Chapter 2

Experimental details: Instrumentation & Methodology

2.1 Synthesis Techniques

2.1.1 Sol-Gel Reflux Method

The sol-gel reflux method is a solution-based approach used for the synthesis of nanoparticles, particularly metal oxides and semiconductors. It involves the formation of a stable colloidal sol from precursor materials, followed by a controlled chemical reaction under reflux conditions.

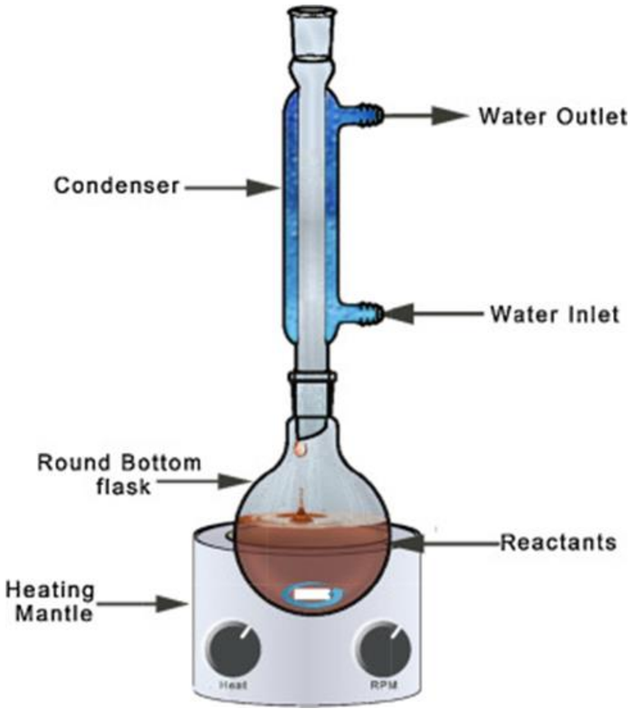


Fig 2.1 Schematic of Sol-gel reflux setup[146]

The process can be summarized in the following steps:

1. **Precursor Solution Preparation:** In this step, precursor materials, typically metal alkoxides or metal salts, are dissolved in a suitable solvent. This solution forms the starting point for nanoparticle synthesis.
2. **Sol Formation:** Through hydrolysis and condensation reactions, the precursor solution undergoes sol-gel transformation, forming a stable colloidal sol. During this stage, the nucleation and growth of nanoparticles take place.

3. **Refluxing:** Refluxing is a critical step in the sol-gel reflux method. The sol is heated under reflux conditions, maintaining a constant temperature and vigorous stirring. This step promotes further growth and crystallization of nanoparticles, leading to the desired properties.
4. **Purification and Drying:** After refluxing, the resulting nanoparticles are typically separated from the solvent and washed to remove any impurities. The collected nanoparticles are then dried to obtain the final product.

Advantages of the Sol-Gel Reflux Method

The sol-gel reflux method offers several advantages for nanoparticle synthesis, making it an attractive choice for researchers and industrial applications:

- **Precise Control:** The sol-gel reflux method allows precise control over the nanoparticle size, shape, and composition by adjusting reaction parameters such as temperature, time, and precursor concentration.
- **Homogeneity:** This method yields nanoparticles with excellent homogeneity, which is crucial for consistent material properties and performance in various applications.
- **Scalability:** The sol-gel reflux method can be easily scaled up for large-scale production, making it suitable for industrial applications.
- **Versatility:** It is adaptable to a wide range of precursor materials, including metal oxides, semiconductors, and hybrid materials, enabling the synthesis of diverse nanoparticles.
- **Enhanced Properties:** The controlled synthesis process often results in nanoparticles with improved physical, chemical, and electronic properties, making them suitable for advanced technologies and applications.

2.1.2 Modified Hummers Method

The modified Hummers method is a chemical oxidation process that transforms graphite into graphene oxide by introducing oxygen-containing functional groups on the graphene layers.

The key principles of this method can be summarized as follows:

1. **Graphite Oxidation:** In the initial step, graphite is subjected to strong oxidative conditions, typically using a mixture of sulfuric acid (H2SO4), potassium permanganate (KMnO4), and a strong oxidizing agent like sodium nitrate (NaNO3).

This mixture initiates the oxidation of the carbon atoms within the graphite lattice, breaking the sp² carbon-carbon bonds.

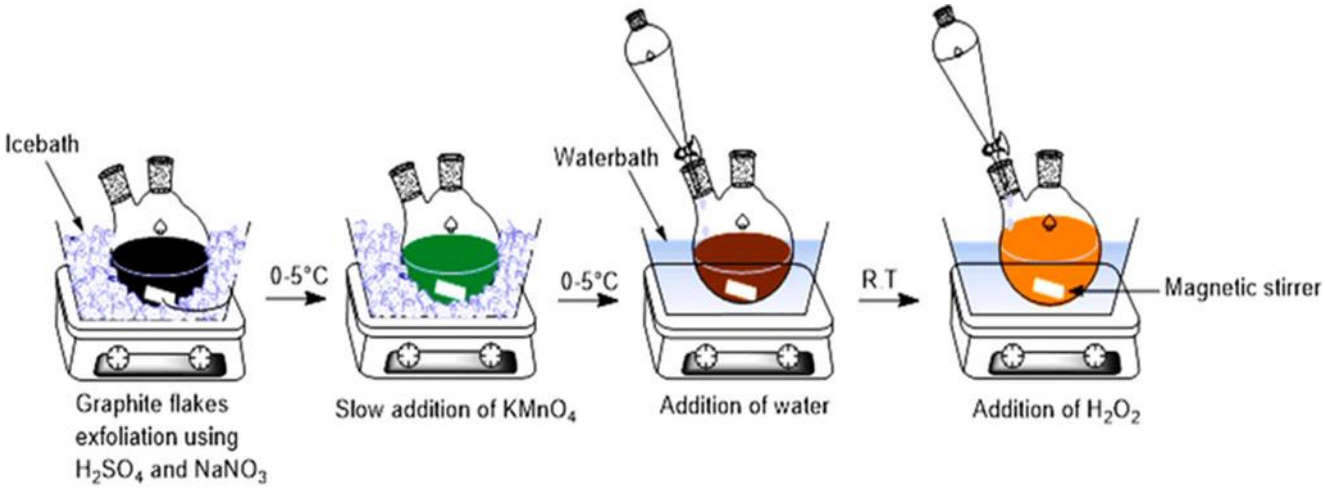


Fig 2.2: Schematic of Modified Hummers Reaction[147]

