CHARACTERIZATION OF NANOPARTICLES

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Introduction

Nanomaterials have garnered significant attention as a rapidly expanding material category with diverse applications, necessitating thorough characterization. Various methods have been used to assess nanoparticle size, crystal structure, elemental composition, and other physical properties. Sometimes, multiple techniques can be used to evaluate specific properties. Choosing the most suitable method can be challenging due to the distinct advantages and drawbacks of eachtechnique, often requiring a combined approach for complete characterization.

Morphology (Size, Shape, Length, Internal Structure)

Morphology stands out as a key factor in nanoparticle characterization. Nanomaterials' size and shape play crucial roles in shaping their physicochemical characteristics, influencing aspects such as catalytic activity, bioactivity, optical properties, magnetic properties, and mechanical properties. To analyze size, distribution, shape, and aggregation, widely used techniques include TEM, SEM, and AFM.

1. Transmission Electron Microscopy (TEM)

Transmission Electron Microscopy serves as a frequently utilized technique for characterizing nano materials. It employs a particle beam of electrons to observe specimens and produce highly magnified images. Operating on similar principles to a light microscope, TEM differs in using electrons rather than light. The electron wavelength being significantly smaller than that of light allows TEM to achieve optimal resolutions many magnitude superior to those achievable with a light microscope.

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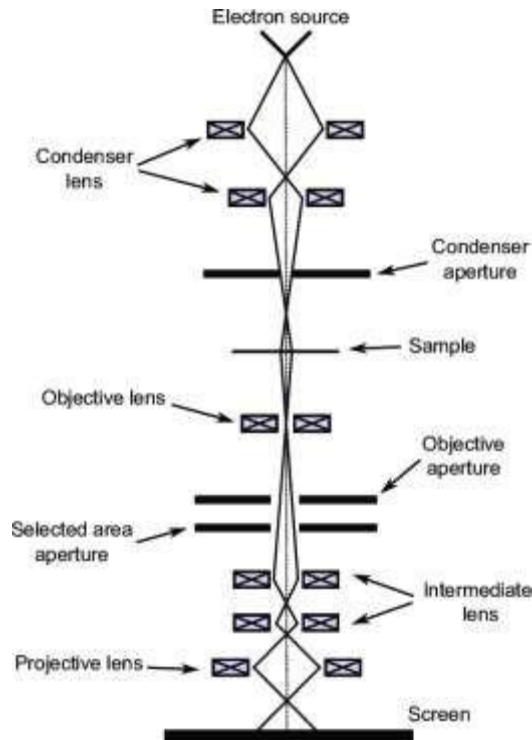
Schematic representation of TEM

Transmission electron microscopes (TEMs) utilize a high-voltage electron beam to generate an image. Positioned at the top of a TEM, an electron gun emits electrons that traverse the microscope's vacuum tube. Unlike light microscopes that use a glass lens for focusing, the TEM employs an electromagnetic lens to concentrate electrons into a finely focused beam. This electron beam then traverses through the exceptionally thin specimen, where electrons either scatter or strike a fluorescent screen located at the bottom of microscope. The resulting image of the specimen displays its various components in distinct shades corresponding to their densities.

High-Resolution TEM (HR-TEM) is a specialized imaging technique within TEM that enables direct visualization of a sample's atomic-level crystallographic structure. This method is instrumental for studying material properties at the atomic scale, revealing crystal structures, defects, and even individual atoms. HR-TEM is applicable in investigating crystal nanoparticles, their spatial arrangement, nanocrystalline features in amorphous films, alignment of nanofibers, and porous materials.

Despite its effectiveness in analyzing nanomaterial's shape, size, heterogeneity, aggregation, and dispersion, TEM has certain limitations. One key drawback is its demand for high vacuum and ultra-thin sample sections, potentially altering the sample's structure during preparation. The high-energy electron beam in TEM can harm or destroy specimens, and artifacts may emerge when probing 3D specimens using a 2D transmission view due to limited depth sensitivity. Additionally, TEM's examination of a small specimen area over a specific period leads to poor statistical analysis.

