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Innovative Nanotechnology Techniques for Exploring Surface Area, Microstructure, Morphology, And Chemical Composition

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Abstract-

Nanomaterials possess a significantly larger surface area compared to the same mass of material produced in bulk. As a result, there is an increased proportion of surface atoms within the nanomaterial's structure. The greater the number of surface atoms, the more pronounced the surface-related effects become. The surface area and pore size of nanomaterials can be accurately measured using the BET method. To analyze the microstructure and morphology of samples with particles at the nanometer scale, scanning electron microscopy (SEM) and transmission electron microscopy (TEM) are commonly employed. TEM is widely regarded as the most effective method when detailed information about morphology and microstructure is required. Additionally, energy-dispersive X-ray spectroscopy (EDX) can be attached to both SEM and TEM for chemical composition analysis.

Keywords: Nanotechnology, Techniques, Brunauer-Emmett-Teller (BET) Analysis, Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM), Energy-Dispersive X-ray Spectroscopy (EDX).

1.0 Introduction

Nanotechnology is a multidisciplinary field of research that has gained significant attention in recent years and has experienced rapid development [1-3]. Nanoscience and nanotechnology have a profound impact on various aspects of human life [4]. However, the exact definitions of nanoscience and nanotechnology are still being established. Different organizations, including the United States National Nanotechnology Initiative (US-NNI), the British Standards Institution (BSI), the International Organization for Standardization (ISO), and the American Society for Testing and Materials (ASTM), have proposed various definitions [4].

Generally, nanoscience is defined as the study of the fundamental principles governing molecules and structures sized between 0.5

and 100 nanometers [5]. These structures are referred to as nanostructures. In simple terms, nanoscience is the scientific study of materials on the nanoscale [6].

According to the United States National Nanotechnology Initiative (US-NNI), nanotechnology involves research and technological development at atomic, molecular, or macromolecular levels within a length scale of approximately 1 to 100 nanometers. It encompasses the creation and use of structures, devices, and systems that possess novel properties and functions due to their small size and the ability to be controlled or manipulated at the atomic level. The Royal Society and the Royal Academy of Engineering define nanotechnology broadly as "the design, characterization, production, and application of structures, devices, and

systems by controlling shape and size at the nanometer scale."

A nanometer is a billionth of a meter (10^{-9} meters), with "nano" derived from the ancient Greek word "nanos," meaning dwarf or very small. The nanoscale refers to systems that are below macroscopic dimensions (bulk materials) and above molecular dimensions (atoms and molecules) [7]. The British Standards Institution (BSI) defines the nanoscale as ranging from approximately 1 to 100 nanometers. It describes a nano-object as a discrete piece of material with one or more external dimensions within this size range. According to BSI, a nanomaterial is defined as a material having one or more external dimensions at the nanoscale or which is nanostructured, the latter being described as possessing a structure with one or more dimensions in the nanoscale. Generally, a nanomaterial has dimensions ranging from 1 to 100 nanometers [8], placing it between molecules (less than 1 nanometer) and bulk materials (greater than 100 nanometers).

Nanomaterials demonstrate unique properties compared to their bulk counterparts [9]. These unique properties arise from several factors:

- (i) Nanomaterials possess a relatively large surface area in relation to their mass when compared to bulk materials. This increases the proportion of surface atoms, enhancing the effects associated with the material's surface.
- (ii) Quantum effects begin to dominate the behavior of matter at the nanoscale, influencing the magnetic, optical, and electrical properties of the nanomaterial [10].
- (iii) The tiny size of nanomaterials allows them to enter the realm where quantum effects predominate.
- (iv) A notable achievement of nanotechnology is the miniaturization of devices [11].

Nanotechnology has applications in fields such as medicine, electronics, biomaterials, energy production, and many others. There

are various methods for characterizing nanoparticles; however, this discussion will focus on Brunauer–Emmett–Teller (BET) analysis, Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM), Energy Dispersive X-ray (EDX) analysis, and Fourier Transform Infrared Spectroscopy.

2.0 Brunauer-Emmett-Teller (BET) Analysis

The BET theory explains the physical adsorption of gas molecules onto a solid surface and is a crucial technique for measuring specific surface area and porosity [12]. Developed by Stephen Brunauer, Paul Hugh Emmett, and Edward Teller in 1938 [13], the BET theory specifically allows for determining the specific external and internal surface area of nanopowders or porous solids. This is achieved by measuring the amount of physically adsorbed gas using the BET method [14].

