

CHAPTER 2

EXPERIMENTAL

2.1 Chemicals

- 2.1.1 Cerium (III) nitrate hexahydrate ($\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$), assay 99.5%, M.W. 434.22 g/mol, ACROS-organics, NEW Jersey, USA
- 2.1.2 Silver nitrate (AgNO_3), M.W. 169.87 g/mol, Merck, Germany
- 2.1.3 Ethylene glycol ($\text{C}_2\text{H}_5(\text{OH})_2$), assay 95%, M.W. 62.07 g/mol, MAY&BAKER DAGENHAM, England
- 2.1.4 Ammonia solution (NH_3), assay 25%, M.W. 17.08 g/mol, BHD, England
- 2.1.5 Ethanol ($\text{C}_2\text{H}_5\text{OH}$), assay 95%, F.W. 46.07 g/mol, Merck, Germany
- 2.1.6 Oxalic acid ($\text{C}_2\text{H}_2\text{O}_4$) assay 99.7%, F.W. 90.05 g/mol, LAB-SCAN, Ireland
- 2.1.7 Formic acid (CH_2O_2) assay 99.5%, F.W. 46.05 g/mol, LAB-SCAN, Ireland

2.2 Apparatus and instrument

2.2.1 Alumina crucible

2.2.2 X-ray diffractometer (XRD), Bruker D8 Advance diffractometer, Germany

2.2.3 Thermogravimetric differential scanning calorimeter (TG/DSC), NETZSCH, Germany

2.2.4 Scanning electron microscope (SEM) and energy dispersive X-ray spectroscopy (EDS), JEOL JSM 5410LV, Japan

2.2.5 Transmission electron microscopy (TEM) and energy dispersive X-ray spectroscopy (EDS), JEOL JSM-2010, Japan

2.2.6 Brunauer-Emmett-Teller (BET) – Quantachrome Autosorb 1 MP, USA

2.2.7 Spiral photoreactor

2.2.8 UV-lamp – NEC 20 watt T10 black light blue

2.2.9 Conductivity meter – JENWAY 4330 and EUTECH PC 5500

2.2.10 Ultrasonic probe, SONICS & MATERIALS VC 750, U.S.A.

2.2.11 Oven, EYELA VOS-300SD, England

2.2.12 Digital balance, HR-200, Japan

2.2.13 Centifuge, Universal 320, Germany

2.2.14 Hotplate, Fisher Scientific

2.3 Sample preparations

2.3.1 Synthesis of pure CeO₂ nanoparticles by the homogeneous precipitation method

Cerium (III) nitrate hexahydrate (Ce(NO₃)₃·6H₂O, 99.5%) was dissolved in 80% EG/water mixed solvents. The reaction was carried out at 50°C, the mixture was stirred at stirring rate of 500 rpm, 25 ml of 3M ammonia solution was added slowly. A slightly yellow precipitate came out first within few minutes. After that, the precipitate turned into purple colour, and finally became light yellow suspension. The time for the complete reaction was approximately 12h. The precipitate was then centrifuged, washed with distilled water and rinsed with 95% ethanol for three times, and dried at 80°C for 48h. The powders was then calcined at 500°C for 1h. The schematic diagram is shown in Figure 2.1.

