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CHAPTER FIVE
Nanomaterials Analytical Tools

5.1 Nano Materials Measurement and Spectroscopy

This chapter describes the general principles of techniques and equipment used to characterize of the nano-size (nanoparticle or nanostructures) by different methods, which have been systematically investigated using;

a) Field emission scanning electron microscopy (FESEM)
b) X-ray diffraction (XRD)
c) Atomic force microscopy (AFM)
d) UV–vis spectrophotometry
e) Photoluminescence spectrum (PL)

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5.1.a Field Emission Scanning Electron Microscope (FESEM)

Field emission scanning electron microscope (FESEM) is a tool used to examine and analyse the surface morphology of the nano-materials. The FESEM has more uses than traditional microscope due to its large field depth which produces images of films with high magnification (as small as 1 nm) and high resolution, as shown in Figure 5.1. In FESEM, an electron beam is used instead of a light beam, which provides sharply pointed beam with high electron energy, thereby reducing charging effects on the sample and enhancing of the spatial analysis.

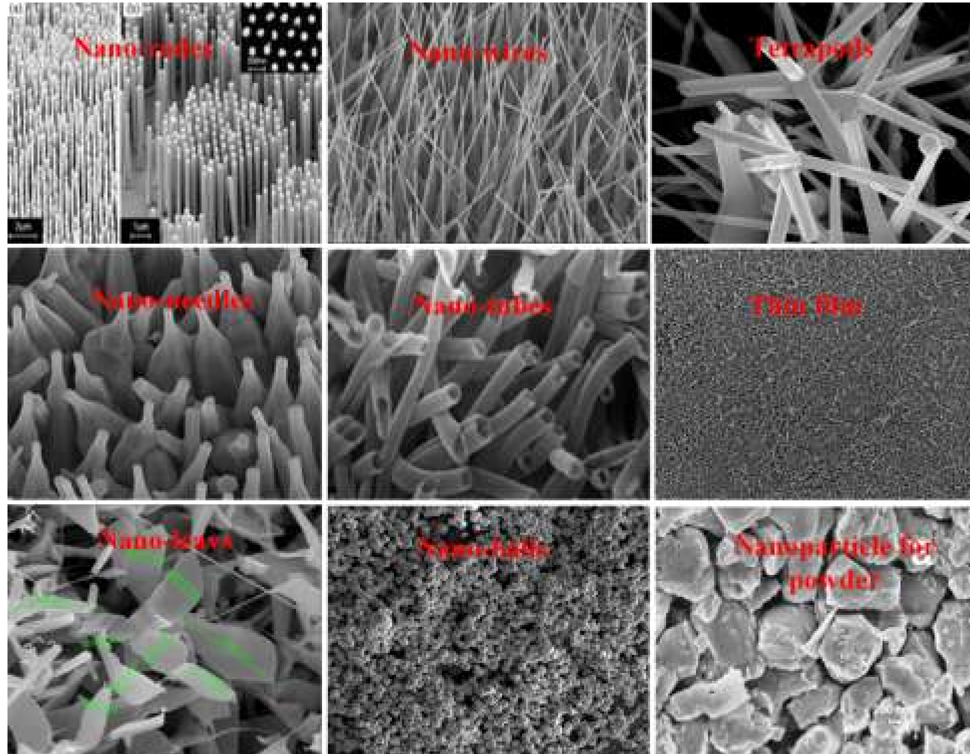

Figure 5.1: FESEM images of nanostructures and nanoparticle with different morphology

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The image of FESEM generated as a result of the electron beam from the field emission gun passes through the electromagnetic lens focusing onto the sample surface [Figure 5.2 (b)].

The high electrons energy of backscattered electrons emission (BSE) is generated from the elastic collision in the deep level of the sample, whereas the secondary electron (SE) emission is created as a result of the inelastic collision on the surface of the sample. The BSE and SE emissions are then collected using a detector. These emissions are used to collect information on the morphology of the samples, such as images of the 3D view, cross section, and surface.