2. Scanning Electron Microscopy (SEM)
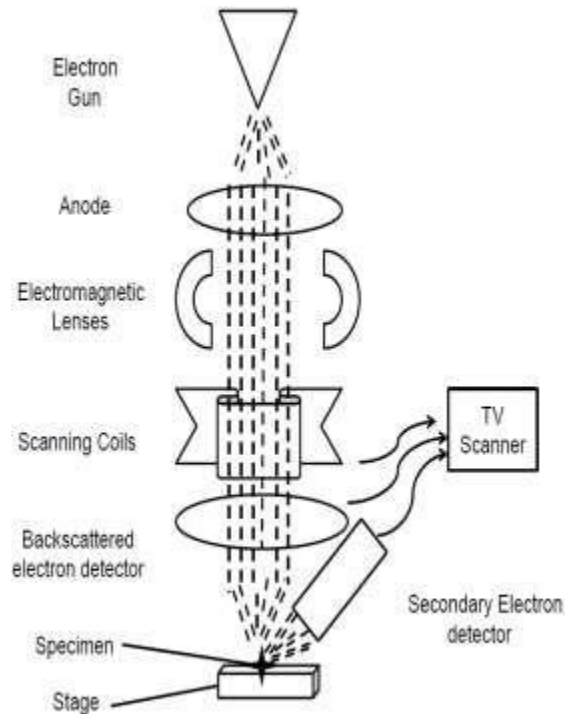
Schematic representation of SEM

A Scanning Electron Microscope (SEM) is an electron microscope that captures images of a sample through the scanning of its surface with a focused electron beam. This electron beam is systematically moved in a raster scan pattern, generating diverse signals that contain details about the sample's surface topography and composition. In SEM, electrons are generated at the apex of the high vacuum column and then accelerated toward the sample. The trajectory of electrons within the microscope column is regulated by the condenser and objective lens, converging the beam twice before it impacts the sample. The interaction of electrons with the sample produces backscattered (BSE) and secondary electrons (SE), which are utilized for SEM imaging. BSEs are part of the primary electron beam, while secondary electrons originate from the atoms of the sample. Various detectors are employed to capture these electrons, and the resulting data is utilized to create images.

The Field Emission Scanning Electron Microscope (FESEM), akin to the SEM, furnishes a wide range of information about the sample surface, but with enhanced resolution and a significantly expanded energy range.

Nevertheless, SEM measurements come with certain limitations. Sample preparation involving drying and contrast can lead to nanomaterial shrinkage, altering their size and shape characteristics. Additionally, because the scanning area contains limited number of particles, biased statistics regarding size distribution are unavoidable for heterogeneous samples.