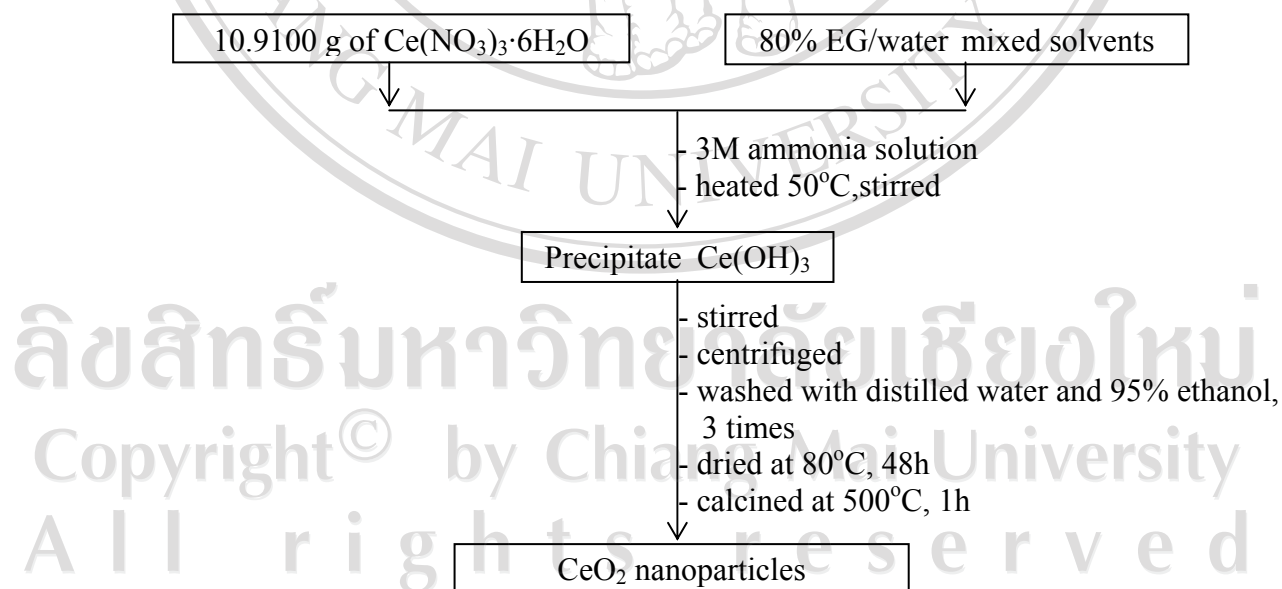


Figure 2.1 Schematic diagrams for synthesis procedures of pure CeO₂

2.3.2 Preparation of Ag-doped CeO₂ nanoparticles by the impregnation method

At room temperature, Ag-doped CeO₂ nanoparticles were prepared by the impregnation method. 0.05125 g of Silver nitrate (AgNO₃) was dissolved in 5.00 ml of distilled water and mixed this solution until the homogeneous solution was obtained. The solution was added into 2.00 g of pure cerium dioxide nanoparticles which were synthesized by homogeneous precipitation method in amount of 0.19, 0.48, 0.96, 1.44 and 1.92 ml for Ag 0.10, 0.25, 0.50, 0.75 and 1.00 mol%, respectively. The content was mixed until it formed smooth uniform slurry and dried in an oven at 80°C for 24h. The powders were calcined at 400°C for 1h. The schematic diagram of the above process is shown in Figure 2.2.

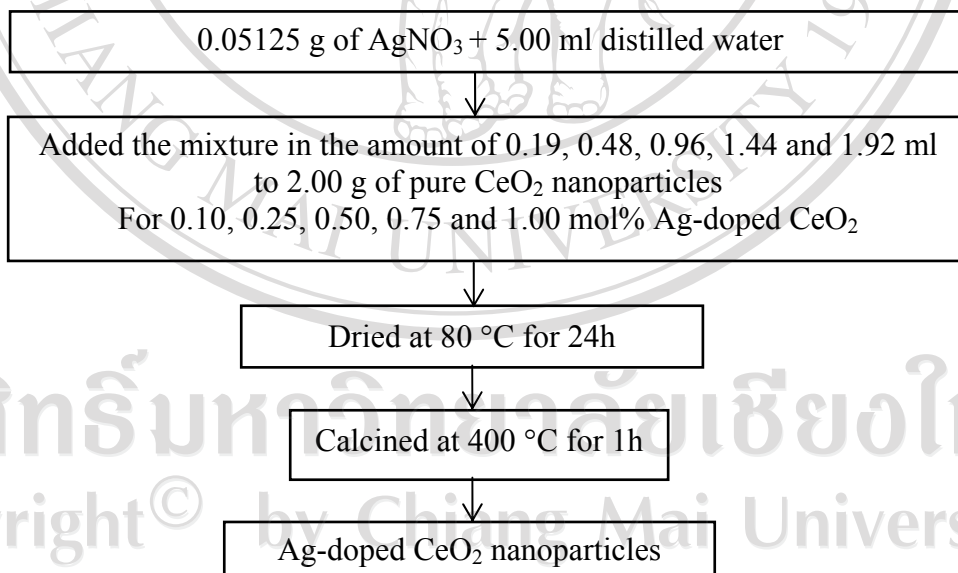


Figure 2.2 Schematic diagrams for preparation procedure of the Ag-doped CeO₂ nanoparticles

