.

2) Analytical balance, Model BP-210S, Satorius AG. Goettingen, Germany

3) pH meter, model 691, Methrom

4) Ultrasonic bath, Bandelin Sonorex, Germany

5) Oven, Model UE-400, Memmert, Germany

6) Table top centrifuge, Model PLC-03, Gemmy Industrial Corp., Taiwan

7) Agate mortar

2.2 Synthesis methods

2.2.1 Sonochemical synthesis, photocatalysis and photonic properties of Ce-doped ZnO nanostructures

0.005 mole $Zn(NO_3)_2 \cdot 6H_2O$ and 0, 1, 2, 3 mole% $Ce(NO_3)_3 \cdot 6H_2O$ were dissolved into 100 ml deionized water under vigorous stirring till complete dissolution. Subsequently, NH_4OH solution was slowly dropped into these solutions until reaching at the pH 9.5 and colorless solutions were achieved. Each of colorless solutions was sonicated in 35 kHz ultrasonic bath at 80 ^{o}C for 5 h. Finally, white precipitates were synthesized, separated by filtration, washed with deionized water and ethanol, and dried at 70 °C for 12 h for further characterization.

2.2.2 Ultrasonic-assisted synthesis of Nd-doped ZnO for photocatalysis

0.005 mole $Zn(NO_3)_2 \cdot 6H_2O$ with 0, 0.5 and 1 mole% $Nd(NO_3)_3 \cdot 6H_2O$ was dissolved in 100 ml deionized water under vigorous stirring until complete dissolution. NH_4OH was slowly dropped into the solutions till they were colorless (pH 9.5). Ultimately, these solutions were irradiated by 35 kHz ultrasonic wave at 80 ^{o}C for 5 h to synthesize precipitates. Finally, white precipitates were synthesized, separated by filtration, washed with deionized water and ethanol, and dried at 70 °C for 12 h for further characterization.

2.2.3 Sonochemical synthesis of Dy-doped ZnO nanostructures and their photocatalytic properties

0.005 mole $Zn(NO_3)_2 \cdot 6H_2O$ and 0, 1, 2, 3 mole% $Dy(NO_3)_3 \cdot 6H_2O$ were dissolved into 100 ml deionized water under vigorous stirring till complete dissolution. Subsequently, NH_4OH solution was slowly added to these solutions until reaching at the pH of 9.5 with the achievement of colorless solutions. Each of colorless solutions was processed in 35 kHz ultrasonic bath at 80 ^{o}C for 5 h in order to have the well mixed solutions and to enhance ultrasonic reaction. In the end, the precipitates were synthesized, collected and dried (70 ^{o}C, 12 h) for further characterization.

2.2.4 Synthesis and characterization of highly efficient Gd-doped ZnO photocatalyst irradiated with ultraviolet and visible radiations

0.005 mole $Zn(NO_3)_2 \cdot 6H_2O$ and 0, 1, 2, 3 mole% $Gd(NO_3)_3 \cdot 6H_2O$ were dissolved in 100 ml deionized (DI) water under vigorous stirring till complete dissolution. Subsequently, NH_4OH solution was slowly added to these solutions until reaching at the pH of 9.5 with the achievement of colorless solutions. Each of the colorless solutions was processed in 35 kHz ultrasonic bath at 80 ^{o}C for 5 h in order to have well mixed solutions. In the end, the precipitates were synthesized, collected and dried (70 ^{o}C, 12 h) for further characterization.