3. Atomic Force Microscopy (AFM)
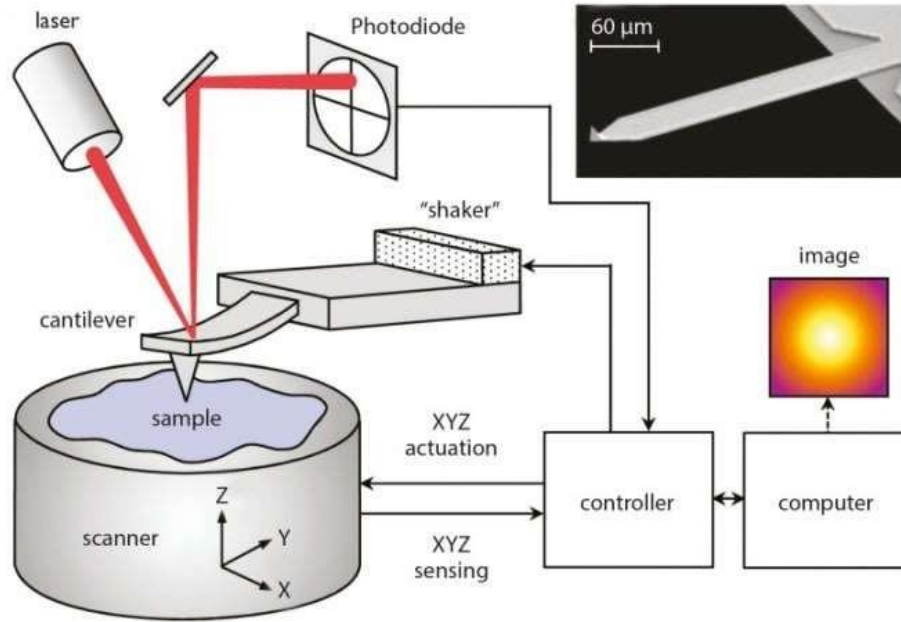
Schematic representation of AFM

Atomic Force Microscopy (AFM) proves to be a potent imaging technique, proficient in mapping the topography of thin film surfaces across a variety of materials. As a high-resolution method, AFM falls under the category of scanning probe microscopy, often referred to as scanning force microscopy (SFM). Its utility extends to assessing different forces, including adhesion strength, magnetic forces, and mechanical properties.

The operation of AFM microscopes involves the utilization of an exceptionally sharp tip situated on a micro-machined silicon probe for surface sensing. This tip scans the sample in a raster pattern, employing distinct methods across various operating modes, with the primary modes categorized as contact mode and dynamic (tapping) mode.

The fundamental concept of AFM revolves around a nanoscale tip connected to a small cantilever, forming a spring-like structure. Upon the contact with the surface cantilever undergoes bending due to the interaction with the tip. This bending is detected through a laser diode and a split photodetector, with the degree of bending serving as a measure of the interaction force between the tip and the sample.

During the scanning process of the sample, using a fine tip attached at the end of the cantilever, there are interactions such as attractive or repulsive forces, mainly Van der Waals forces, and other forces like electrostatic and hydrophobic/hydrophilic forces, between the tip and sample. These interactions lead to a bending of the cantilever. A laser is used to measure this deflection, which is reflected off the cantilever onto photodiodes. The photodiodes produce an output signal based on the varying light collected, indicating the vertical bending of the cantilever. This information is then directed to a scanner that controls the probe's height as it traverses the surface. The scanner's adjustments in height are utilized to generate a three-dimensional representation of the sample's topography.

Structural and Chemical Characterization

Characterization of nanoparticle's structure and composition holds great significance, as these factors strongly affect their physicochemical properties. The analysis of nanoparticle composition, phase, crystallinity, functionalization, chemical state (oxidation), surface charge, polarity, bonding, and electrochemical properties is commonly conducted using various techniques. Techniques used for structural and composition analysis include,

4. X-ray Powder Diffraction (XRD)

X-ray powder diffraction (XRD) stands out as an analytical technique primarily utilized for the phase identification of crystalline materials and can furnish information about unit cell dimensions. The material under analysis undergoes meticulous grinding and homogenization, followed by the determination of the average bulk composition.

Crystalline substances serve as three-dimensional diffraction gratings for X-ray wavelengths that align with the spacing of planes within a crystal lattice. X-ray diffraction hinges on the constructive interference of monochromatic X-rays and a crystalline sample. These X-rays, emanating from a cathode ray tube, undergo filtration for monochromatic radiation, collimation for concentration, and are then directed toward the sample.

