



CHAPTER III METHODOLOGY

3.1 Materials

3.1.1 Chemicals

- Ferric chloride anhydrous (FeCl_3 ; Ajax Finechem, AR grade, $\geq 98.0\%$)
- Ferrous chloride tetrahydrate ($\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$; Sigma Aldrich, AR grade, $\geq 99.0\%$)
- Sodium hydroxide (NaOH ; Lobal Chemie, AR grade, $\geq 98.0\%$)
- Ammonium hydroxide (NH_4OH ; Merck, AR grade, $\geq 25.0\%$ NH_3 in water)
- Sodium chloride (NaCl ; Lab-Scan, AR grade, $\geq 99.0\%$)

3.1.2 Solvent

- Distilled water (H_2O)

3.1.3 Gas

- Nitrogen gas (N_2 ; High purity, 99.99%)

3.2 Equipment

3.2.1 Analytical Instruments

- X-Ray Diffraction Spectrometer (XRD; Bruker AXS, D8 Advance)
- Fourier Transform Infrared Spectrometer (FT-IR; Thermo Nicolet, Nexus 670)
- Thermogravimetric/Differential Thermal Analyzer (TG/DTA; Perkin Elmer, Pyris Diamond)
- Surface Area Analyzer (Thermo finnigan, Sorptomatic 1990)
- Field-Emission Scanning Electron Microscope (FE-SEM; Hitachi, S-4800)
- Electrometer (Keithley, 6517A) with a custom-built two-point probe
- Vibrating Sample Magnetometer (VSM; Lake Shore, 7404)

3.2.2 Glassware and Apparatus

- Three-neck round bottom flask
- Condenser
- Magnetic bar
- Oil bath
- Stand, Clamp and Clamp holder
- Hot-plate/Stirrer (Yellowline, MSH B)
- Thermostat and controller (Maxtech, MC-2438)
- Digital pH meter (Reed, pH-8689)
- Oven (Mettler, U50)

3.3 Experimental

3.3.1 Synthesis of Hematite Nanoparticles

Hematite nanoparticles were synthesized via the chemical precipitation method as described by Liu *et al.* (2007) with some alterations. In a typical preparation, NaOH solution (6.0 M, 25 ml) was added into Fe(III) solution (1.0 M, 50 ml) until reached pH 7 under the condition of vigorous stirring at room temperature. In this mixed system, the brown precipitates precursor (Fe(OH)₃) formed were confirmed to be 2-line ferrihydrite by using XRD. The agitation was continued for an additional 10 min, followed by adding trace amounts of Fe(II) ions ($n_{\text{Fe(II)}}/n_{\text{Fe(III)}} = 0.02$) into the system. The pH of the system was readjusted to the desired pH 7 once again with a dilute NaOH solution (1.0 M) and at the same time the total volume of each system was adjusted to 100 ml so that the total concentration (C) of the precursor reached 0.5 M. The suspension was heated to a boiling point and kept refluxing for 1h under vigorous stirring. All stages of the experiment were carried out under pure N₂ gas to avoid the oxidation of Fe(II). The final product was filtered off, washed thoroughly with distilled water, and then dried at about 70-80 °C.