In the BET method, a volume of gas (adsorbate), typically nitrogen, is adsorbed onto the surface of the particles at the boiling point of nitrogen, which is approximately -196°C . At this temperature, nitrogen gas is below its critical temperature and condenses on the particle surfaces. Assuming that the gas forms a monolayer on the surface and that the size of the gas molecule is known, the amount of adsorbed gas can be correlated to the total surface area of the particles, including any pores on the surface [13].

The major steps involved in a BET measurement include the following:

- i. **Degassing:** This process can be conducted using a vacuum system or by flushing the sample with nitrogen (N_2), often at elevated temperatures.
- ii. **Evacuation:** Both the sample and reference tubes are evacuated, ensuring that they undergo the same treatment throughout the measurement process.
- iii. **Volume Measurement:** Most BET methodologies include a dead-volume measurement using an inert gas, such as

helium. This measurement is essential for determining the quantity of adsorbate that is absorbed. It is important that both the sample and reference tubes have similar dead volumes. Glass rods or glass beads are often used to minimize dead volume and achieve uniformity in dead volumes between the tubes.

- iv. Final Evacuation: At this stage, any gas in the dead volume is removed via vacuum.

Adsorption refers to the adhesion of atoms, ions, or molecules from a gas, liquid, or dissolved solid onto a surface. There are six types of adsorption isotherms, as shown in Figure 1. The BET method applies only to adsorption isotherms of type II, which pertain to disperse, non-porous, or macroporous solids, and type IV, which includes mesoporous solids with pore diameters

ranging from 2 to 50 nm. The BET method is not reliably applicable to solids that absorb the measuring gas instead of adsorbing it.

In BET analysis, the adsorbate gas is introduced into the two tubes either in doses or through a slow, continuous flow. The gas then adsorbs onto the sample, causing the pressure in the confined volume to decrease until equilibrium is reached between the adsorbate and the adsorptive. The amount of gas that was introduced minus the amount remaining in the gas phase at equilibrium is used to calculate the amount of adsorbate. Key parameters for this calculation include pressure, temperature, and the (dead) volume of the system. This stage ultimately generates the adsorption isotherm over a selected range of P/P_0 .

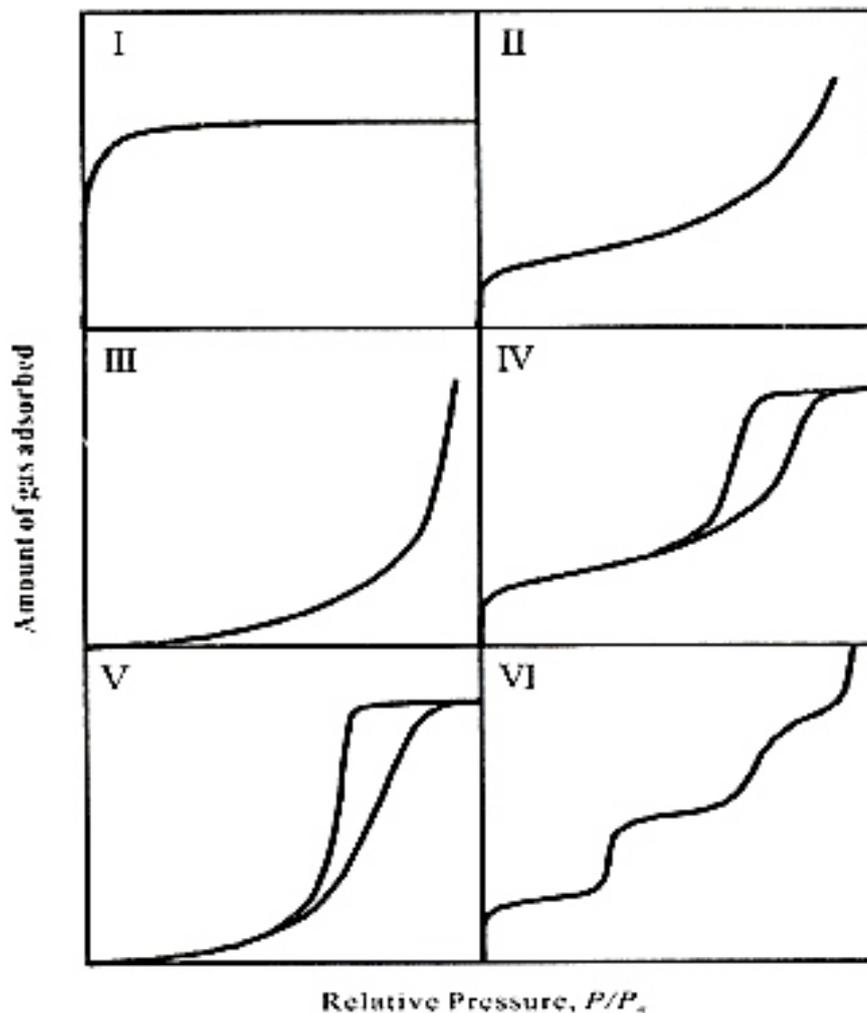


Fig 1: Adsorption isotherms [13].