2.4 Sample characterization

In this research work, calcination temperature of cerium hydroxide nanopowders was obtained from TG/DSC study. Pure CeO₂ and Ag-doped CeO₂ nanoparticles were characterized by using scanning electron microscopy (SEM), energy-dispersive X-ray spectrometry (EDS), X-ray diffraction (XRD), transmission electron microscopy (TEM) and nitrogen adsorption (BET) analysis. SEM and EDS were used to analyze the morphology and chemical compositions of pure CeO₂ and Ag-doped CeO₂ nanoparticles. XRD was used to confirm the phase and crystalline structure of pure CeO₂ and Ag-doped CeO₂ nanoparticles. TEM was selected to determine the accurate size and morphology. BET was a method of choice to evaluate the specific area of pure CeO₂ and Ag-doped CeO₂ nanoparticles. The photocatalytic activity of all samples was tested for the mineralization of oxalic and formic under UVA irradiation using a spiral photoreactor.

2.4.1 Thermogravimetric analysis (TG) and Differential scanning calorimetry (DSC)

Calcination temperature of cerium hydroxide nanopowders and Ag-doped CeO₂ were analyzed by TG/DSC [Thermogravimetric differential scanning calorimeter, NETZSCH]. TG/DSC was done in dry-air atmosphere up to 1000°C using a heating rate of 10°C/min.

2.4.2 X-ray Diffraction (XRD)

The crystalline structure and phase transformation of pure CeO₂ and Ag-doped CeO₂ were analyzed by X-ray diffraction [Bruker D8 advance diffractometer, operated at 40 kV, 20 mA] using CuK α radiation. The detection of 2 θ values was 2-70° with a step size of 0.04° and a scanning speed of 0.72° /minute. Identification of

crystalline phases was carried out by comparison of XRD patterns with JCPDS standards.

2.4.3 Scanning Electron Microscopy (SEM)

The morphology of pure CeO₂ and Ag-doped CeO₂ nanoparticles were observed and analyzed by scanning electron microscopy (SEM) [JSM-5910LV, JEOL] and the elemental compositions of pure CeO₂ and Ag-doped CeO₂ nanoparticles were investigated by energy-dispersive X-ray (EDS) spectrometry [JSM-5910LV, JEOL]. The powder samples were dispersed in distilled water using ultrasonic probe for 20 minutes. The suspension was dropped onto a gold conductive tape attached to the surface of the SEM brass stub. The stub was then coated with palladium-gold by plasma sputtering for 2 minutes, and an acceleration voltage of 20 kV was used.

2.4.4 Transmission Electron Microscopy (TEM)

The morphology and accurate particle sizes of pure CeO₂ and Ag-doped CeO₂ nanoparticles were analyzed by transmission electron microscopy (TEM) [JSM-2010, JEOL] at an acceleration voltage of 200kV. The powder samples were dispersed in distilled water using ultrasonic probe for 20 minutes. The suspension was dropped onto carbon-copper grid. The deposit was dried in air prior to imaging.

2.4.5 BET-Specific surface areas analysis (BET)

The specific surface areas were analyzed from the Brunauer-Emmett-Teller (BET) measurements [Micromeritics Tristar]. The specific surface areas of pure CeO₂ and Ag-doped CeO₂ nanoparticles were calculated and the approximate particle sizes (d_{BET}) were determined by 5-point nitrogen adsorption from the *Brunauer-Emmett-Teller* (BET) measurements at 77 K. All samples were controlled with degassing at

150°C for 1h prior to analysis. The particle diameters of pure CeO₂ and Ag-doped CeO₂ nanoparticles were calculated from specific surface areas and density of Ag and CeO₂ as

$$d_{BET} = 6 / [(\rho_{CeO_2} \times SSA_{CeO_2} \times (\text{mol\% of CeO}_2)) + (\rho_{Ag} \times SSA_{Ag} \times (\text{mol\% of Ag}))]$$

where $\rho_{CeO_2} = 7.65 \text{ g/cm}^3$ and $\rho_{Ag} = 10.49 \text{ g/cm}^3$

2.4.6 Photocatalytic activity measurements

2.4.5.1 Apparatus

Pure CeO₂ and Ag-doped CeO₂ nanoparticles were tested for photocatalytic activity by using the spiral photoreactor. A schematic diagram of the spiral photoreactor was shown in Figure 2.3. The spiral photoreactor consisted of:

- (i) A 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)
- (ii) The glass spiral filtered with the lamp was covered with an aluminum foil to prevent both the intrusions of ambient light and the emission of the harmful UV from the lamp.

