

CHAPTER III

EXPERIMENTAL

This chapter has provided the information of instruments, apparatus, chemicals, sample preparations and measurements employed in this work.

3.1 Instruments and Apparatus

The following is the list of instruments and apparatus utilized in this work.

- 3.1.1 Milli Q water system (Millipore, USA)
- 3.1.2 Ultrasonic bath (Ultrasonik 28H, ESP Chemicals, Inc., USA)
- 3.1.3 Vacuum pump (Gast)
- 3.1.4 Hot plate (HL)
- 3.1.5 Drying oven (Mettler)
- 3.1.6 Furnace (Carbolite RHF 1600)
- 3.1.7 Brunauer, Emmett & Teller (BEL, Japan)
- 3.1.8 Fourier transform infrared spectrophotometer (Nicolet IMPACT 410)
- 3.1.9 X-ray diffraction (Bruker D8 ADVANCE)
- 3.1.10 Scanning electron microscopy (JSM-6400)
- 3.1.11 Transmission electron microscopy (JEM-2100)
- 3.1.12 Ultramicro balance (Sartorius Ultra-Microbalance SC2, Germany)
- 3.1.13 Sonicator (Sonics & Materials)
- 3.1.14 Electrostatic Spray Deposition System (Home made)
- 3.1.15 Multichannel potentiostat/galvanostat
(VMP2, Princeton Applied Research, USA)
- 3.1.16 Wafer coated with Pt as working electrode (Inostek, Republic of Korea)
- 3.1.17 Platinum plate as counter electrode (Goodfellow, USA)
- 3.1.18 Saturated calomel electrode as reference electrode
(CH Instrument, USA)
- 3.1.19 Nylon membrane filters (0.2 μm , Whatman)
- 3.1.20 Universal indicator Merck (Darmstadt, Germany)
- 3.1.21 Thermometer

3.2 Chemicals

List of chemicals and their suppliers is showed in Table 3.1.

Table 3.1 List of chemicals and their suppliers.

Chemical	Suppliers
As received multi-walled carbon nanotubes	Nanomaterial Research Unit, Chiangmai University, Thailand
Ethyl alcohol	Merck (Darmstadt, Germany)
Iron (II) sulfate heptahydrate 99.5%	Merck (Darmstadt, Germany)
Nickel (II) nitrate hexahydrate crystal	Aldrich, USA
Nitric acid 65%	Merck (Darmstadt, Germany)
Potassium bromide	Aldrich, USA
Sulfuric acid 95-97%	Merck (Darmstadt, Germany)
Sodium hydroxide	Merck (Darmstadt, Germany)
Titanium tetraisopropoxide 97%	Aldrich, USA

3.3 Sample Preparations

3.3.1 Purification and Functionalization of MWNTs

To remove the catalyst impurities of MWNTs and generate functional group onto the surface of MWNTs, 1 g of as received MWNTs was sonicated in 40 mL of 65% concentrated nitric acid for 3 hours. Ultrasonication causes the microbubbles from the CNTs porous and improves the nanotube wetting. Then, MWNTs were refluxed in the concentration of HNO₃ at 140⁰C for 6, 12 and 18 hours, respectively. After cooled to ambient temperature, the products were washed repeatedly with milli Q and dried in the air at 80⁰C for 6 hours. These acid treated MWNTs are thus called as functionalized MWNTs.

3.3.2 Synthesis of Nanocrystalline Composites

3.3.2.1 Synthesis of TiO₂/MWNTs Composites

TiO₂/MWNTs nanocomposites were synthesized by sol gel method as the following: 10 mg of functionalized MWNTs were dispersed in 1:1 volume ratio of the ethanol-water system (EWS). This solution was added by 2, 4, 6, 8 and 10 % w/w of titanium tetraisopropoxide respectively and sonicated to form the slurry. The resultant residues were filtered and washed repeatedly with Milli Q at room temperature. As synthesized TiO₂/MWNTs composites were heated at the temperature of 350⁰C for 2 hours.

3.3.2.2 Synthesis of FeO/MWNTs Composites

10 mg of the functionalized MWNTs were dispersed in EWS. The ratios of iron (II) sulfate heptahydrate, which 2, 4, 6, 8 and 10 % w/w, were added respectively into the solution and these mixtures were sonicated for 1 hour. After that, pH of the slurries was adjusted to 9±0.1 by dropwise addition of 0.5 M NaOH at room temperature. The residues were filtered and washed repeatedly with Milli Q to remove

the exceeding sulfate ions. Finally, the synthesized composites were calcined at 350⁰C for 2 hours.