- i. Desorption: This step involves the use of a vacuum in the reverse of step V. This gives desorption, The BET equation is given as

$$\frac{1}{V \left[\left(\frac{p}{p_0} \right) - 1 \right]} = \frac{C-1}{V_m C} \left(\frac{p}{p_0} \right) + \frac{1}{V_m C}$$

Where
 P_0 is the saturation pressure of adsorbate at the temperature of adsorption.
 P is the equilibrium pressure of adsorbate at the temperature of adsorption.
 V is the adsorbed gas quantity in volume units.
 V_m is the monolayer adsorbed gas quantity (monolayer capacity).
 C is the BET constant. A BET plot is shown in Figure 2.

$$1/v[(p_o / p) - 1]$$

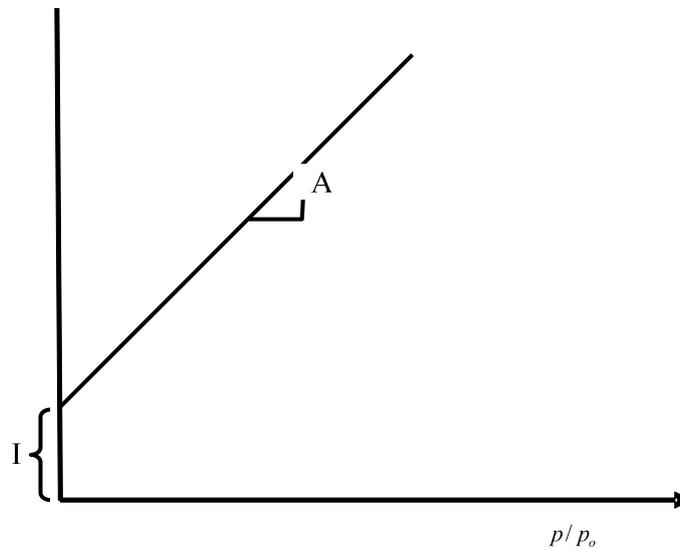


Fig 2: The BET plot [13]
 Using the BET equation;

$$\frac{-1}{\dots} \tag{2}$$

Equation 2 is the slope of the graph in Figure 2.

$$\frac{1}{\dots} \tag{3}$$

Equation 3 is the intercept on the graph in Figure 2.

The V_m and C in the BET Equation and calculated by using Equation 4 below.

$$\frac{1}{\dots} \tag{4}$$

$$1 \dots \tag{5}$$

Equation 5 gives the relationship between BET constant C , the slope, and the intercept.

The linear relationship of equation 1 is maintained only in the range 0.05 to 0.35 . The

total surface area S_{total} is calculated using equation 6.

$$\frac{ms}{\dots} \tag{6}$$

Where V_m is in units of volume which are also the units of the monolayer volume of the adsorbate gas, N is the Avogadro's number, S is the adsorption cross-section of the adsorbing species, and V is the molar volume of the adsorbate gas (for N_2 , $V = 2244\text{cm}^3$). Equation 7 is the specific surface area, S_{BET} .

$$\frac{TOTAL}{7}$$

In equation 7, m is the mass of the solid sample or adsorbent [15].

The value of C (the BET constant) in the BET equation is crucial as it indicates the strength of the interaction between the adsorbent and adsorbate. Typically, the value of C ranges from 100 to 200. A value above 200 suggests the presence of micropores, indicating significant porosity. Conversely, if C falls below 100, it indicates strong interactions between the adsorbent and adsorbate. Particularly, if C is below approximately 20, this indicates very strong interactions,

rendering the BET method invalid [13].

In physisorption, pores are classified based on their sizes: macropores are defined as having widths exceeding 50 nm, mesopores have widths between 2 and 50 nm, and micropores have widths that are less than or equal to 2 nm. Table 1 presents the IUPAC classification of pores.