The interaction of incident rays and the sample results in constructive interference (and a diffracted ray) when conditions satisfy Bragg's Law ($n\lambda = 2d \sin \theta$). These diffracted X-rays are subsequently detected, processed, and tallied. Scanning the sample across a range of 2θ angles ensures the acquisition of all potential diffraction directions of the lattice. The conversion of diffraction peaks to d-spacings facilitates mineral identification, as each mineral possesses a distinctive set of d-spacings.
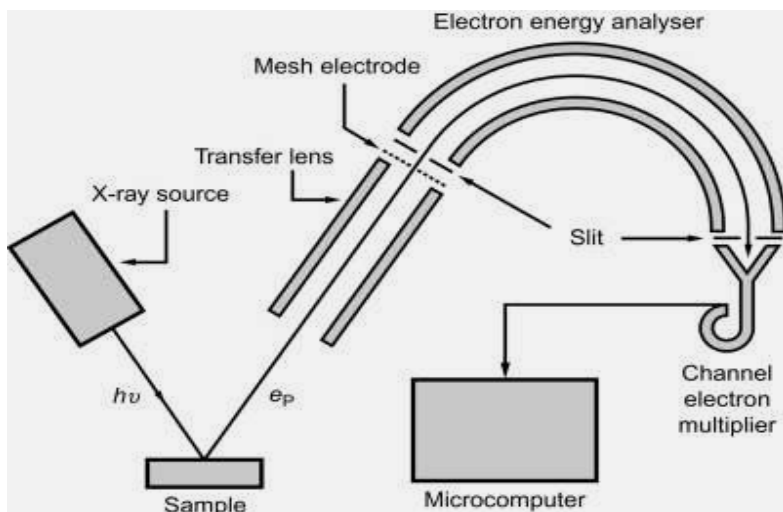
Generally, XRD provides limited information for anisotropic particles and those with unevensize distribution. In such scenarios, supplementary analyses like TEM are necessary for proper interpretation. Additionally, XRD cannot characterize individual particles, and the earlier equation discussed calculates the average particle size for the material rather than the specific particle size.

5. X- Ray Photo Electron Spectroscopy (XPS)

X-ray photoelectron spectroscopy (XPS) relies on the photoelectric effect to discern the elements present in a material, either constituting its elemental composition or coating its surface. Additionally, XPS provides insights into the chemical state, overall electronic structure, and density of electronic states within the material. The acquisition of XPS spectra involves irradiating a solid surface with an X-ray beam and concurrently measuring the kinetic energy of electrons released from the top 1-10 nm of the material under examination. The creation of a photoelectron spectrum

involves counting the ejected electrons across a range of electron kinetic energies. Peaks in the spectrum correspond to atoms emitting electrons with specific characteristic energies. Through analyzing the energies and intensities of these photoelectron peaks, all surface elements can be identified and quantified, with the exception of hydrogen and helium, which lack core electrons.

However, when conducting XPS analysis on nonconductive materials, special attention is necessary as these materialstend to induce undesired shifts in the energy spectrum.

Schematic representation of XPS

6. Fourier-Transform Infrared Spectroscopy (FTIR)

FTIR (Fourier transform infrared spectroscopy) is a quick and reliable method for identifying materials and quantifying their components in a sample. It is based on infrared spectroscopy and utilizes a wide range of infrared spectra (from Near Infrared to Far InfraRed) to gather information. Unlike a dispersive infrared spectrometer, where individual spectral components aremeasured one at a time, FTIR simultaneously collects all wavelengths, making it efficient and easy to use.

The fundamental of FTIR is rooted in the atomic vibrations of molecules that selectively absorb specific frequencies and energies of infrared radiation. Molecules behave like vibrating springs due to their interatomic chemical bonds, with energies close to infrared light. When molecules absorb infrared light, they vibrate. These vibrations are limited to those involving a change in dipole moment, and vibrations cancel out if bond vibrations between atoms oppose each other.

In linear molecules, symmetric stretching vibrations do not absorb infrared light because the dipole moment remains unchanged, while asymmetric stretching vibrations do absorb infrared light due to the dipole moment alteration. In nonlinear molecules, both symmetric and asymmetric stretching vibrations absorb infrared light as the dipole moment changes. Additionally, infrared absorption takes place for bending and rotational vibrations as long as the dipole moment changes.

The absorption spectrum of each molecule is distinct and can identify the molecule due to its absorption of infrared radiation at specific frequencies. Each molecular structure has a unique arrangement of atoms, so when it is exposed to infrared light, generates a unique spectrum. This is even true for molecules with the same number of atoms but varying positions. The infrared absorption spectrum acts like a distinct fingerprint for each molecule.