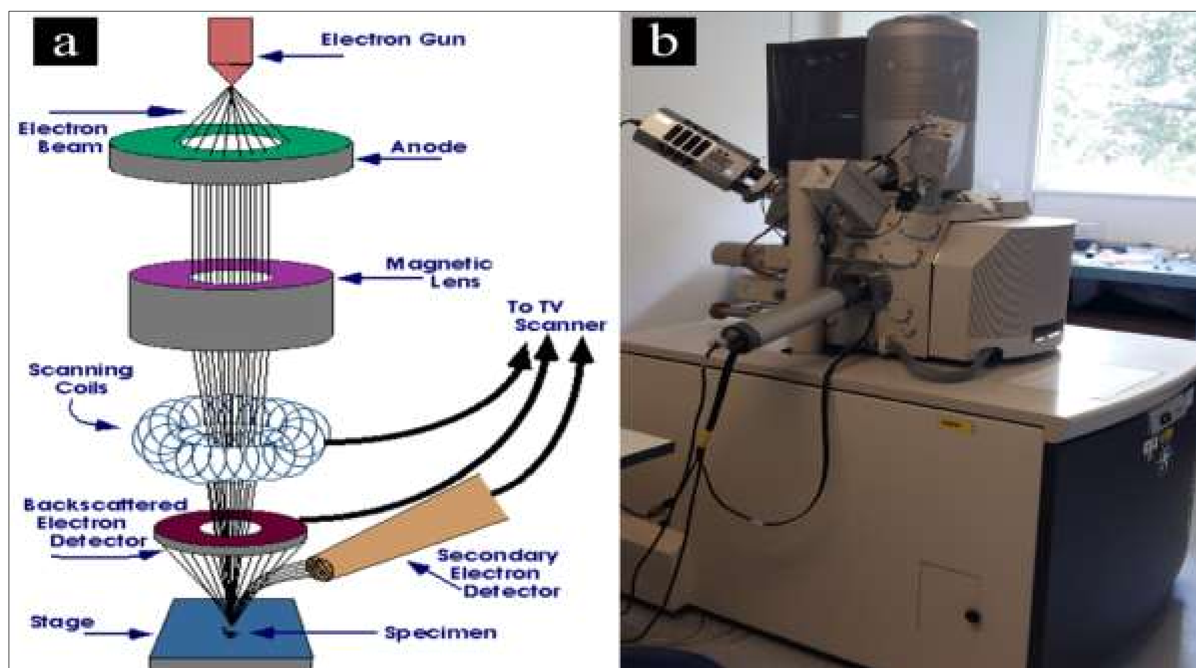

Figure 5.2: (a) Schematic diagram of field emission scanning electron microscope (FESEM), and (b) photograph of FESEM.

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5.1.b X-ray diffraction (XRD)

X-ray diffraction (XRD) is an effective technique used extensively to examine and analyse quality, crystalline structures, orientation, and crystallite size of the nano-materials. Structural information of the crystalline material is a description of the ordered arrangement of atoms. The crystal structure consists of parallel planes of atoms passing through the unit cell. These parallel planes are defined by Miller indices, which form a notation system in crystallography for crystal planes. In particular, a family of lattice planes is determined by three integers h, k, and l, which are used to determine distances and directions within the unit cell of crystal.

When the beam of X-ray radiation incident at a certain angle onto parallel planes of atoms in the material, diffraction occurs at the planes because of coherent scattering from the atoms (Figure 5.3). The wavelength of X-ray resembles the distance between the planes of atoms; therefore, the diffraction pattern produced because of various atom planes that provide information related to the atom arrangement unit cell of crystal. The conditions required for the diffractions coming from different planes are given by Bragg's law:

$$n\lambda = 2d_{hkl} \sin\theta \quad (5.1)$$

where λ is the X-ray wavelength of 1.540 Å, n is the order of reflection (in integer form), θ is the diffraction angle in degree, and d_{hkl} is the inter−planer spacing of the diffraction planes. The d_{hkl} is a function of Miller indices (h, k, and l) and lattice parameters a and c.

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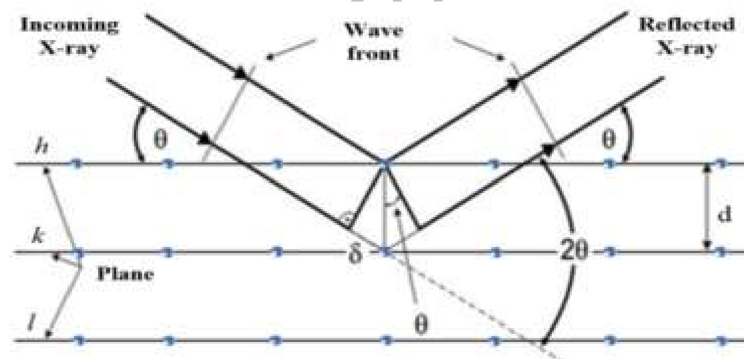

Figure 5.3: Diffraction of an X-ray beam on crystal planes, Bragg's law.