Table 1: IUPAC Classification of Pores

Porosity	Pore diameter (Width) in nm
Macropore	50 or above
Mesopore	2 to 50
micropore	2 or below

Table 2 outlines the characteristics of the six adsorption isotherms along with examples of adsorptive interactions.

Table 2: Features of Adsorption Isotherms

Type	Features	Example of Sample-Adsorptive interaction
	Porosity	
I	Relatively strong	Activated carbon-Nitrogen
II	Relatively strong	Oxide- Nitrogen
III	Weak	Carbon-Water vapour
IV	Relatively Strong	Silica-Nitrogen
V	Weak	Activated carbon-water vapor for micropores
VI	Relatively strong	Graphite-Krypton

All measurements that can be performed by a BET instrument are listed in Table 3.

Table 3: Measurements Available on BET Instrument.

Number	Measurement	Calculation method
1.	Surface area	BET, Temkin, Freund Temkin, Langmuir
2.	Total pore volume	Kelvin equation
3.	Mesopore volume, area distributions	BJH, Dollimore – Heal
4.	Micropore distribution	Dubinin – Radush Kevich and Astakhov, Horvath-Kawazoe, Saito-Foley, Cheng-Yang, MP method.
5.	Pore size modeling	Density functional theory
6.	Surface Energy	Density functional theory

3.0 Scanning Electron Microscopy (SEM)

The scanning electron microscope (SEM) is a highly versatile instrument used for examining and analyzing microstructure, morphology, and chemical composition. It plays a crucial role in materials science. SEM is specifically designed for various applications, including microscopic feature measurements, microstructure studies, thin coating evaluations, surface contamination examination, fracture characterization, and failure analysis of materials.

Electron microscopy offers advantages over light microscopy because it replaces the visible light source with a high-energy electron beam. In light microscopy, the sample's surface is illuminated with visible light, while SEM directs a focused beam of electrons onto a small area of the sample's surface. The instrument collects and displays the electronic signals emitted by the target material. These

electron signals are then converted into a visual representation that can be viewed on a cathode ray tube.

As illustrated in Figure 3, an electron gun generates the electron beam within an evacuated column, which focuses and directs the beam to impact a pinpointed spot on the sample. The scanning coils enable the electron beam to systematically scan a small area of the sample's surface. When low-angle backscattered electrons interact with the surface's features, they generate secondary backscattered electrons, producing an electronic signal that forms an image. This process creates an image with a depth of field up to approximately 300 times greater than that of light microscopy, which has a depth of field of about 10 μ m at a magnification of 10,000 times [16].