FTIR spectroscopy involves an IR beam passing through an interferometer, comprising a beam splitter, fixed mirror, and moving mirror. This device temporally separates the beam's spectral components. Afterward, the beam travels through the sample gas cell before reaching the detector. An interferogram is recorded, reflecting the detector signal over time, from which the corresponding absorbance spectrum is derived.

7. Characterization Of Optical Properties

Studying and characterizing the optical properties of nanoparticles is crucial, as these methods provide insights into the absorption, reflectance, fluorescence, luminescence, electronic state, bandgap, photo activity, and electrical conductance attributes of nanoparticles. In addition, these can be measured using,

7. 1. Ultraviolet-Visible Spectroscopy

Ultraviolet-visible spectroscopy (UV-Vis or Spectrophotometry) involves analyzing the interaction of substances with light in the UV and visible regions of the electromagnetic spectrum. This technique measures the absorbance of light by a sample and helps quantify the substance present. It works by comparing the intensity of light passing through a sample to that of a reference, offering insights into material characteristics.

When light interacts with a substance, it causes electronic transitions where electrons move from lower energy states to higher energy states. This transition is linked to the absorption of ultraviolet or visible radiation, with the energy difference between ground and excited states matching the absorbed radiation. This relationship is the basis for deriving ultraviolet-visible (UV-Vis) spectra.

The Beer-Lambert law establishes a mathematical relationship between absorbance and concentration, enabling the direct determination of absorber concentration in a solution based on absorbance and a fixed path length.

As per the law, the absorbance of a solution is directly proportional to both the concentration of the absorbing substance and the path length. This means that as the concentration of molecules capable of absorbing radiation at a specific wavelength rises, the absorption increases. Moreover, a molecule's effectiveness in absorbing radiation, indicated by its molar absorptivity, also contributes to higher absorption.

In UV-Visible spectroscopy, electromagnetic radiation is emitted from a source and separated into different wavelengths by a monochromator. These wavelengths then pass through a beam separator, dividing them into reference and sample chambers. The radiation penetrates both samples, with some being absorbed by the sample and others transmitting. These transmitted radiations are processed to subtract solvent absorption. Finally, a detector records the transmitted radiation, and the resulting graph plots absorbance against wavelength for easier analysis by experts.
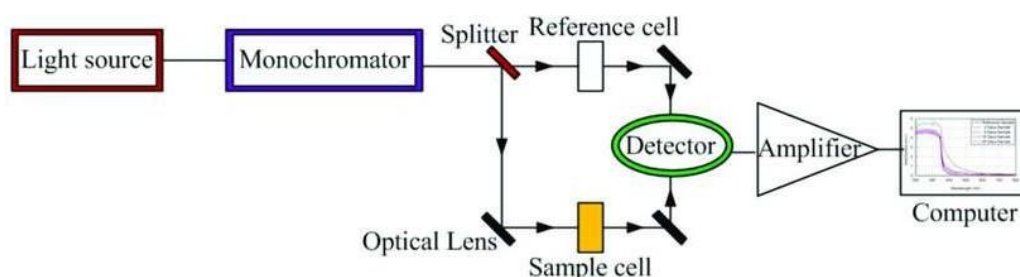
Schematic representation of UV- Vis spectroscopy

8. Fluorescence Spectroscopy

Fluorescence spectrophotometry involves analyzing a molecule's fluorescence based on its distinctive properties. Fluorescence is a form of photoluminescence that occurs when a molecule absorbs energy at a wavelength where it possesses a transition dipole moment. This absorbed energy transfer an electron to an excited state, which then releases thermal energy to the surroundings through vibrations, followed by the emission of a photon from the lowest-lying singlet excited state.

This technique involves illuminating a sample with specific light (typically ultraviolet or visible) that the sample's compounds can absorb. This excites the molecules from their ground state to anexcited electronic state. As the molecules return to the ground state, they emit energy in the form of photons, resulting in fluorescence. The emitted photons' intensities and frequencies are detected and analyzed, providing insights into the molecule's vibrational energy levels and offering information about the molecule's identity, quantity, changes, interactions within the sample, and more.

