

Microscopy in Nanotechnology

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Nowadays science and technology ever seek to build structures of progressively smaller size. This effort at miniaturization has now reached the point where structures and material can be built through “atom-by-atom” engineering. Typical chemical bonds separate atoms by a fraction of a nanometer (10 – 9 m), and the term nanotechnology has been coined for this emerging area of development. By manipulating the arrangements and bonding of atoms, materials can be designed with a far vaster range of physical, chemical and biological properties than has been previously conceived. But how to characterize the relationship between starting composition, which can be controlled, with the resulting structure and properties of a nanoscale-designed material that has superior and unique performance? Microscopy is essential to the development of nanotechnology, serving as its eyes and hands.

In this chapter we discussing about several types of microscopy which are used for characterization of nanomaterials.

Keywords: Nanomaterials; TEM; SEM; AFM; XRD

1. Introduction:

Nanomaterials, specifically nanoparticles, are, without a doubt, key components in the development of new advanced technologies. Although nanoparticles are perhaps the simplest of nanostructures, nanoparticle-based technologies are broadly covering different fields, ranging from environmental remediation, energy generation, and storage all the way to applications in bioscience [1–5].

Much progress in nanoscience and nanotechnology has been made in the past few years thanks to the increased availability of sophisticated physical methods to characterize nanomaterials. The need to know different nanoparticle properties to make them suitable for specific applications has enhanced a large number of worldwide research efforts aimed at their tailoring. However, full use of these structures in these applications requires more detailed information and a feedback of data coming from reliable characterization techniques [6–8]. These techniques comprise local probes, such as scanning electron microscopy (SEM), transmission electronic microscopy (TEM), electron diffraction, scanning tunneling microscopy, and atomic force microscopy, with bulk-sensitive probes such as optical absorption spectroscopy, infrared (IR) spectroscopy (Fourier transform IR), and Raman scattering, and X-ray-based techniques such as X-ray diffraction, X-ray photoelectron spectroscopy, and X-ray absorption (X-ray absorption near edge structure and extended X-ray absorption fine structure).

Characterization of nanomaterials includes the determination not only of size and shape, but also of the atomic and electronic structures and other important properties. In this chapter we describe some of the important methods employed for characterization of nanostructures.

2. Microscopy Techniques:

Structural characterization is essential for nanomaterials research. Since the nanostructures are usually too small to be visualized with conventional optical microscopes, it is important to use appropriate tools which adequately characterize their structure and surface in detail at the molecular or atomic level. This is important not only for understanding their fundamental properties but also for exploring their functional and technical performance in technological applications. There are several experimental techniques that can be used to characterize structural and surface properties of nanomaterials either directly or indirectly, e.g. XRD, STM (scanning tunneling microscopy), AFM (atomic force microscopy), SEM (scanning electron microscopy), TEM (transmission electron microscopy), XAS (X-ray absorption spectroscopy), EXAFS, XANES (X-ray absorption near edge structure), EDX (energy dispersive X-ray), XPS, IR (infrared), Raman, and DLS (dynamic light scattering) [9-13]. Some of these techniques are more surface sensitive than others. Some techniques are directly element-specific while others are not. The choice of techniques depends strongly on the information being sought about the material.

2.1. Scanning probe microscopy (SPM): AFM and STM

Scanning probe microscopy (SPM) is a group of techniques, which includes scanning tunneling microscopy (STM), atomic force microscopy (AFM), and chemical force microscopy (CFM), that has been extensively applied to characterize nanostructures with atomic or subatomic spatial resolution [9, 12, 14-16]. A common characteristic of these techniques is that an atom sharp tip scans across the specimen surface and images are formed by either measuring the

current flowing through the tip or the force acting on the tip. SPM can be operated in a number of environmental conditions, in a variety of different liquids or gases, allowing direct imaging of inorganic surfaces and organic molecules. It allows viewing and manipulation of objects on the nanoscale and its invention is a major milestone in nanotechnology.