2. **Formation of Functional Groups:** During the oxidation process, oxygen-containing functional groups such as epoxides, hydroxyls, and carboxyls are introduced onto the graphene layers. These functional groups impart hydrophilicity and reactivity to GO.
3. **Exfoliation and Delamination:** The intercalated functional groups cause the graphite layers to expand and exfoliate, leading to the formation of individual or few-layered GO sheets.
4. **Purification:** The resulting GO suspension is typically washed and purified multiple times to remove excess reagents, unreacted chemicals, and metal impurities.

Advantages of the Modified Hummers Method

The modified Hummers method for GO synthesis offers several advantages over the traditional Hummers method:

- **Improved Efficiency:** Modifications in the reagent composition and reaction conditions enhance the yield and reproducibility of the GO synthesis process.
- **Control Over Functionalization:** Researchers can tailor the degree of functionalization by adjusting the reaction parameters, enabling the production of GO with specific properties.

- **Enhanced Safety:** Some modifications reduce the use of hazardous and environmentally harmful reagents, improving safety and reducing environmental impact.
- **Scalability:** The modified Hummers method can be scaled up for large-scale production of GO, making it suitable for industrial applications.

2.1.3 Solvothermal Method

The synthesis of advanced nanomaterials with tailored structures and properties is at the forefront of materials science and nanotechnology. One such promising class of materials is heterostructures, which combine two or more distinct materials to exploit synergistic effects and multifunctionality. In this section, we explore the principles, methodology, and advantages of the solvothermal method for the synthesis of reduced graphene oxide/zinc oxide (rGO/ZnO) heterostructures, which have gained considerable attention due to their unique properties and potential applications in various fields.

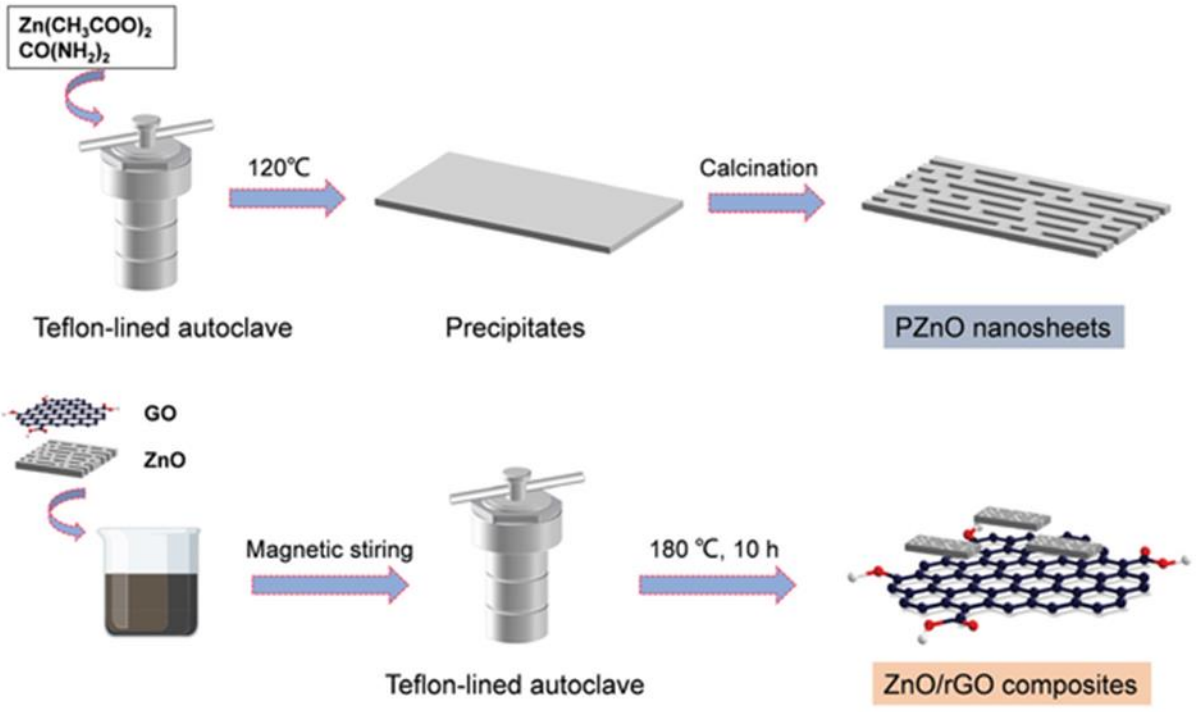


Fig 2.3: Schematic of heterostructure synthesis via Solvothermal reaction[148]

The solvothermal method is a versatile and powerful technique for the synthesis of nanomaterials, including heterostructures like rGO/ZnO. It involves the use of high-temperature and high-pressure conditions within a solvent to drive chemical reactions and control the formation of desired nanostructures. The key principles of the solvothermal synthesis can be summarized as follows:

1. **Precursor Solution Preparation:** Initially, a precursor solution is prepared by dissolving appropriate precursors of graphene oxide and zinc oxide in a suitable solvent. The choice of solvents and precursor concentrations influences the morphology and properties of the resulting heterostructures.
2. **Reaction Under Solvothermal Conditions:** The precursor solution is sealed within a high-pressure vessel and subjected to elevated temperatures and pressures for a specified duration. These conditions facilitate the nucleation, growth, and self-assembly of nanoparticles of both rGO and ZnO.
3. **Reduction of Graphene Oxide:** Simultaneously, graphene oxide undergoes reduction to rGO in the presence of reducing agents such as hydrazine or other suitable reductants. This reduction step is crucial for enhancing the electrical conductivity of the heterostructure.
4. **Heterostructure Formation:** During the solvothermal treatment, ZnO nanoparticles nucleate and grow on the surface of rGO sheets, forming a well-defined heterostructure. The size, shape, and distribution of these nanoparticles can be controlled by adjusting the reaction parameters.
5. **Purification and Drying:** After the solvothermal treatment, the resulting rGO/ZnO heterostructure is typically washed to remove any unreacted precursors and impurities. The collected heterostructure is then dried to obtain the final product.