9. Characterization of Thermal Properties

Various methods are available to characterize the thermal properties of nanoparticles, such as melting points, crystallization, structural-phase transitions, heat capacity, thermal conductivity, and thermal and oxidative stability. Among these, Analysis (TGA) stands outas a primary technique for analyzing thermal properties.

9.1. Thermogravimetric Analysis (TGA)

Thermogravimetric analysis (TGA) is a robust method used to measure the thermal stability of various materials, including polymers. This technique involves tracking weight changes in a sample as its temperature is raised. TGA can also determine the moisture and volatile content within a specimen.

TGA operates by monitoring changes in the mass of a substance while subjecting it to continuous heating. While certain thermal processes like melting and crystallization may not influence mass, other thermal events such as desorption, absorption, sublimation, vaporization, oxidation, reduction, and decomposition can lead to significant mass changes. Hence, it is crucialto optimize the conditions and factors that influence the sample's mass change throughout the experiment.

In this technique, the sample is continuously weighed as it is heated from room temperature to 1000 degrees Celsius under an inert gas atmosphere. Many solids undergo reactions that release gaseous by-products. In TGA, these gaseous by-products are eliminated, and the resulting changes in the remaining sample mass are monitored.

10. Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES)
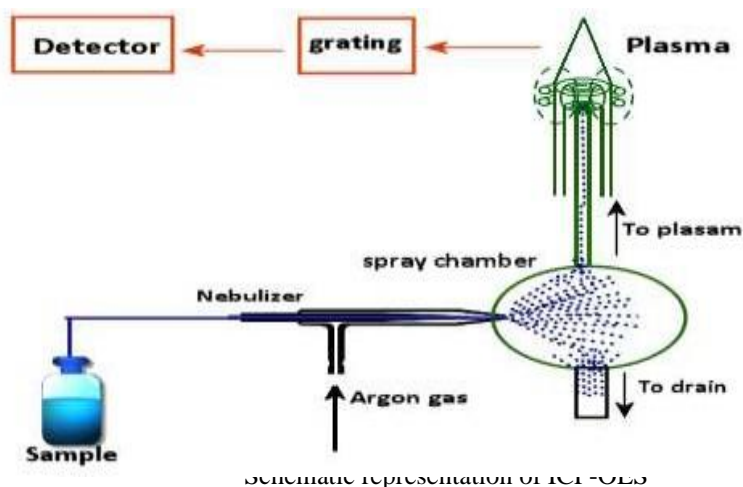
ICP-OES finds application in quantifying ultra-trace metals across various samples, and it's also employed to assess the toxicity of nanoparticles for potential biomedical purposes.

Schematic representation of ICP-OES

ICP-OES is a method utilized for determining the elemental composition of samples, predominantly those dissolved in water, through the application of plasma and a spectrometer. It finds frequent application in the analysis of trace metals in contaminated water samples. The analytical process involves delivering the solution to be analyzed via a peristaltic pump through a nebulizer into a spray chamber. The resulting aerosol is directed into an argon plasma.

In ICP-OES, the plasma is generated at the end of a quartz torch using a cooled induction coil subjected to high-frequency alternating current. This induces an alternate magnetic field, propelling electrons into a circular trajectory. Ionization occurs through collisions between argon atoms and electrons, establishing a stable plasma. The plasma is exceptionally hot, ranging between 6000 and 18,000 K, with the potential to reach 10,000 K in the induction zone of the torch. Within the torch, processes such as desolvation, atomization, and ionization of the sample transpire.

As a consequence of the thermal energy absorbed by the electrons, they attain a higher excited state. Upon their return to ground level, energy is released in the form of light (photons). Each element exhibits a unique emission spectrum that is captured by a spectrometer. The light intensity at specific wavelengths is measured and, through calibration, translated into concentration values.

Conclusion

Numerous factors affect the quality and quantity of synthesized nanoparticles for their potential applications. So, effective characterization techniques are required to efficiently assess synthesized nanoparticles, enhancing their applicability in environmental, electronic, biomedical,and drug delivery contexts.

References

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