2.1.1 Atomic force microscopy (AFM):

AFM is based on measuring the force between the tip and the solid surface. The interaction between two atoms is repulsive at short-range and attractive at long-range. The force acting on the tip reflects the distance from the tip atom(s) to the surface atom, thus images can be formed by detecting the force while the tip is scanned across the specimen. A more generalized application of AFM is scanning force microscopy, which can measure magnetic, electrostatic, frictional, or molecular interaction forces allowing for nano-mechanical measurements. For nonconductive nanomaterials, AFM is a better choice [17, 18]

A typical AFM setup involves a sharp tip mounted on a microscale cantilever, a laser, a position sensitive detector, a piezoelectric tube (PZT) scanner, and control electronics [16]. The cantilever is typically silicon or silicon nitride with a tip radius or curvature on the order of nanometers. When the tip is brought near a sample surface, forces between the tip and the sample lead to a deflection of the cantilever according to Hooke's law. Depending on the situation, forces that are measured in AFM include mechanical contact force, electrostatic forces, chemical bonding, van der Waals forces, capillary forces and magnetic forces. Typically, the deflection is measured using a laser beam reflected from the top of the cantilever into an array of position sensitive photodiodes. To avoid possible collision between the tip and sample surface, a feedback mechanism is often employed to adjust the tip-to-sample distance to maintain a constant force between the tip and the sample. Traditionally, the sample is mounted on a PZT that can move the sample in the z direction for maintaining a constant force and in the x and y directions for scanning the sample. The resulting map of the area $s = f(x,y)$ represents the topography of the sample. The AFM can be operated in a number of modes, depending on the application. In general, possible imaging modes are divided into static (also called contact) modes and a variety of dynamic (or non-contact) modes.

AFM is capable of directly providing unprecedentedly detailed information on the atomic scale, which is important for understanding chemical bonding and electronic structure of atoms and molecules.

2.1.2. Scanning tunneling microscopy (STM):

Another powerful SPM technique is STM, discovered in the 1980s [19]. STM is based on measuring the tunneling current between a sharp metallic tip and specimen. The STM tip does not actually touch the surface of the sample measured. A voltage is applied between the tip and the specimen, typically between a few mV and a few V. If the tip touches the surface of the specimen, the voltage will result in an electrical current. If the tip is far away from the surface, the current is zero since it is essentially an open circuit. STM operates in the regime of extremely small distances between the tip and the surface of only 0.5 to 1.0 nm, or only a few atomic diameters. At these distances, electrons can tunnel from the probe tip to the surface or vice versa, which is why it is named tunneling microscopy. Since tunneling is a weak process, the tunneling current is thus very low.

STMs typically operate at tunneling currents between a few picoAmperes (pA) and a few nanoAmperes (nA). The tunneling current depends strongly on the distance between the tip and the specimen. Therefore, tunneling current provides a highly sensitive measure of the distance between the tip and the surface. The STM tip is attached to a piezoelectric element used to control the precise distance between the tip and the surface with an electrical voltage. This voltage is adjusted such that the tunneling current is a constant in the z direction, which means that the distance between the tip and the specimen surface is kept at constant. This distance control is achieved using feedback electronics. While distance control is active, the tip can be moved in directions (e.g. x and y) parallel to the sample surface to scan over the surface using two other parts of the piezoelectric element. As the tip scans, the tip needs to be moved in the z direction perpendicular to x and y , through the piezoelectric voltage control, to ensure a constant current. In doing so, the control voltage in the feedback electronics contains information about the surface topology of the specimen. This information is usually transformed into 3D images and plotted on a computer for easy visualization [20]. STM is applicable mainly for conductive samples.

2.2. Electron microscopy:

Since diffraction effects restrict the resolution of optical microscopy, structures smaller than 1 μm cannot be observed with light. Therefore, if imaging at considerably higher resolution is required, electromagnetic radiation of shorter wavelengths must be used. Electron beams present this possibility. The development of electron microscopes has resulted in instruments that are able to routinely achieve magnifications of the order of 1 million and that can disclose details with a resolution of up to about 0.1 nm.

When an electron beam interacts with a sample, many measurable signals are generated and electrons can be transmitted, backscattered, and diffracted. TEM uses the transmitted electrons to form a sample image, while SEM uses

backscattered electrons and secondary electrons emitted from the sample. Depending on the sample thickness, transmitted electrons pass through it without suffering significant energy loss. Since the attenuation of the electrons depends mostly on the density and thickness of the sample, the transmitted electrons form a two dimensional projection of the sample. This is the basis for TEM imaging. Electrons can also get diffracted by particles if these are favorably oriented toward the electron beam; the crystallographic information that can be obtained from these diffracted electrons is the basis for electron diffraction. Finally, the electrons in the primary beam can collide with atoms in the sample and be scattered back or, in turn, remove more electrons from these atoms (secondary electrons). These two processes (backscattering and generation of secondary electrons) are more effective as the atomic number of the atom increases. If the primary electron beam is targeted over the sample surface and the yield of secondary or backscattered electrons is plotted as a function of the position of the primary electron beam, it is possible to obtain three-dimensional images of the samples analyzed; this method is the basis for SEM.