Advantages of the Solvothermal Method

The solvothermal method offers several advantages for the synthesis of rGO/ZnO heterostructures:

- **Control Over Morphology:** The solvothermal method enables precise control over the size, shape, and distribution of ZnO nanoparticles on rGO sheets, which is essential for tailoring the heterostructure properties.

- **Enhanced Electrical Conductivity:** The reduction of graphene oxide to rGO during the synthesis process improves the electrical conductivity of the heterostructure, making it suitable for various electronic applications.
- **Scalability:** The method can be scaled up for the production of rGO/ZnO heterostructures in larger quantities, making it suitable for industrial applications.
- **Synergistic Properties:** The combination of rGO and ZnO in a heterostructure leads to synergistic effects, such as enhanced photocatalytic, electrochemical, and optoelectronic properties.

2.1.4 Solution-Processed Spin Coating

Solution-processed spin coating is a versatile technique that involves the deposition of a polymer solution containing nanoparticles onto a substrate. The process can be broken down into the following key steps:

1. **Polymer Solution Preparation:** A polymer matrix, often in the form of a solution or dispersion, is prepared by dissolving a polymer in a suitable solvent. To synthesize polymer nanocomposites, nanoparticles are typically dispersed in this solution to form a homogeneous mixture.
2. **Spin Coating Deposition:** The prepared polymer-nanoparticle solution is dispensed onto a substrate, which is typically a flat and smooth surface such as glass or silicon. The substrate is then rotated at high speeds, causing the solution to spread uniformly due to centrifugal forces.
3. **Solvent Evaporation:** As the substrate spins, the solvent begins to evaporate, leaving behind a thin film of the polymer-nanoparticle composite. The speed of rotation, solution concentration, and solvent evaporation rate can be controlled to influence film thickness and nanoparticle distribution.
4. **Annealing or Curing:** After the deposition process, the film is often subjected to an annealing or curing step to remove any remaining solvent and enhance polymer cross-linking or crystallinity. This step is crucial for achieving the desired properties of the nanocomposite.

Advantages of Solution-Processed Spin Coating

The solution-processed spin coating method offers several advantages for the synthesis of polymer nanocomposites:

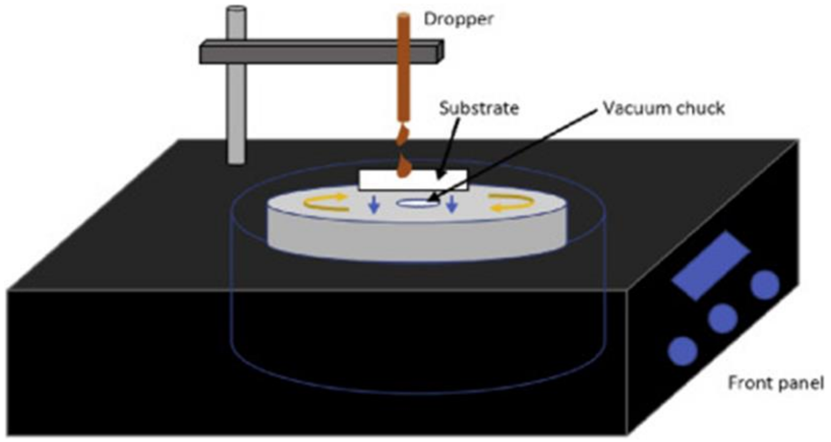


Fig 2.4: Schematic of Spin-coating process for thin-film deposition

- **Nanoparticle Dispersion Control:** Spin coating provides excellent control over the distribution and alignment of nanoparticles within the polymer matrix, leading to enhanced properties and performance.
- **Thin Film Formation:** The technique enables the production of thin, uniform films with precise thickness control, making it suitable for various applications, including coatings, sensors, and electronic devices.
- **Scalability:** Solution-processed spin coating can be easily scaled up for large-scale production, making it suitable for industrial applications.
- **Reduced Waste:** It is a solvent-efficient process, reducing waste compared to other deposition methods.
- **Versatility:** The method is compatible with a wide range of polymers and nanoparticles, allowing for the synthesis of diverse polymer nanocomposites with tailored properties.

2.2 Characterization & Measurement methods

2.2.1 X-ray diffraction

X-ray diffraction (XRD) is a powerful analytical technique widely employed for the characterization of crystalline materials. This method provides valuable insights into the atomic and molecular structure of materials, making it indispensable in various fields, including materials science, chemistry, physics, geology, and biology. This section will provide a comprehensive overview of the X-ray diffraction characterization method, elucidating its working principle, instrument details, and application in the research.

Fig 2.5 Digital image of the XRD setup

Working principle:

X-ray diffraction relies on the interaction of X-rays with the crystal lattice of a sample. When monochromatic X-rays of a specific wavelength are directed at a crystalline material, the X-rays undergo constructive and destructive interference as they interact with the atoms within the crystal lattice. The resulting diffraction pattern, characterized by a series of discrete spots or diffraction peaks, contains information about the arrangement of atoms in the crystal lattice.