For the hexagonal structures, d_{hkl} values for various sets of atomic planes in the materials given as follows:

$${d_{hkl}}^2 = \frac{4}{3}\frac{h^2+hk+k^2}{a^2} + \left(\frac{l}{c}\right)^2 \quad (5.2)$$

where a and c are lattice constant. The lattice constant c given as follows:

$$c = \frac{\lambda}{2 \sin \theta} \tag{5.3}$$

The grain sizes were derived from the X-ray diffraction spectra following the Scherer equation as follows:

$$D = \frac{0.94\, \lambda}{\beta\, cos\theta} \tag{5.4}$$

where λ is the incident X- ray wavelength (λ= 1.5406 Å), β is the full width at half maximum (FWHM), and θ is the angle of the incident X-rays.

The strains (ε_{zz}) along the c-axis can be calculated using the following formula.

$$\varepsilon_{zz}(\%) = \frac{c - c_o}{c_o} \times 100 \tag{5.6}$$

where c_o is 0.5206 nm which represent standard lattice constant.

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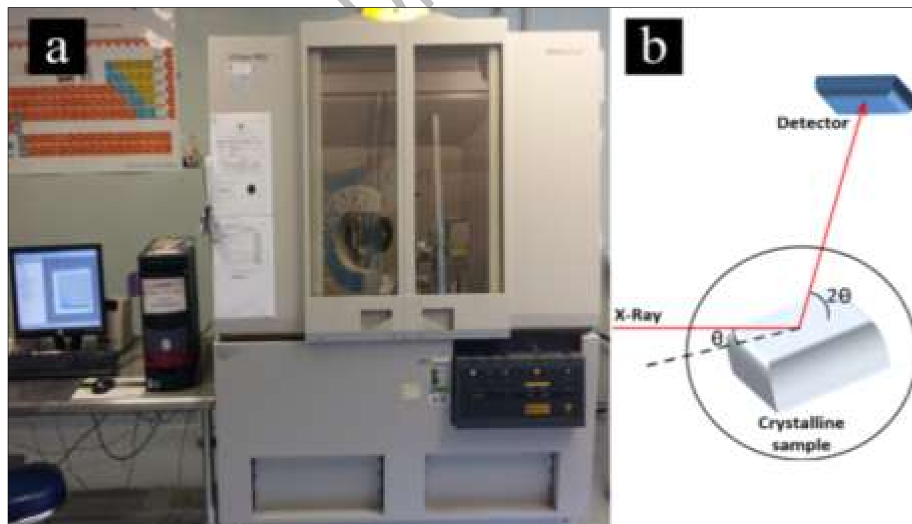

Figure 5.5: (a) HR-XRD system, and (b) schematic diagram of an X-ray diffraction experiment.

5.1.c Atomic force microscopy (AFM)

Atomic force microscopy (AFM) is a common technique used to examine and analyse surface features of materials, such as surface roughness, agglomeration, progression of grain size, and appearances of void and islands with its ability to scan a surface in three dimensions, as shown in Fig.5.6. The advantage of AFM over other microscopy techniques is its ability to scan a surface of materials in 2D and 3D.

The basis of the AFM system is Van der Waals force between the probe tip and the sample surface. When the tip scans the surface of film, it senses the inter-atomic forces with the surface. Therefore, when the tip approaches the surface, the difference between the force and signal is generated between the probe tip and the film surface.

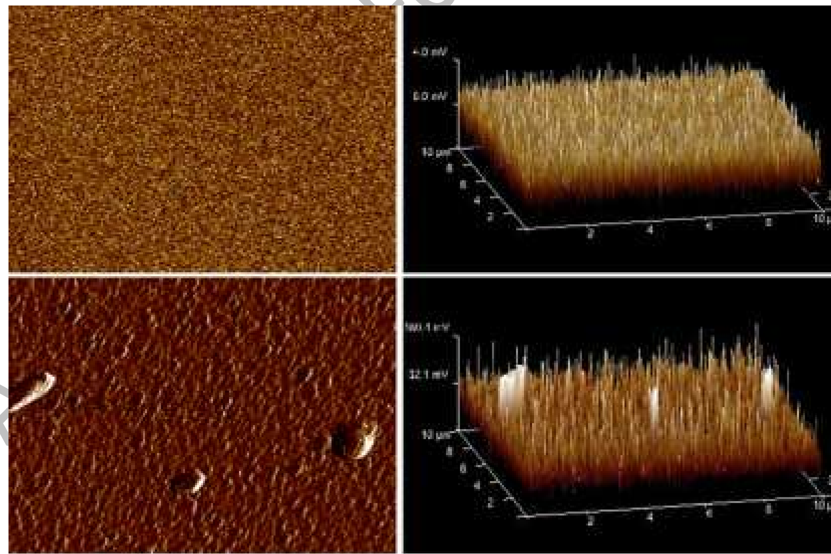

Figure 5.6: AFM images 2D and 3D of nanomaterials.