2.2.1. Transmission Electron Microscopy (TEM):

The development made in TEM has enabled the direct imaging of atomic structures in solids and surfaces. Nanometer-sized particles are commonly present in many different types of materials and the use of TEM allows for gathering information about particle size, shape, and any surface layers or adsorbates [21, 22]. More recently, changes in nanoparticle structure as a result of interactions with gas-, liquid-, or solid-phase substrates can now be monitored by this technique [23].

In recent years, a large number of new developments have been made in electron microscopy for nanotechnology. This includes new techniques such as in situ microscopy used for imaging dynamic processes, quantitative chemical mapping, holographic imaging of electric and magnetic fields, and ultra high resolution imaging [24]. For instance, the study of nanoparticles can be greatly improved with the use of aberration-corrected lenses, enabling image resolutions at levels sometimes lower than 1 Å [25, 26]. This level of image resolution yields a new level of understanding of the behavior of matter at the nanoscale.

TEM is a high spatial resolution structural and chemical characterization tool [27]. A modern TEM has the capability to directly image atoms in crystalline specimens at resolutions close to 0.1 nm, smaller than interatomic distance. An electron beam can also be focused to a diameter smaller than ~ 0.3 nm, allowing quantitative chemical analysis from a single nanocrystal. This type of analysis is extremely important for characterizing materials at a length scale from atoms to hundreds of nanometers. TEM can be used to characterize nanomaterials to gain information about particle size, shape, crystallinity, and interparticle interaction [10, 28].

A stream of monochromatic electrons produced by an electron gun is focused into a small, thin, coherent beam by two condenser lenses. The electron beam is restricted by the condenser aperture to remove high angle electrons before it reaches the specimen. It is important in this case that the specimen is thin enough to allow some electrons to transmit through the sample. Interaction between the electron beam and specimen generates elastically and inelastically scattered electrons, along with some unscattered electrons, in the forward direction after the sample has been detected. The detected signal contains information about the sample. The detection involves several lenses to focus the electrons to be detected before they reach the detection phosphor screen. Optional objective and selected area metal aperture that can be used to restrict the beam, with the objective aperture enhancing contrast by blocking out high-angle diffracted electrons and the selected area aperture enabling the user to examine the periodic diffraction of electrons by ordered arrangements of atoms in the sample examined.

An important precaution to be taken into consideration when performing TEM measurements on nanoparticle-containing samples; that is they can be susceptible to the highly energetic electron beam of the TEM instrument [29]. Beam susceptibility makes it very difficult sometimes to carry out electron diffraction studies on nanoparticles that are prone to beam damage. In this case, by using low electron beam currents, it is possible to obtain lattice fringe images and electron diffraction.

In spite of all these advantages, TEM imaging still presents a series of challenges. For instance, image overlap is a typical problem during observation. When this occurs, the surrounding matrix usually tends to mask the supported nanoparticles. In some special cases, however, the existence of an epitaxial relationship between the nanoparticles and their support can be used to obtain size and shape information [30]. Moreover, nanoparticles can be susceptible to damage under the electron beam irradiation conditions normally used for high-resolution imaging.

2.2.2. Scanning Electron Microscopy:

SEM is, to a certain extent, a limited tool to characterize nanoparticles. The main problem with the application of SEM to nanoparticle characterization analysis is that sometimes it is not possible to clearly differentiate the nanoparticles from the substrate. Problems become even more exacerbated when the nanoparticles under study have tendency to adhere strongly to each other, forming agglomerates. In contrast to TEM, SEM cannot resolve the internal structure of these domains.

SEM is a powerful and popular technique for imaging the surfaces of almost any material with a resolution down to about 1 nm [10, 11]. The image resolution offered by SEM depends not only on the property of the electron probe, but

also on the interaction of the electron probe with the specimen. The interaction of an incident electron beam with the specimen produces secondary electrons, with energies typically smaller than 50 eV, the emission efficiency of which sensitively depends on surface geometry, surface chemical characteristics and bulk chemical composition [31]. SEM can thus provide information about the surface topology, morphology and chemical composition. The high resolution capability afforded by SEM makes it convenient for probing nanomaterials of which the structural features on the nanoscale are critical to their properties and functionalities.