3.3.2.3 Synthesis of NiO/MWNTs Composites

NiO-supported MWNTs composites were prepared by dissolving 10 mg of the treated MWNTs in EWS. Then 2, 4, 6, 8 and 10 % w/w of nickel (II) nitrate hexahydrate crystal were added respectively to the above solution, and ultrasonication was continued for 1 hour at room temperature. The homogenous mixtures were adjusted to pH 9±0.1 by the addition of 0.5 M NaOH. The blank of products were filtered and washed repeatedly with Milli Q water until the pH was neutral to ensure that the solutions were free of nitrate ions. The final products were heated at the temperature of 350⁰C for 2 hours in the air.

3.3.2.4 Synthesis of FeO-TiO₂/MWNTs Composites

FeO-TiO₂ /MWNTs composites, as listed in Table 3.2, were prepared by using iron (II) sulfate heptahydrate and TiO₂/MWNTs composites. First, the ratios of TiO₂ nanocomposite were dispersed in EWS. After that, the ratios of FeSO₄.7H₂O were added into the composite solutions. These mixtures were sonicated continuously for 1 hour and adjusted slowly to a constant pH value of 9.0±0.1 by dropwise addition of 0.5 M NaOH. After the precipitation, the precipitates were filtered and washed repeatedly with Milli Q to remove the exceeding sulfate ions. The final composites were calcined at 350⁰C for 2 hours.

Table 3.2 The ratios of FeO-TiO₂/MWNTs composite

Sample	TiO ₂ /MWNTs composites (%w/w)	Iron (II) sulfate heptahydrate (%w/w)
1	8/90	2
2	6/90	4
3	4/90	6
4	2/90	8

3.3.2.5 Synthesis of NiO-TiO₂/MWNTs Composites

NiO-TiO₂ /MWNTs nanocrystalline composites, as listed in Table 3.3, were synthesized by dissolving of the ratios of nickel (II) nitrate hexahydrate crystal in EWS. Subsequently, the ratios of TiO₂ /MWNTs composite were dispersed in the above solutions. The mixtures were sonicated for 1 hour. Then, 0.5 M NaOH solution was added simultaneously into the mixtures to adjust the pH to 9.0±0.1. The products of this reaction were filtered and washed with Milli Q until the pH was 7 to ensure that the solutions were free nitrate ions. The synthesized nanocomposites were calcined at 350⁰C for 2 hours in air.

Table 3.3 The ratios of NiO-TiO₂/MWNTs composite

Sample	TiO ₂ /MWNTs composites (%w/w)	Nickel (II) nitrate hexahydrate crystal (%w/w)
1	8/90	2
2	6/90	4
3	4/90	6
4	2/90	8

3.3.3 Capacitor Electrode Preparations

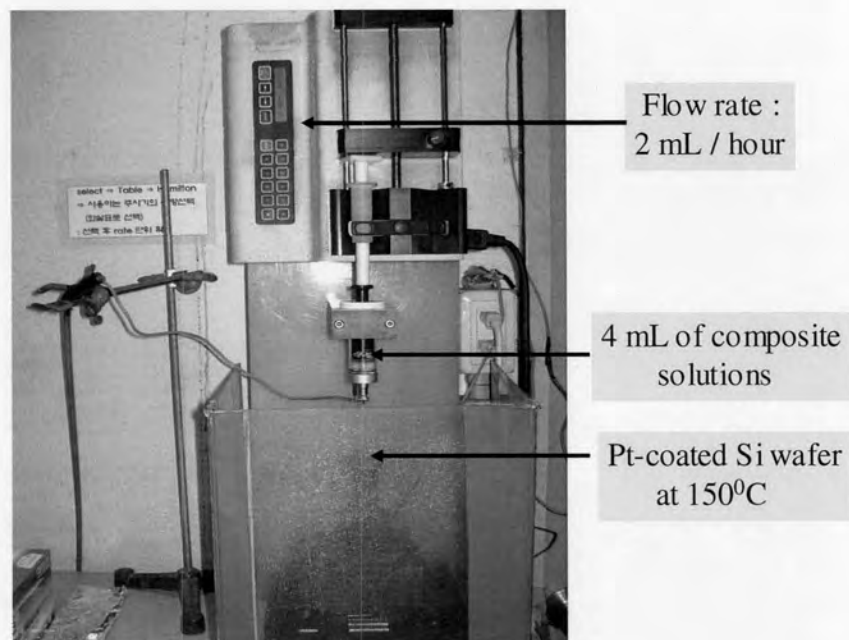


Figure 3.1 Electrostatic spray deposition.