AFM system contains of a cantilever and a sharp tip (nanometre probe) usually made from SiN, SiO_2, or Si which are used to scan the film to detect surface features (Figure 5.7).

The AFM technique does not need to focus beam on electrons or photons on the film surface to builds a topographic map, but the AFM probe physically feels the surface to collect data.

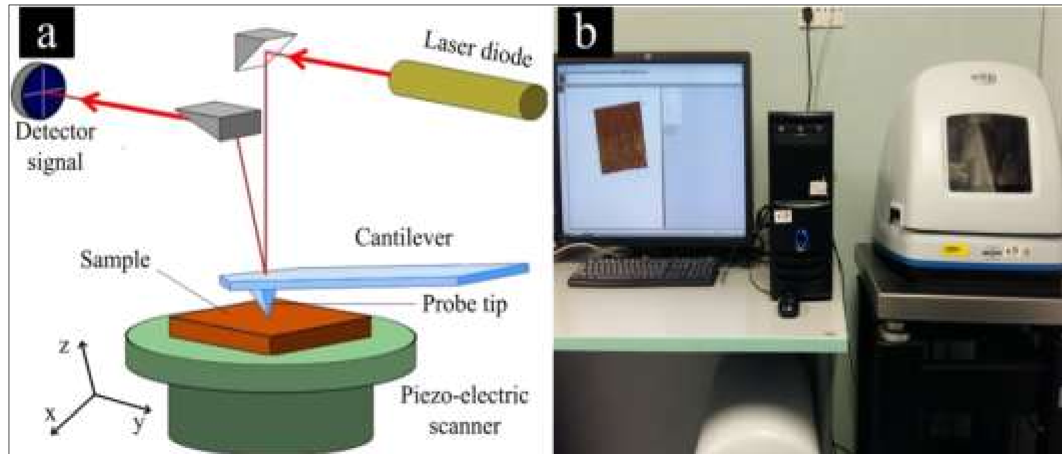

Figure 5.7: (a) Schematic diagram of atomic force microscopy (AFM), and (b) photograph of AFM.

5.1.d Photoluminescence (PL) spectroscopy

Photoluminescence spectroscopy (PL) is a powerful tool used to examine and analyse the optical properties of materials; this method provides information about the energy band gap value *Eg*, impurity densities, and possible presence of defect.

When a laser beam incident in the material, the laser photons ($E_{exc} > E_g$) encourage electrons to transport from valence band (VB) to conduction band (CB) leaving holes within the material. The excess energy after recombination of the excited electrons with the holes can emit photons that have the same energy of the tested sample energy band gap. The CCD detector collects these photon emissions, and the intensity is recorded as a function of emission energy to produce a PL spectrum (Figure 5.8).

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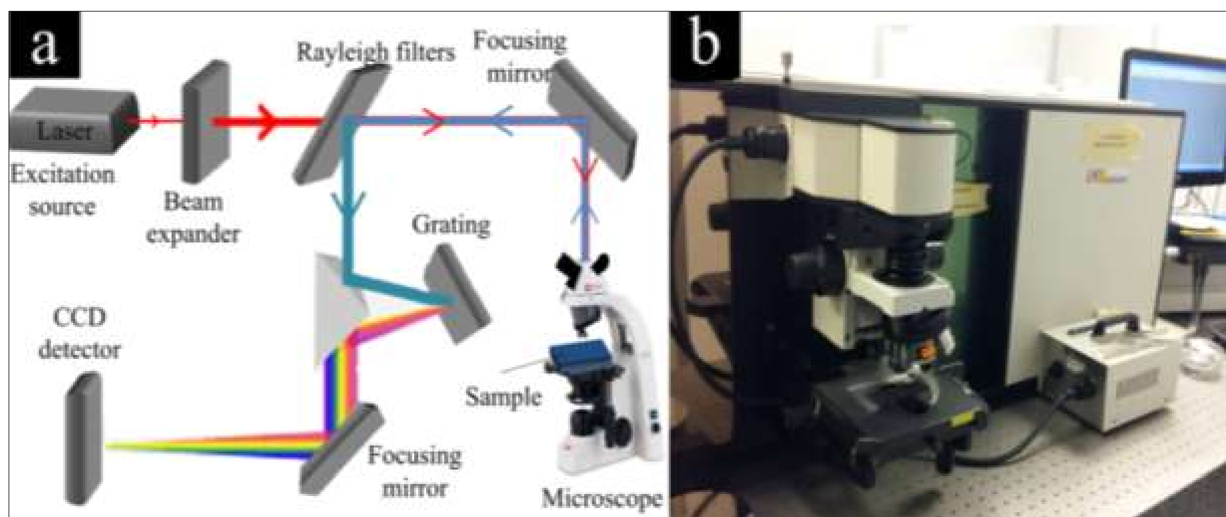

Figure 5.8: (a) Schematic diagram of photoluminescence (PL) spectroscopy, and (b) photograph of PL spectroscopy.