A typical scanning electron microscope starting from the electron source; a stream of monochromatic electrons generated by an electron gun is condensed by the first condenser lens to both form the beam and limit the amount of current, as well as, in conjunction with the condenser aperture, to eliminate the high-angle electrons from the beam. The second condenser lens focuses the electrons into a thin, tight, coherent beam and an objective aperture is used to further eliminate high-angle electrons from the beam. A set of coils is used to scan the beam in a grid fashion. The objective lens focuses the scanning beam onto the specimen desired, one point at a time. Interaction between the electron beam and the sample generates back scattered electrons (BSE), X-ray, secondary electrons (SE), and Auger electrons in a thick or bulk sample. These various electrons are detected and the signal detected contains information about the specimen under investigation. BSE is more sensitive to heavier elements than SE. The X-ray radiation can be detected in a technique called energy dispersive X-ray (EDX) spectroscopy that can be used to identify specific elements [32, 33].

Nevertheless, SEM can yield valuable information regarding the purity of a nanoparticle sample as well as an insight on their degree of aggregation. Moreover, when nanoparticles are part of secondary and tertiary nanostructures, SEM becomes a valuable tool to assess their location [34]. The location of the metal nanoparticles over the support is evident. Furthermore, the SEM micrograph clearly reveals the high degree of dispersion and uniformity of these metallic nanoparticles over the substrate.

While both TEM and SEM techniques can provide topological, morphological and compositional information about the sample, TEM can provide crystallographic information as well. In addition, TEM allows for diffraction patterns to be detected that also contain useful crystallographic information about the sample.

The big disadvantage of both SEM and TEM in this context is that one can never be sure that the observed image is truly representative of the bulk nanoparticle sample. Consequently, bulk-sensitive methods that provide information regarding the quality, size, and structural properties of a given sample must be employed. Among these methods, Raman spectroscopy and optical absorption deliver the most comprehensive results.

2.3. X-ray:

Nowadays several X-ray techniques are used for nanomaterial characterization like XRD, XPS, XAFS, SAXS etc. X-ray based spectroscopies are useful in determining the chemical composition of materials. These techniques include X-ray absorption spectroscopy (XAS) such as extended X-ray absorption fine structure (EXAFS) and X-ray absorption near edge structure (XANES), X-ray fluorescence spectroscopy (XRF), energy dispersive X-ray spectroscopy (EDX), and X-ray photoelectron spectroscopy (XPS) [35, 36]. They are mostly based on detecting and analyzing radiation absorbed or emitted from a sample after excitation with X-rays, with the exception that electrons are analyzed in XPS. The spectroscopic features are characteristic of specific elements and thereby can be used for sample elemental analysis.

2.3.1. X-ray Diffraction (XRD):

XRD is a powerful and routine technique for determining the crystal structure of crystalline materials [37-39]. By examining the diffraction pattern, one can identify the crystalline phase of the material. Small angle scattering is useful for evaluating the average interparticle distance while wide-angle diffraction is useful for refining the atomic structure of nanoclusters [40]. The widths of the diffraction lines are closely related to the size, size distribution, defects and strain in nanocrystals. As the size of the nanocrystals decreases, the line width is broadened due to loss of long range order relative to the bulk. This XRD line width can be used to estimate the size of the particle via the Debye– Scherrer formula.

$$D = \frac{0.9\lambda}{\beta \cos\theta} \quad \dots\dots(1)$$

where D is the nanocrystal diameter, λ is the wavelength of light, β is the full width half at maximum (FWHM) of the peak in radians, and θ is the Bragg angle.