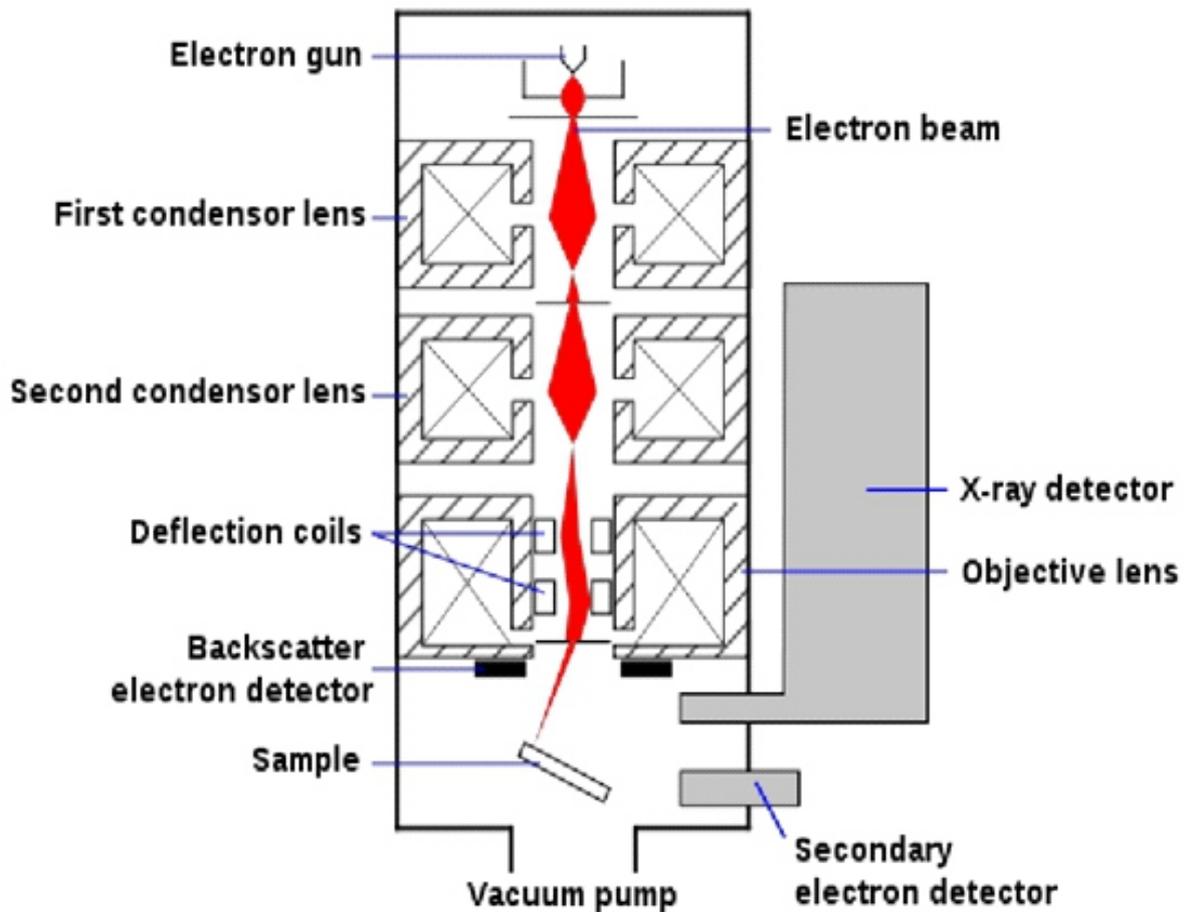


Fig.3: Schematic diagram of a typical scanning electron microscope (<https://www.nanoscience.com/techniques/scanning-electron-microscopy/>).

Many scanning electron microscope (SEM) instruments have a resolution of approximately 5 nm and can achieve a magnification range of about 15 to 100,000 times. Image formation in SEM relies on the signals generated from the interactions between the electron beam and the sample. These interactions can be broadly classified into two categories: elastic and inelastic scattering.

Elastic scattering occurs when the incident electrons are deflected by the atomic nucleus or by valence shell electrons of the sample, resulting in a negligible loss of energy during the collision. This scattering is characterized by a wide-angle directional change of the scattered electrons. Those incident electrons that are scattered elastically at angles greater than 90° are termed backscattered electrons, which provide valuable signals for imaging the sample.

In contrast, inelastic scattering involves a variety of interactions between the incident electrons and the sample's electrons and atoms. This type of scattering occurs when primary beam electrons transfer substantial energy to the sample's atoms. The energy loss during inelastic scattering depends on whether the specimen electrons are excited singly or collectively, as well as on the binding energy of the electrons to the atoms. The excitation of specimen electrons during the ionization of the sample atoms generates secondary electrons that possess energies of less than 50 eV, which can be used for imaging and analysis. In addition to the signals used for imaging, other signals produced when the electron beam strikes the sample include the emission of characteristic X-rays, cathodoluminescence, and Auger electrons.

For SEM analysis, samples are often coated

with carbon. However, standard SEM procedures may use gold coatings or other heavy metal coatings to enhance resolution and signal quality. Coating is particularly important for non-conductive materials.

When an SEM is equipped with an X-ray spectrometer, it can provide both quantitative and qualitative information about the sample's formation [16].