The binder-free nanocrystalline composite electrodes were deposited onto Pt-coated Si wafer (Pt/Si wafer) current collecting substrates by ESD technique as illustrated in Figure 3.1. First, 5 mg of the synthesized composites were dissolved in 30 mL of ethanol. The mixtures were sonicated continuously by sonicator, presented in Figure 3.2, at 60% of amplitude for 30 minutes to form the slurry. After that, 4 mL of each precursor solution was pumped at a flow rate of 2 mL/hour into a needle of a syringe placed about 10 cm above the substrates which were heated to 150°C. The voltage between the stainless needle and the substrates was maintained at 10 kV.

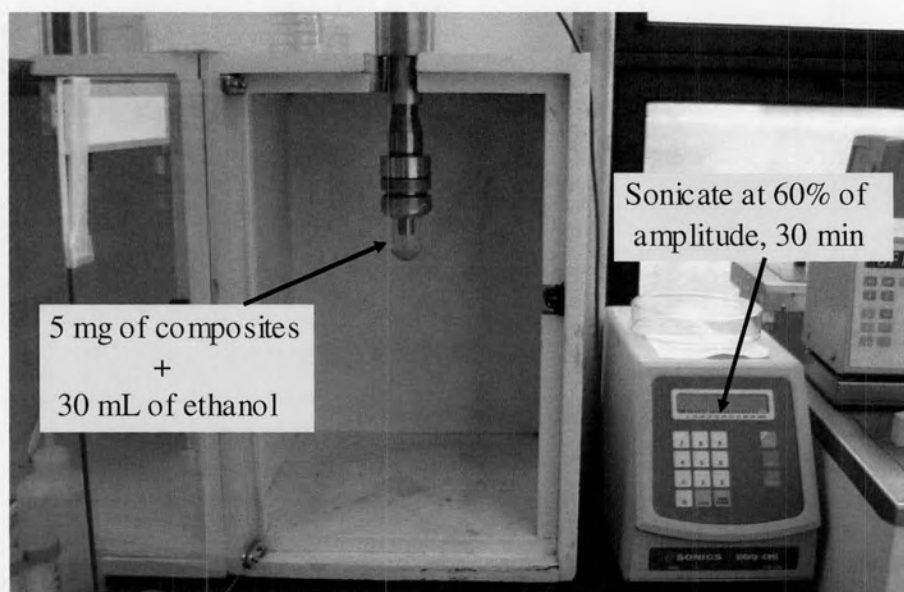


Figure 3.2 Sonicator.

The result of the electrode preparations was the attachment of composite samples to the collecting substrates [16]. Moreover, the area of the composite thin films as the working electrode in electrochemical measurements was 1 cm^2 as showed in Figure 3.3.

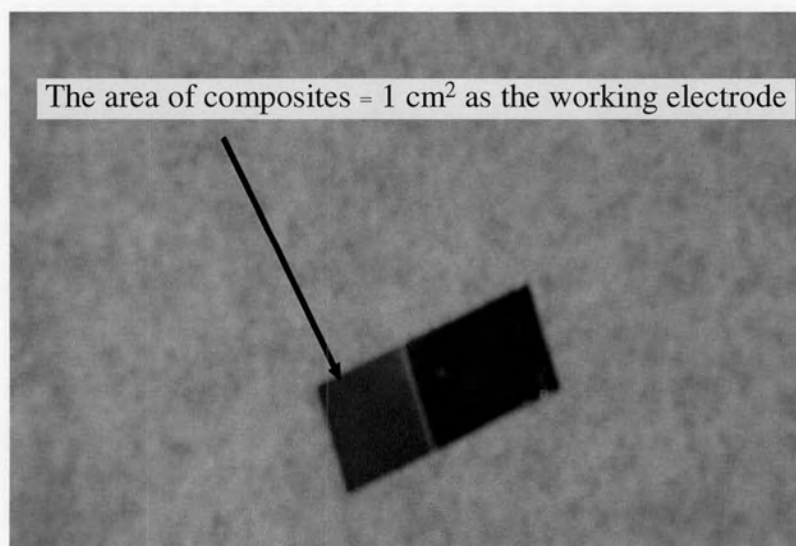


Figure 3.3 Working electrode prepared by ESD.