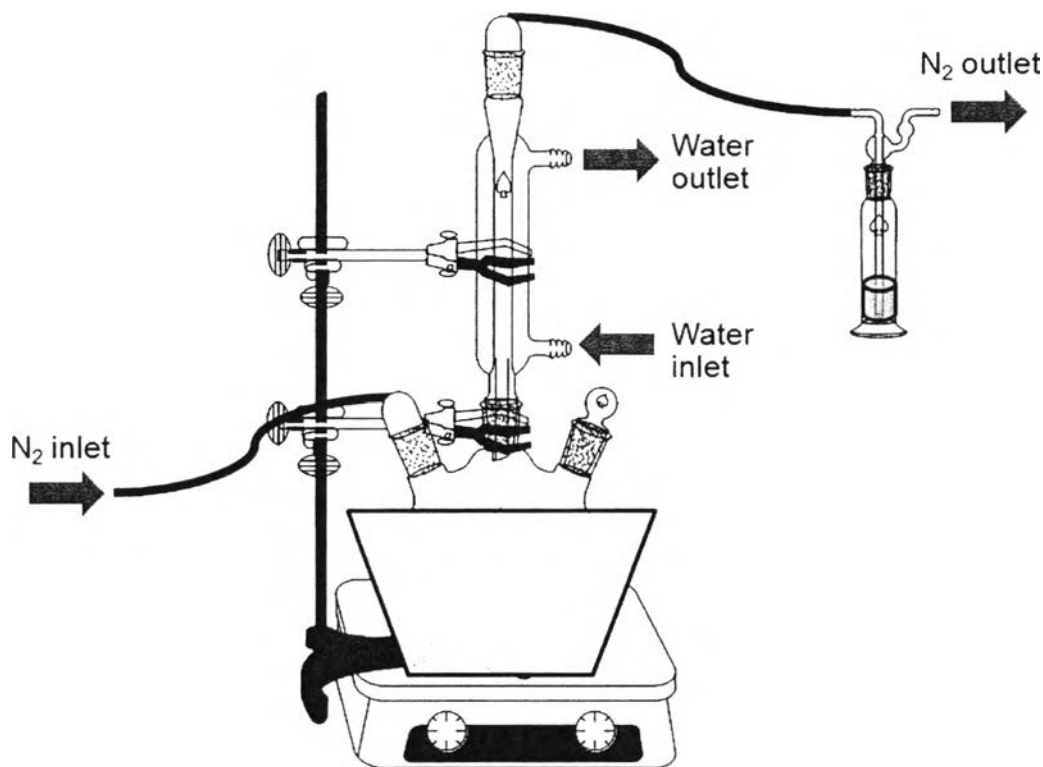


Figure 3.1 Experimental setup of the chemical precipitation method.

3.3.2 Particle Size and Morphology Control

The various sizes and morphologies of hematite particles influenced by the precursor concentration, the solution pH, the amount of catalyst, the ionic strength, the reaction temperature, and the reaction time were systematically investigated by holding the other parameters constant. The precursor concentrations were changed by diluting the prepared 1.0 M Fe(III) solution. The pHs of the solutions were adjusted by changing the volume of dilute NaOH solution (1.0 M) added. The amounts of Fe(II) used were calculated in term of Fe(II) to Fe(III) molar ratio ($n_{\text{Fe(II)}}/n_{\text{Fe(III)}}$). The ionic strength (I) values of the reaction systems were controlled by adding a certain amount of 5.0 M NaCl solution. The experiments were performed through the same procedure as described in the above section, excepted in some conditions the suspensions were heated at various temperatures (in the range of 60-100 °C) for a certain time varying from 10 min to 2 hours. The amounts of chemicals used to synthesize hematite particles at various synthesis conditions are provided in details in Appendix A.

3.4 Characterization and Measurement

3.4.1 Characteristics of Hematite Nanoparticles

3.4.1.1 X-Ray Diffraction (XRD)

A powder X-ray diffractometer (Bruker AXS, D8 Advance) was used to examine the crystal structure of the synthesized hematite particles which were below the nanometer scale. The Cu K α ($\lambda = 1.5406 \text{ \AA}$) radiation source was operated at 40 kV/30 mA and used the K β filter to eliminate the interference peak. Divergence slit and scattering slit 0.5 deg together with 0.3 mm of receiving slit were set on the instrument. The hematite powder was placed into a sample holder and the measurement was continuously run. The experiments were recorded by monitoring the diffraction in the diffraction angle (2θ) range from 10.000 to 80.000 deg with a scan speed of 1.000 deg/min and a scan step of 0.020 deg.

The crystallite sizes of the synthesized hematite nanoparticles could be estimated from the XRD patterns by using Scherrer's equation (3.1) as follows:

$$D = \frac{k\lambda}{\beta \cos\theta} \quad (3.1)$$

where D is the crystallite size (nm), k is the grain shape dependent constant (assumed to be 0.89 for the spherical particles), λ is the wavelength of X-ray beam (nm) ($\lambda = 0.15406 \text{ nm}$ for Cu K α radiation), β is the full width at half maximum (FWHM) for the considered diffraction peak (rad), and θ is the diffraction angle ($^{\circ}$). For hematite, the crystallite sizes calculated from (104) diffraction peak located at $2\theta = 33.2^{\circ}$

3.4.1.2 Fourier Transform Infrared Spectroscopy (FT-IR)

A Fourier transform infrared spectrometer (Thermo Nicolet, Nexus 670), with a deuterated triglycine sulfate detector, was used to characterize the functional groups of the synthesized hematite particles. For the KBr-pellet technique, optical grade KBr (Carlo Erba Reagent) was used as the background material. The hematite powder was grounded in a mortar and mixed with dried KBr at ratio of the sample:KBr was about 1:20, then the mixed powder was compressed into the pellets

under the pressure of 7 tons. The absorption mode was run 64 scans with a resolution of $\pm 4 \text{ cm}^{-1}$ in the wave number in range of 4000-400 cm^{-1} .

3.4.1.3 Thermogravimetric/Differential Thermal Analysis (TG/DTA)

A thermogravimetric/differential thermal analyzer (Perkin Elmer, Pyris Diamond) was used to determine the thermal behavior of the synthesized hematite particles. The experiment was carried out by weighting a powder sample of 1-5 mg and loaded into a platinum pan. The mass change under the temperature scan from 30 to 600 °C at a heating rate of 10 °C/min and under the nitrogen flow was monitored and recorded.