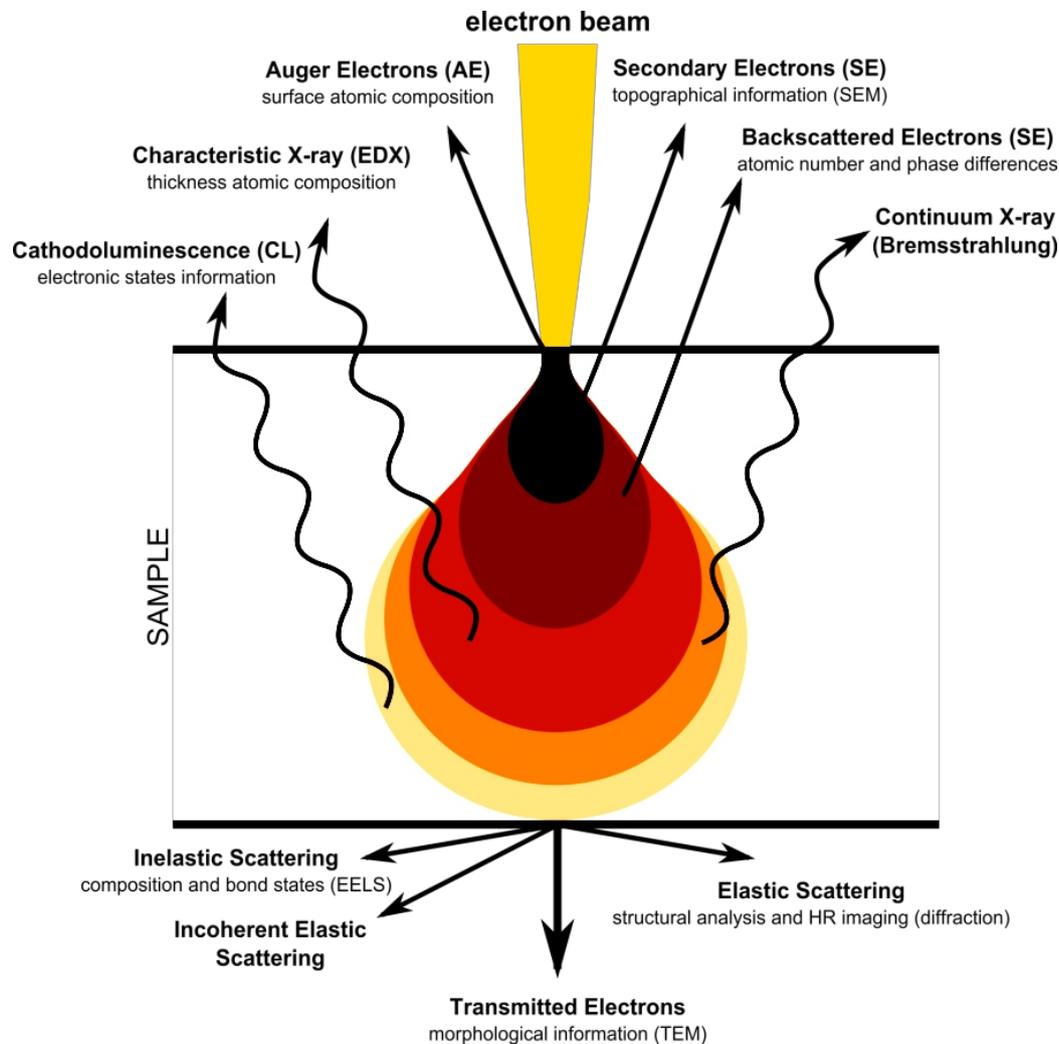


Figure 4: Signals generated by the electron-beam-specimen interaction (<https://blog.phenom-world.com/sem-electrons>).

4.0. Transmission Electron Microscopy (TEM)

Transmission electron microscopy (TEM) is a microscopy technique that involves transmitting a beam of electrons through an ultra-thin specimen, allowing the electrons to interact with the material as they pass through [17]. This method is crucial for studying defects, precipitates, and secondary phases in materials. Preparing samples for TEM

analysis is complex and requires specialized instruments, unlike optical microscopy and scanning electron microscopy (SEM) techniques, which have simpler sample preparation processes.

For TEM analysis, specimens should be no thicker than several hundred nanometers, depending on the operating voltage of the equipment. Properly prepared specimens

must be thin and have flat, parallel surfaces. The operation of TEM (see Figure 5) begins with a heated tungsten filament located at the top of an evacuated column, which produces the electron beam. This beam is accelerated down the column by high voltage, typically ranging from 100 to 300 kV. Electromagnetic coils condense the electron beam before it passes through the thin specimen placed on the specimen stage.

As the electrons traverse the specimen, some are absorbed and others are scattered, changing direction. This is why the sample needs to be thin; if the sample is too thick, it will excessively absorb and diffract the

electrons, preventing their passage. The electron beam that passes through the specimen is focused using a magnetic lens (objective coil) and then enlarged and projected onto a fluorescent screen.

An image is created by collecting either direct or scattered electrons. To choose between the two, an aperture is inserted into the back focal plane of the objective lens. The aperture can be adjusted to allow either the direct electrons or the scattered electrons to pass through it. Selecting the direct beam produces a bright-field image while choosing the scattered electrons results in a dark-field image [16].