The attachments 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))
- (v) A gas-liquid separator

All components were connected together using Masterflex flexible tubing which was resistant to leaching of any organics.

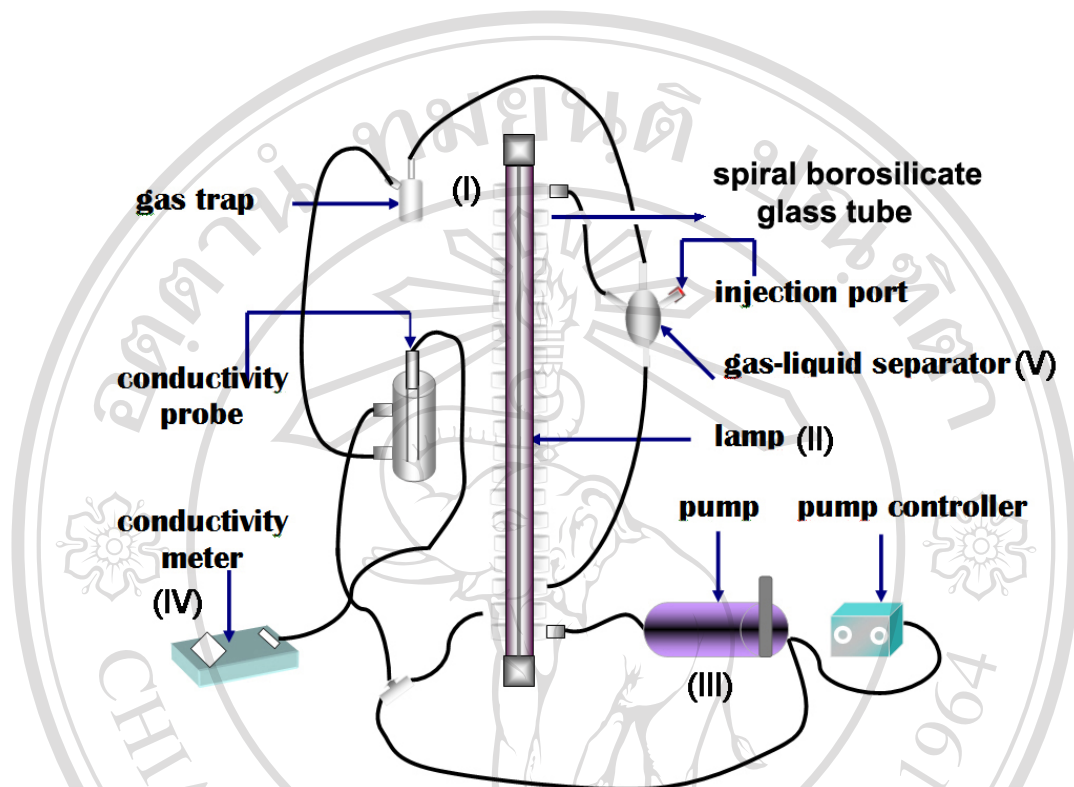


Figure 2.3 Schematic diagram of the spiral photoreactor

2.4.5.2 Preparation of photocatalyst suspension and operation

A 50 mL suspension of pure CeO_2 and Ag-doped CeO_2 nanoparticles having a loading of 1 g/L was prepared. 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 $\mu\text{Siemens/cm}$. 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 oxalic and formic 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 spiral tube. The lamp was then switched on. Subsequently, the increase in conductivity value was recorded every 1 second until the reaction ended. At the end of the photoreaction, the lamp was switched off and the system flushed several times with distilled water. All runs were repeated at least twice.

2.4.5.3 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 pure CeO_2 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 oxalic acid (500 μg of carbon) to the system and the lamp switched on. The conductivity value increased and the final conductivity reading was recorded as in the 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.