3.4 Measurements

3.4.1 Electrochemical Measurements

The electrochemical and capacitive measurements were performed with an electrochemical workstation as illustrated in Figure 3.4. A conventional three-electrode cell in which functionalized MWNTs or composite thin film was used as the working electrode, platinum plate as the counter electrode and saturated calomel electrode (SCE) as the reference electrode in 1 M H₂SO₄ aqueous electrolyte solution. The mass of prepared samples, measured with a microbalance in Figure 3.5, was 0.03 mg/cm².

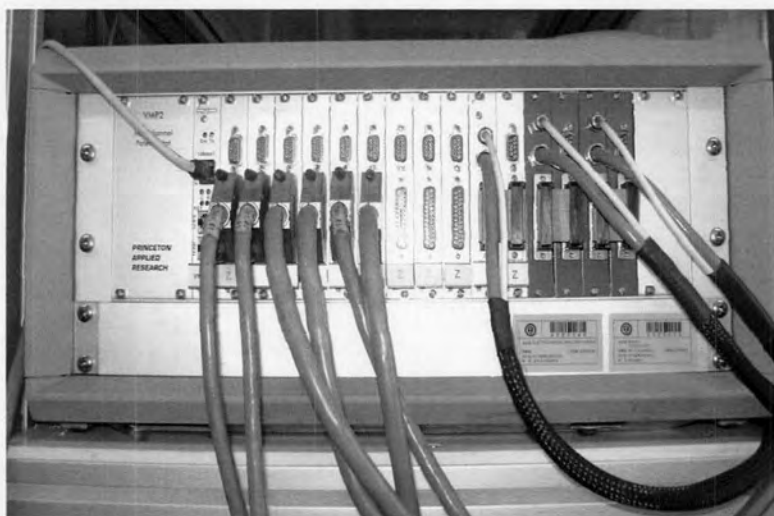


Figure 3.4 The electrochemical workstation (Multichannel potentiostat/galvanostat).



Figure 3.5 Ultramicro balance.

3.4.1.1 Cyclic Voltammetry

The electrochemical properties of pure MWNTs, FeO/MWNTs composites, NiO/MWNTs composites, TiO₂/MWNTs composites, FeO-TiO₂/MWNTs composites and NiO-TiO₂/MWNTs composites were studied by cyclic voltammetry (CV). CV testing was carried out at scan rate of 10 mV/s in the potential range between 0.5 – 1 V. In addition, the specific capacitance (C_p) of the samples was calculated from the cyclic voltammograms by the following equation:

$$C_p = \frac{q_a + |q_c|}{2m\Delta V} \quad 3.1$$

where q_a and q_c are the sum of anodic and cathodic voltammetric charges on the anodic and cathodic scans (A), ΔV is the potential sweep rate (V/s) and m is the mass of each thin film (g).

3.4.1.2 Electrochemical Impedance Spectroscopy

Electrochemical impedance spectroscopic (EIS) measurements of the synthesized samples were carried out with sinusoidal signal of 10 mV over frequency range from 10 kHz to 10 mHz. The capacitance value was obtained from fixed curves calculated by electrochemical software (EC-Lab).

3.4.1.3 Galvanostatic charge-discharge

Galvanostatic charge-discharge method was carried out with an applied constant current of 10 mA in the potential range between 0.5 and 1 V. The capacitance value (C_p) of samples has been evaluated from the charge-discharge curve according to the following equation:

$$C = \frac{I}{m(dV/dt)} \quad 3.2$$

where I is applied current (A) and m is the mass of each thin film (g).

3.4.2 Structural and Morphological Measurements [22]

The prepared samples were characterized in structure and morphology by brunauer, Emmett & teller, fourier transform infrared spectrophotometer, x-ray diffraction, scanning electron microscopy and transmission electron microscopy.

3.4.2.1 Brunauer, Emmett & Teller (BET)

BET is a rule for the physical adsorption of gas molecules on a solid surface and serves as the basis for an important analysis technique for the measurement of the specific surface area of a material [23-26]. In 1938, Stephen Brunauer, Paul Hugh Emmett, and Edward Teller published an article about the BET

theory in a journal for the first time; BET consists of the first initials of their family names.