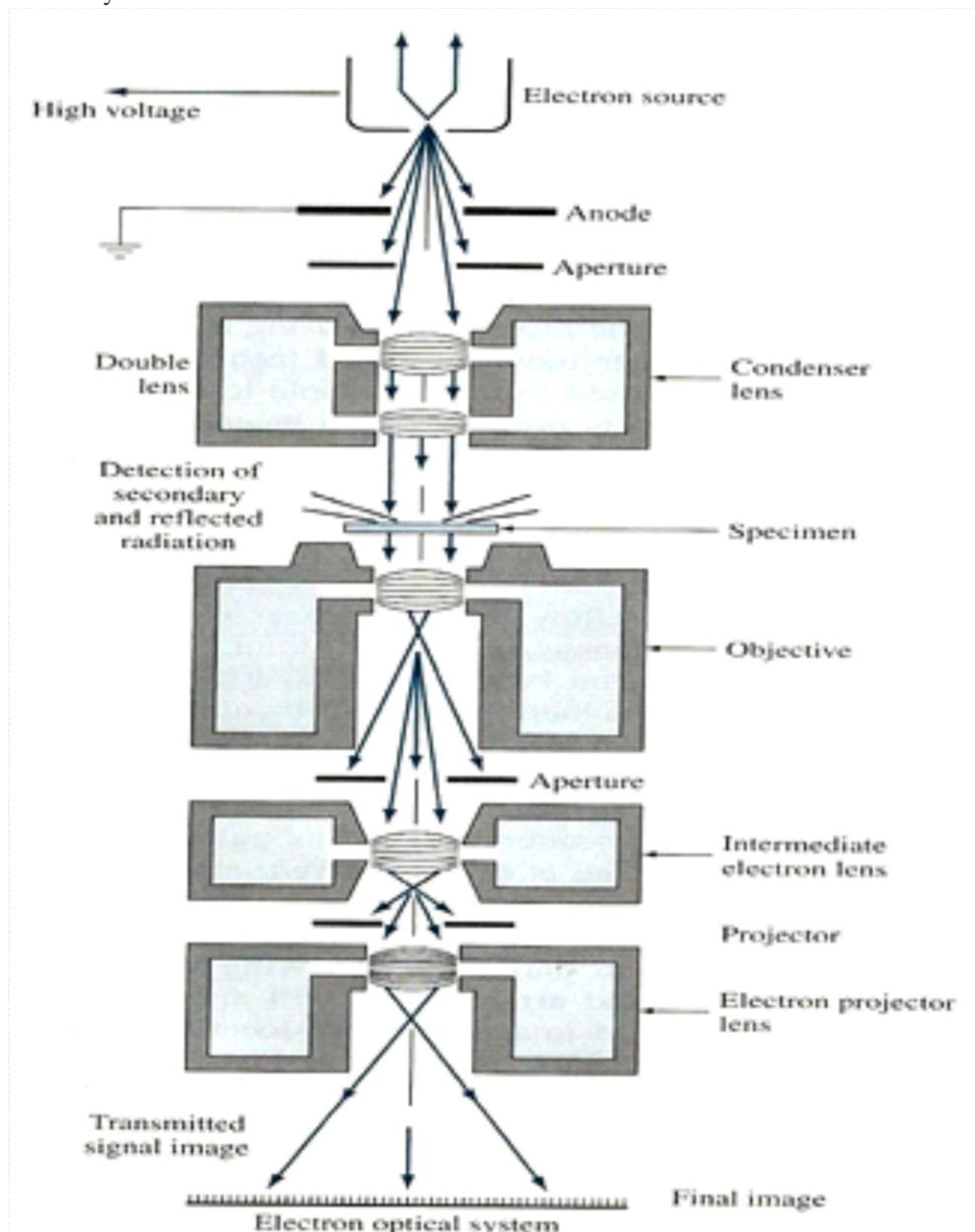


Fig 5: Schematic diagrams of a transmission electron microscope [16].

5.0 Energy -dispersive X-ray spectrometry (EDX or EDS)

This technique utilizes the X-ray spectrum emitted by a solid sample that has been bombarded with a focused beam of electrons to perform a localized chemical analysis of the sample [18]. In principle, it can detect elements with atomic numbers ranging from 4 to 92, that is, from beryllium (Be) to uranium (U). However, some equipment may not be suitable for detecting light elements with atomic numbers less than 10 ($Z < 10$).

The quantitative analysis in this technique involves identifying the spectral lines. To determine the concentrations of the elements present, it is necessary to measure the line intensities for each element in the sample and compare them to the same elements in calibration standards of known composition. X-ray spectrometers are typically integrated into most Scanning Electron Microscopes (SEM) and Transmission Electron Microscopes (TEM) for this analysis, and they do not require special sample preparation.