According to Bragg's law, the angles at which the X-rays are diffracted are related to the spacing between planes of atoms within the crystal and the wavelength of the incident X-rays:

$$n\lambda = 2d\sin\Theta \qquad (2.1)$$

Where n is an integer representing the order of the diffraction peak, λ is the wavelength of the incident X-rays, d is the spacing between crystal planes and Θ is the diffraction angle.

By measuring the diffraction angles and knowing the wavelength of the X-rays, it is possible to determine the interatomic spacing within the crystal lattice, which, in turn, provides information about the crystal structure.

Instruction details:

Model: Rigaku SmartLab 9kW Powder type
Company: RIGAKU Corporation

The X-ray diffraction instrument, commonly referred to as an X-ray diffractometer, comprises several essential components:

- *X-ray Source:* This component produces a beam of monochromatic X-rays. Common sources include X-ray tubes, which emit X-rays when high-energy electrons bombard a target material (e.g., copper or molybdenum).
- *Sample Stage:* The sample to be analyzed is mounted on a goniometer, which allows precise rotation and tilt of the sample. This flexibility is crucial for obtaining diffraction data from different crystallographic planes.
- *Detector:* X-ray detectors, such as scintillation detectors or solid-state detectors (e.g., silicon or germanium), capture the diffracted X-rays and convert them into electrical signals. Modern detectors provide high sensitivity and resolution.
- *Collimation System:* A collimator focuses the incident X-ray beam onto the sample and ensures that only a well-defined portion of the sample is irradiated.
- *Analyzer Crystals:* In some advanced XRD setups, analyzer crystals are employed to select specific diffraction orders, enhancing data quality and selectivity.
- *Data Acquisition System:* A computer-based data acquisition system records the diffraction pattern by measuring the intensity of diffracted X-rays at different angles. The data are then processed to generate a diffraction pattern or a crystal structure.

2.2.2 Transmission Electron Microscopy (TEM) and Selected Area Electron Diffraction (SAED)

Transmission Electron Microscopy (TEM) and Selected Area Electron Diffraction (SAED) are advanced microscopy techniques that have revolutionized the field of materials characterization. These methods offer unparalleled resolution and the ability to probe nanoscale structures, making them indispensable tools in various scientific disciplines, including materials science, biology, and condensed matter physics. This section will provide a comprehensive overview of TEM and SAED characterization methods, elucidating their working principles, instrument details, and application in the research.

Working principles:

TEM is based on the principle of transmitting a beam of electrons through a thin specimen to form a high-resolution image. The key components and steps involved in TEM are as follows:

- *Electron Source:* A thermionic or field-emission electron gun produces a beam of high-energy electrons.
- *Condenser System:* A series of electromagnetic lenses focus and converge the electron beam onto the specimen.
- *Specimen:* The sample must be ultra-thin (typically less than 100 nanometers) to allow electrons to pass through. It is typically prepared by cutting and thinning using specialized techniques such as focused ion beam (FIB) milling or ultramicrotomy.
- *Objective Lens:* The objective lens, another electromagnetic lens, forms a magnified image of the specimen. This image contains information about the sample's internal structure.
- *Projector Lens:* The projector lens further magnifies the image and projects it onto a fluorescent screen or a digital camera sensor.
- *Image Formation:* The interaction of electrons with the sample leads to the formation of an image based on electron scattering, providing information about the sample's morphology, crystal structure, defects, and more.

Selected Area Electron Diffraction (SAED): SAED is a technique employed within the TEM to characterize the crystallography of small, localized regions within a sample. The process involves the following steps:

- *Specimen Area Selection:* Using a selected area aperture, a specific region of the sample is illuminated with a convergent electron beam.

Fig 2.6 Digital image of the HRTEM setup

- *Diffraction Pattern Formation:* Electrons interacting with the crystalline structure in the selected area scatter in accordance with Bragg's law, resulting in the formation of a diffraction pattern on a screen or detector.
- *Pattern Analysis:* The resulting diffraction pattern provides information about the crystal lattice parameters, orientation, and symmetry, allowing for the identification of crystal structures and defects.

Instrument details:

Model: Tecnai G2 20 TWIN
Company: FEI Company of USA (S.E.A.) PTE, LTD
EDS:TEAM EDS SYSTEM with Octane Plus SDD Detector

2.2.3 Field-Emission Scanning Electron Microscopy (FESEM) & Energy-Dispersive X-ray Spectroscopy (EDX)

Field-Emission Scanning Electron Microscopy (FESEM) coupled with Energy-Dispersive X-ray Spectroscopy (EDX) is a powerful combination of techniques used for the characterization of materials at the micro- and nanoscale. This section will provide a comprehensive overview of FESEM and EDX characterization methods, elucidating their working principle, instrument details, and application in the research.

Working principle:

FESEM is a microscopy technique that employs a focused beam of electrons to generate high-resolution images of a sample's surface morphology. The key components and steps involved in FESEM are as follows:

- *Electron Gun:* FESEM uses a field-emission electron gun, which generates a narrow, high-energy electron beam. The field emission occurs when a sharp tungsten or other suitable emitter tip is subjected to a strong electric field.
- *Electron Lenses:* Electromagnetic lenses are used to focus and control the electron beam, allowing for precise imaging.
- *Sample and Stage:* The sample is placed on a movable stage, allowing for precise positioning and manipulation during imaging.
- *Electron-Beam Scanning:* The focused electron beam scans the sample's surface in a raster pattern. Secondary electrons and backscattered electrons are generated during this process.
- *Detectors:* Secondary electron detectors and backscattered electron detectors capture the emitted electrons to create images. These detectors provide information about the sample's topography and composition.

Fig 2.7 Digital image of the FESEM setup

EDX is often integrated with FESEM to provide information about the elemental composition of the sample. The process involves the following steps:

- *X-ray Emission:* When the high-energy electron beam interacts with the sample's atoms, it can displace inner-shell electrons, creating vacancies. Electrons from higher energy levels fill these vacancies, emitting characteristic X-rays in the process.
- *X-ray Detection:* An energy-dispersive X-ray detector is used to capture the emitted X-rays. The detector measures the energy (wavelength) of the X-rays.
- *Spectrum Analysis:* The resulting X-ray spectrum provides information about the elements present in the sample and their relative concentrations. Peaks in the spectrum correspond to specific elements.