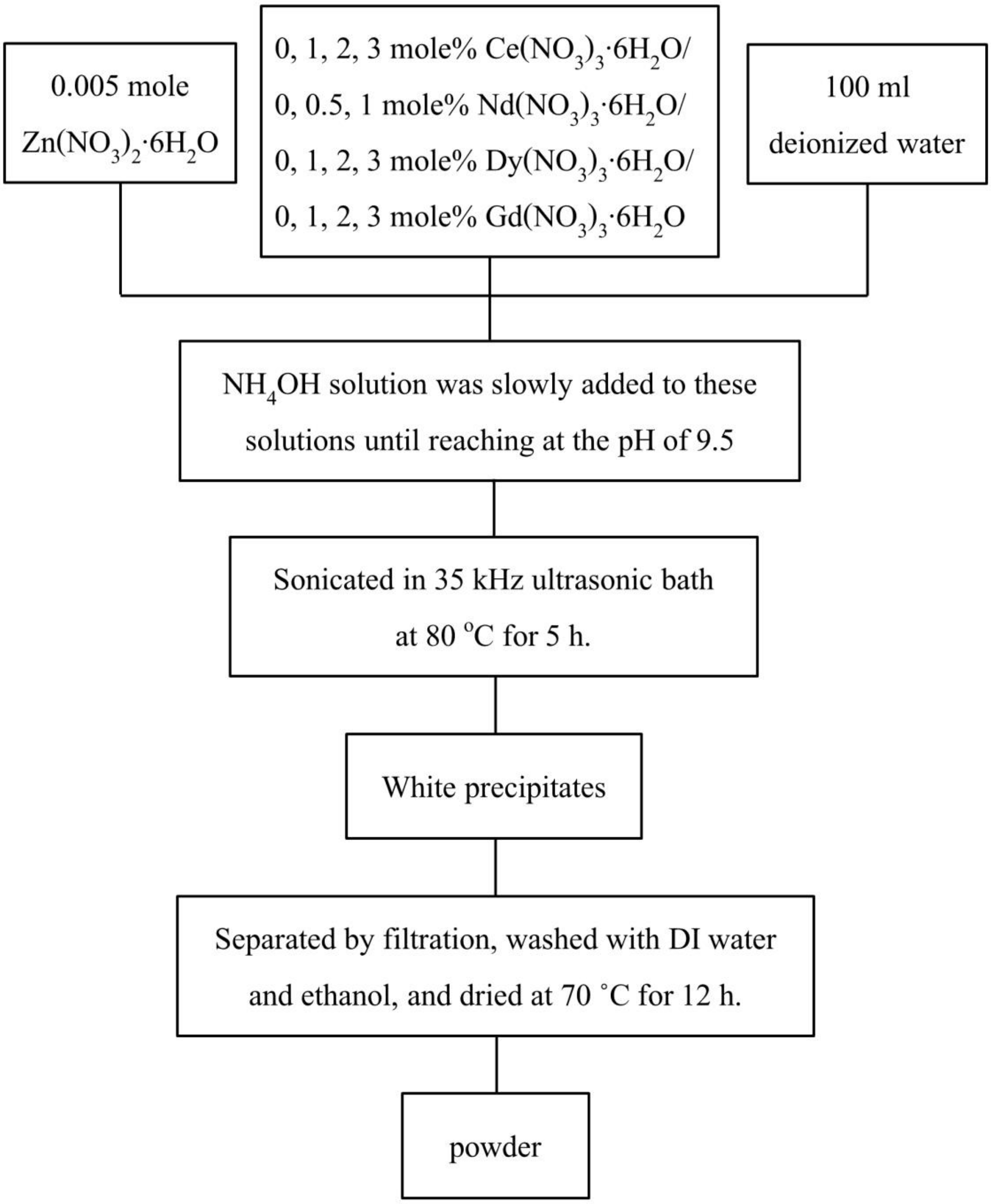

Figure 2.1 Schematic diagram used for preparing zinc oxide and lanthanide-doped zinc oxide by sonochemical method.

2.3 Photocatalytic testing

The photocatalytic activities of the as-synthesized samples were determined by measuring the degradation of methylene blue (MB) solution under UV light irradiation. The 500 mg photocatalyst was added to 100 ml 10^{-5} M MB aqueous solution. The solution was magnetically stirred for 60 min in the dark environment to establish adsorption/desorption equilibrium of MB on surfaces of the photocatalyst. Then the light was turned on to initiate the photocatalytic reaction with keeping the light on until 300 min completion. During testing, the solutions were stirred all the time and the photocatalytic suspensions appeared as nanosized particles floating inside the solutions. The solutions of both before and after testing were analyzed by a Perkin Elmer Lambda 25 UV-Vis spectrometer. The concentration of methylene blue dye during degradation was determined by Lambert-Beer law at 664 nm wavelength. In this research, absorption intensities were assumed to be in linear proportion with the concentration of MB. The decolorization efficiency (%) was calculated by

$$\text{Decolorization efficiency (\%)} = \frac{C_o - C}{C_o} \text{x}100 \tag{2.1}$$

, where C_o and C are the concentrations of MB before and after light irradiation.