2.3.2. X-ray photoelectron spectroscopy:

XPS is based on the measurement of the kinetic energy of photoelectrons generated when the sample is illuminated with soft (1.5 kV) X-ray radiation in an ultrahigh vacuum (UHV) [41]. If one X-ray photon with energy $h\nu$ is used to excite

an atom in its initial state with energy E_i and to eject an electron with kinetic energy, KE , with the atom resulting in a final state with energy E_f , one would have the following equation based on total energy conservation:

$$h\nu + E_i = KE + E_f \dots\dots\dots(2)$$

The difference between the photon energy and the electron kinetic energy is called the *binding energy* of the orbital from which the electron is ejected, which, based on Eq. (2), is equal to $E_f - E_i$. Since the photon energy is known from the X-ray radiation source used and the electron kinetic energy can be measured, the binding energy can be determined, which gives the energy difference between the final and initial states of the atom involved in the transition. This binding energy is characteristic for different orbitals of specific elements and is roughly equal to the Hartree–Fock energy of the electron orbital. Therefore, peaks in the photoelectron spectrum can be identified with specific atoms and surface composition can be analyzed. Because the photoelectrons are strongly attenuated by passage through the sample material itself, the information obtained comes from the sample surface, with a sampling depth on the order of 5 nm. Chemical bonding in molecules will cause binding energy shifts, which can thus be used to extract information of a chemical nature (such as atomic oxidation state) from the sample surface.

2.3.3. X-ray fluorescence spectroscopy (XFS):

XFS is similar to XPS in terms of the excitation mechanism but differs in its detection mechanism. While XPS detects photoelectrons, XFS detects “secondary” or “fluorescent” X-rays from a material that has been excited by high-energy X-rays (or sometimes γ -rays) [42]. The principle behind XFS is relatively straightforward. When a material is exposed to high energy or short wavelength X-rays, ionization or electron ejection can take place if the X-ray photon energy is greater than its ionization energy. Due to the high energy of X-rays or γ -rays, tightly bound electrons in the inner, low energy orbitals of the atom in the material can be expelled. The resulting ionized atom is not unstable and electrons in outer, higher energy orbitals may fall or make a transition into the lower orbital to fill the hole left behind. In doing so, energy may be released in the form of a photon (usually with energy in the X-ray region still) with energy equal to the energy difference of the two orbitals involved. Because the orbitals are specific to individual atoms, the energy of the emitted photon that can be easily detected has energy characteristic of the atoms involved. The term “fluorescence” refers to the emitted X-ray photons, not visible light, even though visible light can also be generated and observed sometimes when a sample is subject to X-ray radiation.

2.3.4. X-ray absorption fine structure (XAFS):

Another powerful X-ray based spectroscopic technique is extended XAFS [35]. EXFAS is based on measuring the fine structure near the absorption edge of a sample when subject to X-ray radiation. It is similar to UV-visible electronic absorption spectroscopy, in principle, except that the spectral range is in the X-ray region and EXAFS focuses on the fine structure specifically since it provides local structural information about specific atoms or ions. EXAFS relates to the details of how X-rays are absorbed by an atom at energies near and above the core-level binding energies of that atom. EXAFS measurements reflect the modulation of an atom’s X-ray absorption probability due to the chemical and physical states of the atom. EXAFS spectra are especially sensitive to the formal oxidation state, coordination chemistry, and the local atomic structure of the selected element. One advantage of EXAFS is that it works for crystalline as well as noncrystalline or even highly disordered materials, including solutions. It is thus well suited for studying nanomaterials [43–46]. EXAFS measurements are relatively straightforward but require an intense and energy-tunable source of X-rays, which usually means the use of synchrotrons. While the experimental measurements can be simple, analysis of EXAFS data is somewhat involved and requires specific expertise and good knowledge of relevant physical principles. For convenience of data interpretation, the X-ray absorption spectrum is typically divided into two regimes: X-ray absorption near-edge spectroscopy (XANES) and EXAFS. While XANES is more sensitive to formal oxidation state and coordination chemistry of the absorbing atom, EXAFS is usually used to determine the distances, coordination number, and species of the neighbors of the absorbing atom.

2.3.5. Small Angle X-ray Scattering (SAXS):

A final example of X-ray related techniques useful for nanomaterials research is SAXS [47, 48]. SAXS is an analytical technique often used for the structural characterization of solid and fluid materials in the nanometer range. In SAXS measurements, the sample is irradiated by a well-defined, monochromatic X-ray beam. Intensity distribution of the scattered beam at very small scattering angles is measured and it contains structural information of the scattering particles. SAXS can be used to study both monodisperse and polydisperse systems. Information about size, shape and internal structure of the particles can be determined for monodisperse systems and size distributions can be calculated for polydisperse systems. SAXS has been applied to investigate structural details of a variety of nanoparticles of inorganic, organic, as well as biological materials in the size range of 0.5 to 50 nm, usually with high intensity X-ray radiation.

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