Instrument details:

Model: Nova Nano SEM 450
Company: FEI Company of USA (S.E.A.) PTE, LTD
EDS:Team Pegasus Integrated EDS-EBSD with Octane Plus and Hikari Pro

2.2.4 Atomic Force Microscopy (AFM)

Atomic Force Microscopy (AFM) is a powerful and versatile characterization technique used to investigate the surface properties of materials at the nanoscale. It offers exceptional spatial resolution and the ability to probe a wide range of surface features, making it an invaluable tool in diverse fields, including nanotechnology, materials science, biology, and chemistry. This section provides a comprehensive overview of the AFM characterization method, elucidating its working principle, instrument details, and application in the research.

Working principle:

AFM is based on the principle of using a sharp probe, typically a cantilever with a nanoscale tip, to scan the surface of a sample. The interaction forces between the tip and the sample surface are measured, allowing for the creation of high-resolution images and the characterization of various surface properties. The key components and steps involved in AFM are as follows:

- *Cantilever and Tip:* The cantilever is a flexible beam with a sharp tip at its end. The tip is brought in close proximity to the sample surface, and forces between the tip and surface govern the cantilever's deflection.
- *Laser and Photodetector System:* A laser beam is directed onto the back of the cantilever, and a photodetector monitors the position of the laser spot on the detector. The deflection of the cantilever alters the position of the laser spot, enabling precise measurements of the cantilever deflection.
- *Feedback Control:* A feedback loop maintains a constant force or distance between the tip and the sample by adjusting the vertical position of the sample stage. This control mechanism is essential for achieving topographic imaging and measuring surface forces.
- *Surface Scanning:* The cantilever, with the tip attached, is raster-scanned across the sample's surface. As the tip interacts with the surface, the cantilever's deflection is recorded at each position, creating a topographic map of the sample.

Fig 2.8 Digital image of the AFM setup

Instrument details:

Model: Park XE7

Company: Park Systems, South Korea

Modes of Atomic Force Microscopy

Atomic Force Microscopy (AFM) offers several modes of operation, each tailored to specific experimental requirements and sample characteristics. These modes enable researchers to obtain a wide range of information beyond topographical imaging. Two of the primary AFM modes are Contact Mode and Non-Contact Mode, which are described below:

Contact Mode AFM: In Contact Mode AFM, the tip of the cantilever is in continuous contact with the sample surface throughout the scan. The cantilever is deflected as it interacts with the sample's surface, and this deflection is used to maintain a constant setpoint force. The feedback mechanism adjusts the z-position of the sample stage to keep the cantilever deflection constant, resulting in topographical imaging.

Applications:

- Surface topography imaging: Contact Mode AFM is widely used for high-resolution topographical imaging of various surfaces.
- Mechanical property mapping: It can be used to assess mechanical properties of materials, such as stiffness or adhesion.
- Force-distance spectroscopy: Contact Mode allows for the measurement of force-distance curves, which can reveal information about material properties and interactions.

Non-Contact Mode *AFM:* Non-Contact Mode, often referred to as Tapping Mode, operates with the cantilever oscillating close to, but not touching, the sample surface. The tip taps the surface intermittently, and the amplitude of the cantilever's oscillation is maintained at a set level by adjusting the tip-sample distance. The frequency shift or phase shift of the cantilever oscillation provides information about the interaction forces, allowing for topographical imaging.

Applications:

- Gentle imaging: Non-Contact Mode is suitable for imaging soft or delicate samples without causing significant damage.
- Reduced tip-sample interaction: It minimizes lateral forces and wear on the tip.
- Surface chemistry mapping: It can be used to study surface properties and chemical composition via frequency or phase shifts.

2.2.5 UV-Vis spectroscopy

UV-Vis spectroscopy is a widely utilized analytical technique that provides valuable insights into the electronic structure, concentration, and properties of molecules and materials. This section provides an in-depth examination of UV-Vis spectroscopy as a characterization method, outlining its working principle, instrument details, and application in the research.

Fig 2.9 Digital image of the UV-Vis Spectrometer

Working principle:

UV-Vis spectroscopy relies on the interaction between ultraviolet (UV) and visible (Vis) light and the molecules or substances being analyzed. The working principle is based on the absorption of photons by electrons in atoms or molecules, which leads to electronic transitions between energy levels. Key aspects of the working principle include:

- *Light Source:* A UV-Vis spectrophotometer employs a light source that emits a broad spectrum of UV and visible light, typically in the range of 190 to 800 nanometers.
- *Sample Interaction:* The incident light passes through a sample containing the analyte. If the analyte absorbs certain wavelengths of light, the transmitted light will exhibit reduced intensity at those wavelengths.
- *Detector:* A detector measures the intensity of light that exits the sample. By comparing this intensity to that of the incident light, the spectrophotometer quantifies the extent of absorption.

- *Beer-Lambert Law:* UV-Vis spectroscopy follows the Beer-Lambert Law, which relates the absorbance (A) of a sample to its concentration (C), molar absorptivity (ε), path length (l), and the intensity of incident light (I_o) as follows:

$$A = \log(I/I_0) = \varepsilon c l \tag{2.2}$$

- The absorbance is directly proportional to the concentration and path length and inversely proportional to the molar absorptivity.

Instrument details:

Model: Biospectrometer Kinetic
Company: Eppendorf AG, Germany

2.2.6 Fourier-transform Infrared (FTIR) spectroscopy

Fourier-transform infrared (FTIR) spectroscopy is a powerful analytical technique used for the characterization of organic and inorganic compounds, polymers, biomolecules, and materials. This section provides an in-depth examination of FTIR spectroscopy as a characterization method, including its working principle, instrument details, and application in the research.