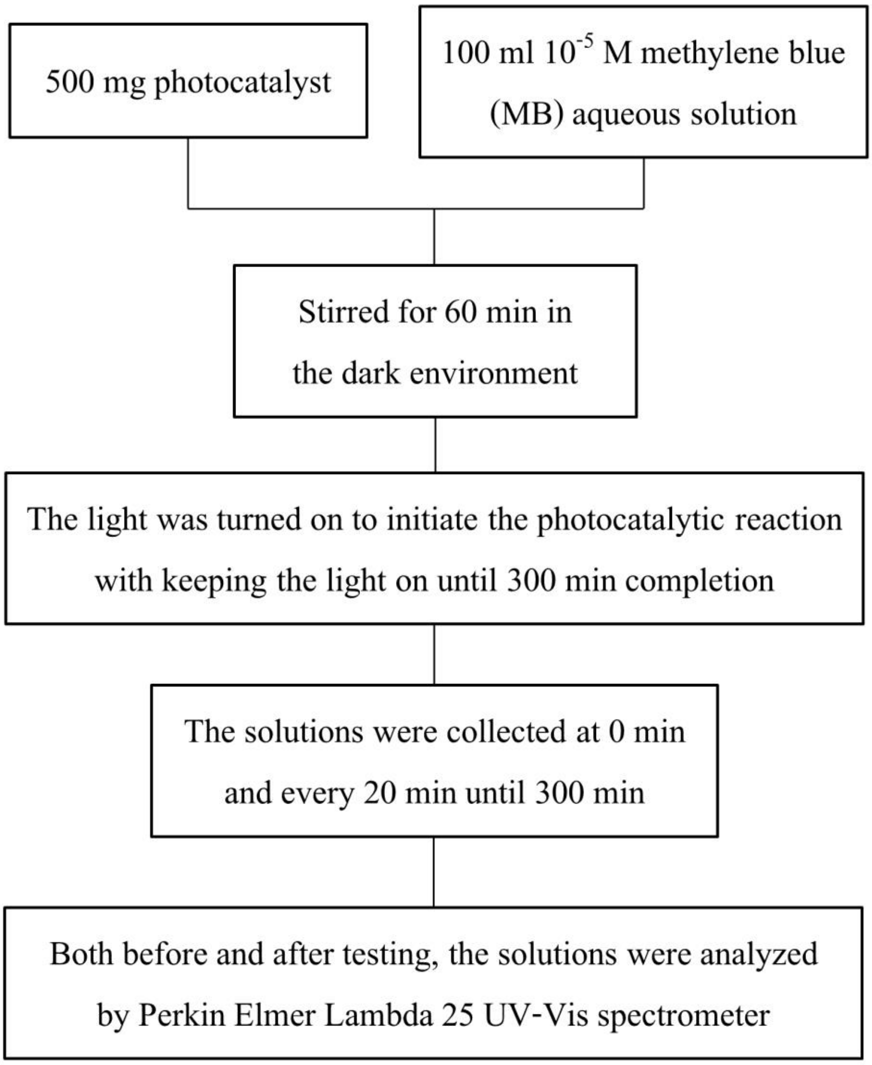

Figure 2.2 Schematic diagram used for photocatalytic testing.

2.4 Characterization

2.4.1 X-ray diffraction (XRD)

The crystallinity and phase purity of the products were analyzed by using X-ray diffractometry (XRD) with Cu K_α radiation (λ = 1.5418 Å) operating at 20 kV-15 mA, at a scanning rate of 5°/min in the 2θ range of 10°-60°. The identification samples were assisted by Philips X'Pert Highscore Computer Software (search-match program) on the database of JCPDS software [34].

Figure 2.3 X-ray diffractometer.

2.4.2 Fourier transform infrared (FTIR) spectroscopy and Raman spectroscopy

The vibration modes of products were analyzed by Fourier transform 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.