An Energy-Dispersive Spectrometer (EDS) employs pulse height analysis, using a detector that generates output pulses proportional in height to the energy of the X-ray photons. This method provides better energy resolution. When X-ray photons interact with the detector, they cause ionization, which results in the production of an electrical charge. This charge is then amplified by a sensitive preamplifier located near the detector. To minimize electronic noise, both the detector and preamplifier are cooled with liquid nitrogen. The most common detectors used today are silicon lithium (Si (Li)) detectors or silicon drift detectors (SDD).

6.0 Fourier Transforms Infrared (FT-IR) Spectroscopy

FTIR stands for Fourier Transform Infrared spectroscopy. It is one of the most important analytical techniques for studying samples in various states, including liquids, pastes, solutions, powders, films, fibers, gases, and surfaces. FTIR spectroscopy represents a significant advancement in infrared spectroscopy, utilizing Fourier transform spectrometers to achieve improved performance. These machines employ interferometers and the well-established mathematical process known as the Fourier Transform. Most modern FTIR instruments are computerized, making them faster and more sensitive compared to older dispersive instruments.

Infrared spectroscopy is unique because it is based on the vibrations of atoms within a molecule. In this technique, infrared (IR) radiation is directed onto a sample, which absorbs some of the radiation while transmitting the rest. The resulting spectrum indicates the molecular absorption and transmission properties, effectively creating a molecular fingerprint for the sample. Each fingerprint is distinct and differs from that of a sample with a different molecular structure. Typically, an infrared spectrum displays absorption peaks that correspond to the vibrational frequencies between the bonds of the atoms composing the material. Since each type of material has a unique combination of atoms, no two compounds will produce identical infrared spectra. Figure 6 illustrates a schematic diagram of a typical Fourier Transform infrared spectrometer.

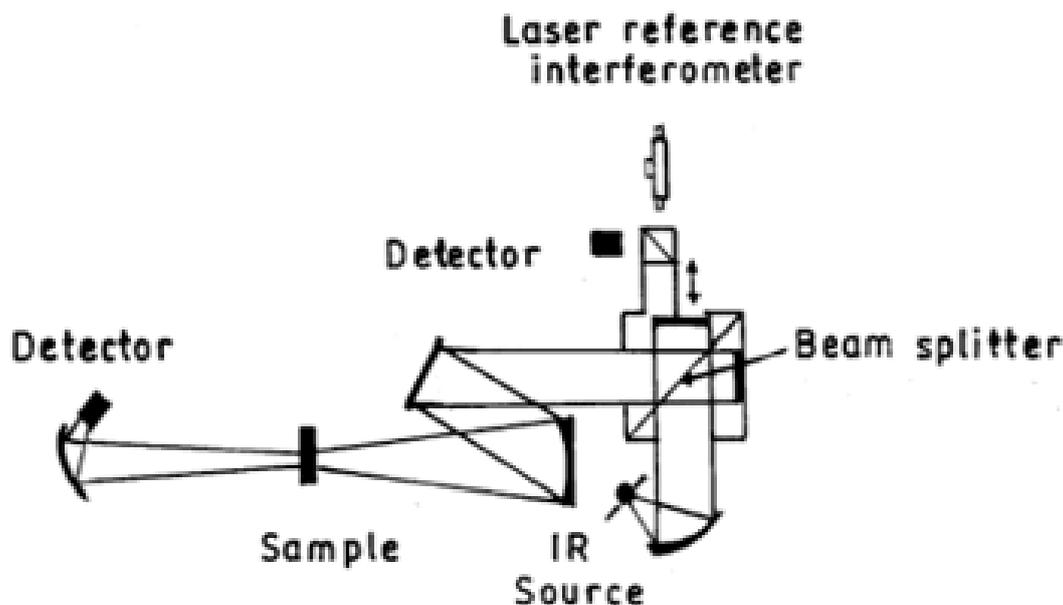


Fig 6: Schematic diagram of a typical Fourier Transforms Infrared Spectrometer [19].

Infrared spectroscopy is applicable for the qualitative identification of every different kind of material. The size of the peaks in the spectrum is a direct measure of the amount of material present [20].

7.0 Conclusion

The BET method can be conveniently used to measure the surface area and pore size of nanomaterials. To determine the microstructure and morphology of samples with nanometer-scale particles, techniques such as scanning electron microscopy (SEM) and transmission electron microscopy (TEM) can be employed. However, TEM is widely accepted as the most effective method when detailed information about morphology and microstructure is required. Additionally, energy-dispersive X-ray spectroscopy (EDX), which can be attached to both SEM and TEM, is utilized for analyzing the chemical composition of samples.

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