The concept of the theory is an extension of the Langmuir theory, which is a theory for monolayer molecular adsorption, to multilayer adsorption with the following hypotheses: (a) gas molecules physically adsorb on a solid in layers infinitely; (b) there is no interaction between each adsorption layer; and (c) the Langmuir theory can be applied to each layer. The resulting BET equation is expressed by the following equation:

$$\frac{1}{v \left[\left(\frac{P_0}{P} \right) - 1 \right]} = \frac{c - 1}{v_m c} \left(\frac{P}{P_0} \right) + \frac{1}{v_m c} \quad 3.3$$

where P and P_0 are the equilibrium and the saturation pressure of adsorbates at the temperature of adsorption, v is the adsorbed gas quantity and v_m is the monolayer adsorbed gas quantity. (C) is the BET constant which is expressed by the following equation:

$$c = \exp \left(\frac{E_1 - E_L}{RT} \right) \quad 3.4$$

E_1 is the heat of adsorption for the first layer and E_L is that for the second and higher layers and is equal to the heat of liquefaction.

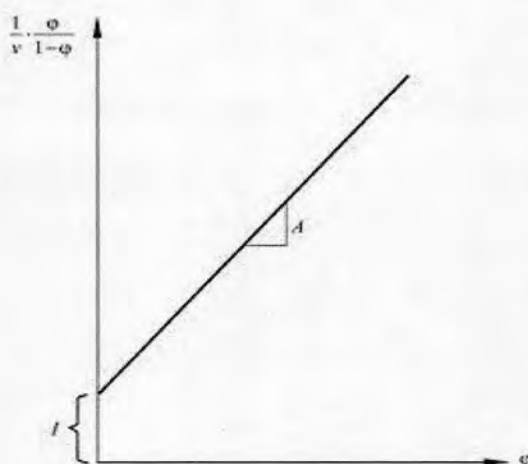


Figure 3.6 BET plot

Equation 3.3 is an adsorption isotherm and can be plotted as a straight line with $1 / v [(P_0 / P) - 1]$ on the y-axis and $f = P / P_0$ on the x-axis according to experimental results. This plot is called a BET plot. The linear relationship of this equation is maintained only in the range of $0.05 < P / P_0 < 0.35$. The value of the slope A and the y-intercept (I) of the line are used to calculate the monolayer adsorbed gas quantity (v_m) and the BET constant (c). The following equations can be used:

$$v_m = \frac{1}{A + I} \quad 3.5$$

$$c = 1 + \frac{A}{I} \quad 3.6$$

The BET method is widely used in surface science for the calculation of surface areas of solids by physical adsorption of gas molecules. A total surface area (S_{total}) and a specific surface area (S) are evaluated by the following equations:

$$S_{BET, total} = \frac{(v_m N s)}{V} \quad 3.7$$

$$S_{BET} = \frac{S_{total}}{a} \quad 3.8$$

where N is Avogadro's number, s is adsorption cross section, V is molar volume of adsorbent gas and a is molar weight of adsorbed species.

3.4.2.1 Fourier Transform Infrared Spectroscopy (FTIR)

Infrared spectroscopy was used to confirm the functional groups of substances and products after preparation process by observing the positions and intensities of IR peaks

The infrared spectra of all films were recorded using a KBr disc method. The dried sample was mixed with potassium bromide in agate mortar and pestle by geometric technique. The mixture was then transferred to a hydraulic press

to a thin disc. In this work, the KBr disc was measured within the wave numbers of $4000 - 1000 \text{ cm}^{-1}$ in transmittance mode.

3.4.2.2 X-Ray Diffractometry (XRD) [27]

When an x-ray beam strikes a surface of crystalline sample at an angle θ , a portion of the radiation is scattered by the layer of atoms at the surface. The effect of scattering from the regularly spaced centers of the crystal is a diffraction of the beam. The data of x-ray diffraction indicates that the spacing between layers of atoms and the scattering centers must be spatially distributed in a higher regular way. The diffraction of x-rays by crystals is showed in Figure 3.7.

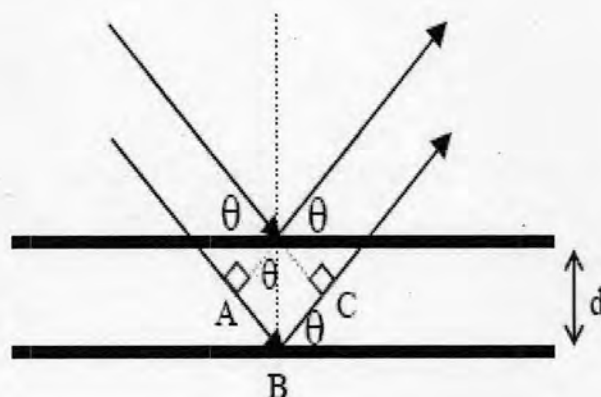


Figure 3.7 Diffraction of x-rays by a crystal.