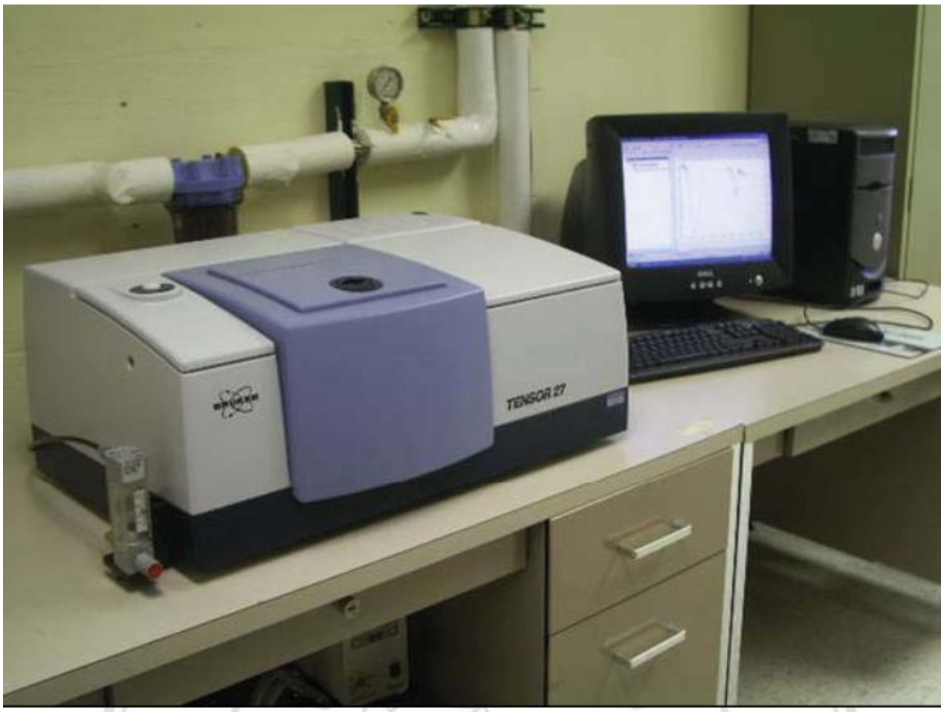

Figure 2.4 Fourier transform inferred spectrometer.

Figure 2.5 Raman spectrometer.

2.4.3 Field Emission Scanning Electron Microscopy (FESEM)

The morphology of the products were analyzed by Field Emission Scanning Electron Microscope, JEOL model SEM, JSM-6335F operating at 15 kV as a 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.

Figure 2.6 Field Emission Scanning Electron Microscope.

2.4.4 Transmission Electron Microscopy (TEM)

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.

Figure 2.7 Transmission Electron Microscope.

2.4.5 Photoluminescence Spectroscopy

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.

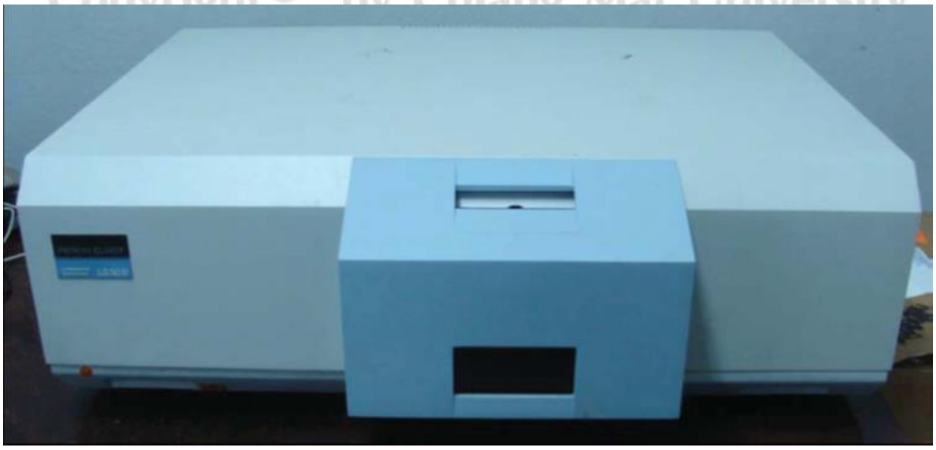

Figure 2.8 Luminescence spectrometer.

2.4.6 UV–visible Spectroscopy

UV–visible properties of products were investigated by a Lambda 25 spectrometer using UV lamp with the resolution of 1 nm.

Figure 2.9 UV-visible spectrometer.