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5.1.e UV–visible (vis) spectroscopy

UV–visible (vis) spectroscopy is another useful, powerful technique that can measure (i) light beam intensity as a function of wavelength, (ii) evaluate the electronic structure and (iii) band gap energy of semiconductor materials. In UV-vis spectroscopy, photons of sufficient energy of visible or ultraviolet light source are absorbed by the semiconductor materials. The absorption characteristics are conducive to important information on the optical properties of a semiconductor, such as energy band gap refractive index, absorption coefficient, and optical transmission, which lead to the determination of the defect levels within the band gap of the semiconductor. The UV-vis spectroscopy measurements can be divided into two classes: a single-beam spectrophotometer measures the absolute light intensity, and a double-beam spectrophotometer measures the ratio of the light intensity on two diverse light paths.

Figure 5.9 shows the schematic of double-beam UV-vis spectrometer. In a deuterium lamp for UV light (190–350 nm) with a quartz window and a tungsten iodide lamp for visible light (330–1100 nm) with a quartz window, where after the UV and visible light source bounce off a mirror (1), the light beam passes through a slit (1) and hits a diffraction grating; the lamp can be rotated allowing selection of a specific wavelength to be selected. Only single wavelength (monochromatic) can successfully pass through the slit at any specific orientation of the diffraction grating. A filter is used to remove or block high-order diffracted beam or other unwanted light. The beam of light hits a mirror (2) before it splits through a half mirror into two beams; one is allowed to pass through the sample, whereas the other beam passes through the reference.

UV-vis spectroscopy measures the intensities of the light beams as a function of wavelength and compares it to the intensity of the reference at the same wave length.

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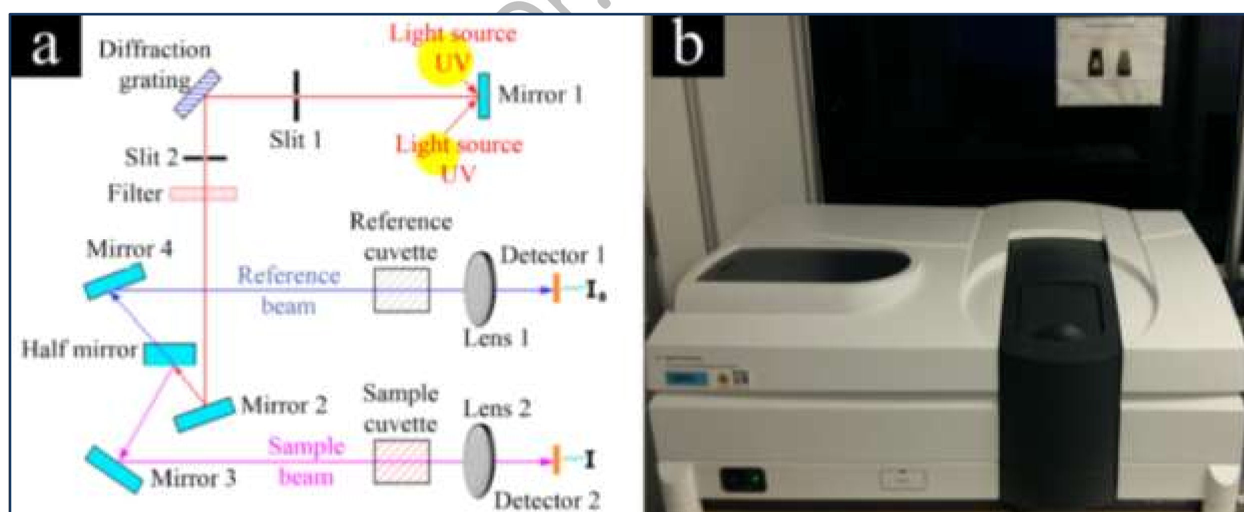

Figure 5.9: (a) Schematic diagram of a double-beam UV-vis spectrometer, and (b) photograph of UV-vis spectrometer.