Working principle:

FTIR spectroscopy is based on the interaction between infrared (IR) radiation and molecules. It operates on the principle that when molecules absorb IR radiation, they undergo changes in vibrational energy levels. Key aspects of the working principle include:

- *Light Source:* An FTIR spectrometer typically employs a broadband IR light source. This source emits a continuous spectrum of IR radiation.
- *Interferometer:* The heart of the FTIR spectrometer is an interferometer, which splits the broadband IR beam into two paths. One beam is directed through the sample, and the other serves as a reference beam.
- *Sample Interaction:* The IR radiation interacts with the sample, causing molecular vibrations that result in the absorption of specific IR frequencies. These frequencies are characteristic of the chemical bonds and functional groups in the sample.

- *Interference Pattern:* After interacting with the sample and the reference beam, the two beams recombine at the interferometer. The interference between the two beams creates an interferogram, which contains information about the sample's absorption spectrum.
- *Fourier Transformation:* The interferogram is subjected to a Fourier transformation to convert it from the time domain to the frequency domain. This process yields the sample's IR spectrum, which displays absorbance as a function of wavenumber (cm^{-1}).
- *Spectral Analysis:* The resulting IR spectrum is analyzed to identify functional groups, chemical bonds, and molecular structures within the sample.

Instrument details:

Model: Nicolet iS5
Company: THERMO Electron Scientific Instruments LLC

Fig 2.10 Digital image of the Fourier Transform Infrared Spectrometer

2.2.7 Raman spectroscopy

Raman spectroscopy is a powerful and versatile analytical technique employed for the characterization of molecular structures, chemical compositions, and crystalline properties of various materials. This section provides a comprehensive examination of Raman spectroscopy as a characterization method, elucidating its working principle, instrument details, and application in the research.

Working principle:

Raman spectroscopy is based on the interaction between monochromatic light, typically from a laser, and the molecular vibrations of a sample. The working principle is rooted in the scattering of photons by molecules, where a small fraction of scattered light undergoes a change in energy due to vibrational transitions. Key aspects of the working principle include:

- *Light Source:* A laser emits monochromatic light of a specific wavelength, which is directed onto the sample.
- *Sample Interaction:* When the laser light interacts with the sample, some of the incident photons are scattered. The majority of these photons scatter elastically, maintaining the same energy (Rayleigh scattering). However, a small portion undergoes inelastic scattering, resulting in a shift in energy corresponding to molecular vibrations (Raman scattering).
- *Spectral Analysis:* The Raman scattered light is collected and analyzed using a spectrometer. The Raman spectrum is generated by plotting the intensity of scattered light as a function of energy shift, typically reported in wavenumbers (cm^{-1}) or frequency (cm^{-1}).
- *Spectral Interpretation:* Peaks in the Raman spectrum correspond to specific vibrational modes within the sample, revealing information about molecular bonds, chemical composition, and crystal structures.

Instrument details:

Model: Alpha 300RA

Company: WITec Instruments, Germany

Fig 2.11 Digital image of the Raman Spectroscope

2.2.8 Photoluminescence spectroscopy

Photoluminescence spectroscopy is a powerful and versatile characterization technique used to investigate the electronic and optical properties of materials. This section provides a comprehensive overview of photoluminescence spectroscopy as a characterization method, elucidating its working principle, instrument details, and application in the research.

Working principle:

Photoluminescence spectroscopy is based on the interaction between photons and materials. The working principle is rooted in the emission of light by materials (photoluminescence) when they absorb photons (typically from a laser or other light source). Key aspects of the working principle include:

- *Light Source:* A light source, often a laser, emits photons with specific energies (wavelengths).

Fig 2.12 Digital image of the Photoluminescence Spectrometer

- *Sample Interaction*: The incident photons are directed onto the sample. When absorbed by the material, the photons excite electrons from the ground state to higher energy states.
- *Relaxation:* After excitation, the electrons eventually return to their ground state, releasing energy in the form of emitted photons. This process is known as photoluminescence.
- *Spectral Analysis:* The emitted photons, which can be at longer wavelengths than the excitation source (Stokes shift) or at shorter wavelengths (anti-Stokes shift), are collected and analyzed using a spectrometer.
- *Spectral Interpretation:* The photoluminescence spectrum is generated by plotting the intensity of emitted light as a function of wavelength or energy. It reveals information about the electronic structure, bandgap, and optical properties of the material.

Instrument details:

Model: F-4600 Fluorescence Spectrophotometer

Company: Hitachi Ltd. Tokyo, Japan

2.2.9 Dynamic Light Scattering (DLS) and Zeta Potential analysis

Dynamic Light Scattering (DLS) and Zeta Potential analysis are essential techniques used to characterize nanoparticles, colloids, and macromolecules in various scientific and industrial applications. This section provides an in-depth examination of DLS and Zeta Potential as characterization methods, elucidating their working principle, instrument details, and application in the research.