3.4.2 Particle Size and Morphology of Hematite Nanoparticles

3.4.2.1 Field-Emission Scanning Electron Microscopy (FE-SEM)

A field-emission scanning electron microscope (Hitachi, S4800) was used to examine the morphological structure and to determine the particle size of the synthesized hematite particles. The sample powder was placed on the holder with an adhesive tape and coated with a thin layer of platinum using an ion sputtering device (Hitachi, E-1010) for 100 sec prior to observation under FE-SEM. The scanning electron images were investigated by using an acceleration voltage of 5.0 kV with a magnification in the range of 50.0-200k times.

The particle size and particle size distribution of the synthesized hematite particles were determined by the professional image processing and analysis software of SemAfore over 2-3 FE-SEM images by the quantitative statistical method. There are multiple definitions for mean diameter value because this value is associated with the basis of the distribution calculation (number, surface, volume). The general form of the mean particle diameter is defined by using equation (3.2) as follows:

$$D[p, q] = \left(\frac{\sum_{i=1}^n n_i D_i^p}{\sum_{i=1}^n n_i D_i^q} \right)^{\frac{1}{p-q}} \quad (3.2)$$

where $D[p,q]$ is the general form of the mean diameter, n_i is the number of the i^{th} particle, D_i is the diameter of i^{th} particle, and $(p-q)$ is the algebraic power of $D[p,q]$.

The particle size of hematite could be characterized by $D[1,0]$ and $D[4,3]$ which are the number mean diameter (D_n ; equation (3.3)) and volume mean diameter (D_v ; equation (3.4)), respectively.

$$D_n = D[1,0] = \frac{\sum_{i=1}^n n_i D_i}{\sum_{i=1}^n n_i} \quad (3.3)$$

$$D_v = D[4,3] = \frac{\sum_{i=1}^n n_i D_i^4}{\sum_{i=1}^n n_i D_i^3} \quad (3.4)$$

In addition, the particle size distribution index could be determined by the polydispersity index (PDI) using equation (3.5) as follows:

$$PDI = \frac{D_v}{D_n} = \frac{D[4,3]}{D[1,0]} \quad (3.5)$$

3.4.2.2 Surface Area Measurement

A surface area analyzer (Thermo finnigan, Sorptomatic 1990) was used to measure the specific surface area of the synthesized hematite particles. The absorbent sample was weighed and outgassed at 300°C for 12 h under vacuum to eliminate volatile adsorbate on the surface. The data were obtained by adsorption and desorption with He and N₂ gases. The BET surface area was determined by using the static volumetric method.

3.4.3 Properties of Hematite Nanoparticles

3.4.3.1 Electrical Conductivity Measurement

An electrometer (Keithley, 6517A), with a custom-built two-point probe, was used to measure the electrical conductivity which is the inversion of specific resistivity (ρ) that indicates the ability of material to transport electrical charge. The meter consisted of a probe making contact on the surface of the sample

in a disc shape. This probe was connected to a power supplier source for a constant source and for reading current. The applied voltage was plotted versus the resultant current to determine the linear Ohmic regime of each sample based on the Van der Pauw method. The applied voltage and the current in the linear Ohmic regime were converted to the electrical conductivity of the sample using equation (3.6) as follows:

$$\sigma = \frac{1}{\rho} = \frac{1}{R_s \times t} = \frac{I}{K \times V \times t} = \frac{\text{slope}}{K \times t} \quad (3.6)$$

where σ is the specific conductivity (S/cm), ρ is the specific resistivity ($\Omega \cdot \text{cm}$), R_s is the sheet resistivity (Ω), I is the resultant current (A), K is the geometric correction factor, V is the applied voltage (V), and t is the thickness of the disc sample (cm).

The geometrical correction factor was taken into account of geometric effects, depending on the configuration and the probe tip spacing; it was determined by using standard materials where specific resistivity values were known; silicon wafer chips (SiO_2). In the present case, the sheet resistivity was measured by using the two-point probe and then the geometric correction factor was calculated by equation (3.7) as follows:

$$K = \frac{\rho}{R \times t} = \frac{I \times \rho}{V \times t} = \text{slope} \times R_s \quad (3.7)$$

where K is the geometric correction factor, ρ is the known resistivity of standard silicon wafer ($\Omega \cdot \text{cm}$), t is the film thickness (cm), R is the film resistance (Ω), and I is the resultant current (A).

3.4.3.2 Vibrating Sample Magnetometry (VSM)

A vibrating sample magnetometer (LakeShore, 7404), with a 4-inch electromagnet, was used to study the magnetic properties of the synthesized hematite particles. The magnetization curves were measured under the maximum magnetic field strength of 8000.0 Oe at room temperature to determine the hysteresis loops. The data were taken with a scan speed of 10 sec/point to complete the 280 points of the hysteresis loop.