A narrow beam strikes the crystal surface at angle θ ; scattering occurs as a consequence of interaction of the radiation with atoms located at B. The distance was calculated from following equation:

$$AB + BC = n\lambda \quad 3.9$$

The scattered radiation will be in phase, and the crystal will appear to reflect the x-radiation. It is investigated with equation:

$$AB = BC = d \sin\theta \quad 3.10$$

Thus the condition for constructive interference of the beam at angle θ is expressed by the equation 3.11, called Bragg's law.

$$2d \sin\theta = n\lambda \quad 3.11$$

where n is an integer, d is interplanar distance of the crystal (\AA ; $1 \text{\AA} = 10^{-10} \text{ m}$), θ is angle between x-ray and crystal planes (degree) and λ is wavelength (\AA)

In this study, XRD was used for the characterization of crystalline pattern of the synthesized nanocomposites, which are nanocrystalline metal oxide and the functionalized MWNTs, in the range 10-80 two theta.

3.4.2.3 Scanning Electron Microscope (SEM)

The scanning electron microscope (SEM) has unique capabilities for analyzing surface and morphology of materials. It is analogous to the reflected light microscope, although different radiation sources serve to produce the required illumination. Whereas the reflected light microscope forms an image from light reflected from the sample surface, the SEM uses electrons for image formation. The different wavelength of these radiation sources result in different resolution levels: electron have much shorter wavelength than light photons, the shorter wavelength is capable of generating the higher resolution information. Enhanced resolution in turn permits higher magnification without loss of detail. The maximum magnification of the light microscope is about 2,000 times; beyond this level is empty magnification, or the point where increased magnification doesn't provide additional information. The upper magnification limit is a function of the wavelength of visible light, 2,000 \AA , which equal the theoretical maximum resolution of conventional light microscope. In comparison, the wavelength of electron is less than 0.5 \AA and theoretically the maximum magnification of electron beam instrument is beyond 800,000 times. Because of the instrument parameter, practical magnification and resolution limits are about 75,000 times and 40 \AA in a conventional SEM. The SEM consists basically of 4 systems:

1. The illuminating/imaging system produces the electron beam and directs it onto the sample.
2. The information system includes the data released by the sample during electron bombardment and detectors which discriminate among these analytic information signals.
3. The display system consists of one or two cathode-ray tubes for observing and photographing the interested surface.
4. The vacuum system removes gas from the micropore column which increases the free path of electron, hence the better image quality.

In this work, the JSM-6400 scanning microscope was used for the observation of surfaces of the synthesized composites at a magnification of 10,000X.

3.4.2.4 Transmission Electron Microscope (TEM)

A schematic TEM instrument is showed in Figure 3.8. High energy electron beam passes through a condenser lens to produce parallel rays which affect the sample. The transmitted beam represents a two-dimensional image of the sample which is subsequently magnified by electron optics. It produces a so-called bright field image. Typical operating conditions of a TEM instrument are 100-200 keV, 10^{-6} mbar vacuum, 1 nm resolution and a magnification of 10^5 to 10^6 .

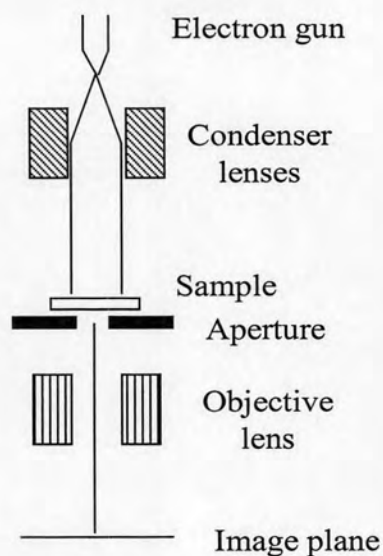


Figure 3.8 Schematic diagram of transmission electron microscope.

In this study, TEM technique is used to determine nanoparticle sizes. The reduced nanocrystalline metal oxides have a broad distribution of sizes and shapes. An average particle size can be calculated by the equation:

$$d_s = \frac{\sum n_i d_i^3}{\sum n_i d_i^2} \quad 3.12$$

where d_s is the average particle diameter (m), d_i is particle diameter (m) and n_i is amount particle (m).

TEM was performed with a JEM-2001 instrument at 200 kV. Samples for TEM were prepared by placing a drop of the ethanol suspension of the nanopowders onto carbon grids and pre-dried before insertion.