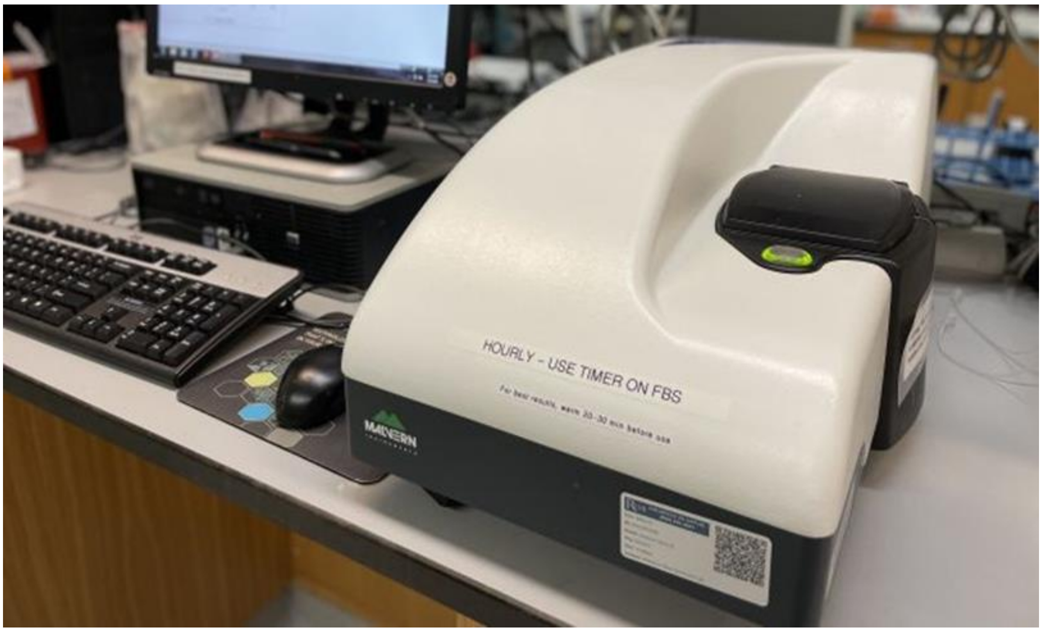


Fig 2.13 Digital image of the DLS and Zeta Potential setup

Working principle:

DLS, also known as Photon Correlation Spectroscopy (PCS), characterizes the size and size distribution of particles in a solution. The working principle is based on the Brownian motion of particles in a fluid. Key aspects of the working principle include:

- *Laser Light Scattering:* A laser beam is directed into the sample, and the scattered light is collected at an angle. The scattering intensity is recorded as a function of time.
- *Brownian Motion:* Particles suspended in the solution undergo Brownian motion due to thermal energy. Larger particles move more slowly than smaller ones.

- *Correlation Function:* The autocorrelation function of the intensity fluctuations is calculated, which provides information about the time-dependent fluctuations in scattered light caused by the movement of particles.
- *Size Determination:* Analysis of the autocorrelation function yields the diffusion coefficient of particles, which can be used to calculate the hydrodynamic radius (size) of particles using the Stokes-Einstein equation.
- *Zeta Potential Analysis:* Zeta potential measures the electrokinetic potential at the shear plane of particles in a colloidal suspension. It provides information about particle stability and interactions. Key aspects of the working principle include:
- *Electrophoretic Mobility:* An electric field is applied to the sample, causing charged particles to move. The velocity of particle movement is recorded.
- *Zeta Potential Calculation:* Zeta potential is calculated using the measured electrophoretic mobility and the Smoluchowski equation or the Henry equation, depending on the system.
- *Electrokinetic Behavior:* The Zeta potential reflects the electrokinetic behavior of particles, indicating their surface charge and potential interactions with other particles or surfaces.

Instrument details:

Model: Zetasizer Nano ZS
Company: Malvern Panalytical, United Kingdom

2.2.10 X-ray Photoelectron Spectroscopy (XPS)

X-ray Photoelectron Spectroscopy (XPS), also known as Electron Spectroscopy for Chemical Analysis (ESCA), is a powerful surface-sensitive technique used for the characterization of materials in terms of their chemical composition, elemental identity, chemical states, and electronic properties. This section provides an in-depth examination of XPS as a characterization method, elucidating its working principle, instrument details, and application in the research.

Fig 2.14 Digital image of the X-Ray Photoelectron Spectroscope

Working principle:

XPS operates on the principle of detecting emitted electrons from a sample's surface due to interactions with X-ray photons. The working principle is rooted in the photoelectric effect and the binding energy of electrons in atomic orbitals. Key aspects of the working principle include:

- *X-ray Excitation:* A monochromatic X-ray source emits X-ray photons that are directed onto the sample's surface. The instrument is equipped with a monochromatic X-ray source, commonly using Al Kα (1486.6 eV) or Mg Kα (1253.6 eV) X-rays.
- *Photoelectric Effect:* When X-ray photons interact with the sample, they can eject inner-shell electrons from atoms near the surface through the photoelectric effect. The energy of the emitted electrons is characteristic of the binding energy of the core electrons.
- *Electron Detection:* An electron analyzer measures the kinetic energy and emission angle of the ejected electrons. The energy distribution of emitted electrons is used to construct an XPS spectrum. The electron analyzer consists of a hemispherical or cylindrical analyzer that measures the kinetic energy and emission angle of the emitted photoelectrons.

- *Binding Energy Analysis:* XPS spectra are plotted as intensity vs. binding energy. The binding energy of each peak in the spectrum corresponds to specific electron shells and chemical states within the material.
- *Chemical State Identification:* The binding energy information allows for the identification of the chemical elements present and their chemical states, oxidation states, and chemical environment.

Instrument details:

Model: K-Alpha
Company: Thermo Fisher Scientific

2.2.11 Thermal evaporation vacuum chamber

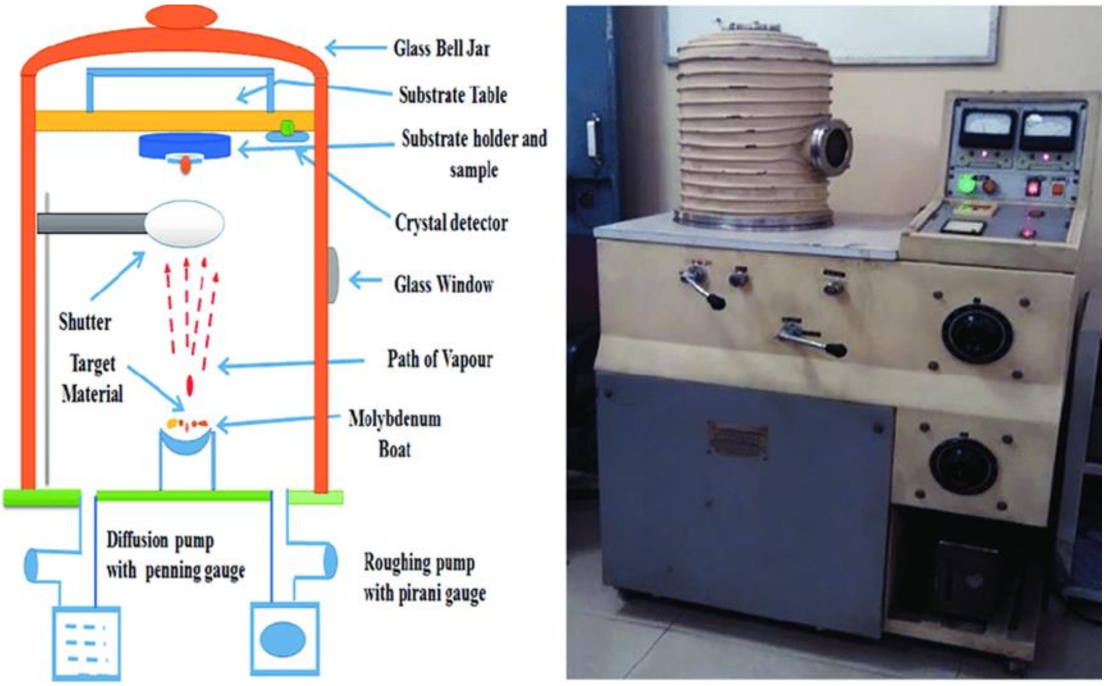
Thermal evaporation in a vacuum chamber is a fundamental technique for depositing thin films and coatings onto substrates. This section provides a detailed examination of a thermal evaporation vacuum chamber used for electrode deposition, elucidating its working principle, instrument details, and application in the research.

Working principle:

Thermal evaporation is a physical vapor deposition (PVD) technique used to deposit thin films by heating a solid material (source) in a vacuum until it vaporizes and condenses onto a substrate. Key aspects of the working principle include:

- *Vacuum Environment:* The vacuum chamber is evacuated to a low-pressure environment to minimize the presence of gas molecules that can interfere with film deposition.
- *Heating the Source Material:* The source material, typically a metal or semiconductor, is placed in a crucible or boat within the vacuum chamber. It is heated using resistive or electron beam heating methods.
- *Vaporization:* As the source material is heated, it undergoes sublimation, transforming from a solid to a vapor phase. The vaporized atoms or molecules rise and condense onto a substrate, forming a thin film.

- *Substrate Placement*: The substrate, which may be a wafer or another material, is positioned in the vacuum chamber in proximity to the source material. The film deposition occurs on the substrate surface.
- *Film Growth:* The rate of film growth depends on parameters such as the heating temperature, pressure, and the distance between the source and substrate. Control of these parameters allows for precise film thickness and uniformity.



(a)

(b)

Fig 2.15 a) Schematic of thermal evaporation technique for electrode deposition; b) Digital image of the thermal evaporator [149]

Instrument details:

Thermal evaporation vacuum chambers for electrode deposition consist of several critical components:

- *Vacuum Chamber:* The chamber is made of materials compatible with high vacuum, often stainless steel or glass, and includes ports for introducing and evacuating gases.
- *Source Material Holder:* The source material is placed in a crucible or boat within the chamber, which can be resistively heated or electron beam heated.

- *Substrate Holder:* Substrates are held in a separate holder, which may be heated to control film properties further.
- *Deposition Rate Monitor:* Some systems incorporate deposition rate monitors or quartz crystal microbalances to monitor and control the rate of film deposition.
- *Vacuum Pump:* A high-vacuum pump (e.g., turbo molecular pump or diffusion pump) is used to evacuate the chamber and maintain a low-pressure environment.
- *Gas Inlet System:* A gas inlet system allows for the introduction of specific gases or reactive gases during deposition processes like co-evaporation or sputtering.

2.2.12 Semiconductor Parameter Analyzer

A Semiconductor Parameter Analyzer is a sophisticated laboratory instrument designed to characterize and evaluate the electrical properties of semiconductor devices and materials. This section provides an in-depth examination of the Semiconductor Parameter Analyzer, elucidating its working principle, instrument details, and application in the research.

Working principle:

The working principle of a Semiconductor Parameter Analyzer is rooted in the measurement and analysis of electrical parameters, such as current (I), voltage (V), resistance (R), capacitance (C), and inductance (L), for semiconductor devices and materials. Key aspects of the working principle include:

- *Signal Generation:* The instrument generates stimulus signals, typically voltage or current, which are applied to the semiconductor device under test.
- *Data Acquisition:* The Parameter Analyzer measures the response of the device, capturing data on current and voltage as a function of time or applied voltage/current.
- *Data Analysis:* The collected data is analyzed to extract relevant electrical parameters, such as carrier mobility, carrier concentration, threshold voltage, on/off ratio, capacitance-voltage (C-V) characteristics, and more.
- *Characterization Modes:* The Parameter Analyzer operates in different characterization modes, such as DC measurements, pulsed measurements, small-signal AC measurements, and transient measurements, to cover a wide range of device behaviors and properties.

Fig 2.16 Digital image of the Semiconductor Parameter Analyzer

Instrument details:

Model: B1500A

Company: Keysight Technologies, US

Semiconductor Parameter Analyzers are equipped with several essential components:

- *Stimulus Generators:* These produce the required voltage or current signals for device testing. They may also provide specialized signals, such as pulsed or AC signals.
- *Measurement Units:* These units capture and digitize the response signals, allowing for precise measurement of current and voltage.
- *Data Analysis Software:* The instrument is connected to a computer running specialized software for data acquisition, analysis, and visualization.
- *Sample Holder:* A sample holder or probe station facilitates the connection of semiconductor devices or materials to the Parameter Analyzer.
- *Communication Ports*: Interfaces like USB, Ethernet, or GPIB enable communication with external devices and control systems.