

# Chapter 1

## Fundamentals of Nanotechnology and Nanobiotechnology



### 1.1 Introduction

Nanotechnology is a very interesting scientific discipline and has versatile practical applications. It depends majorly on manufacturing novel, and promising materials at the level of the nanoscale (Rastogi et al. 2018). The Japanese Professor Norio Taniguchi was the first to coin the term nanotechnology (Taniguchi et al. 1974). Particles with dimensions of 100 nm or less are referred to as nanoparticles and are considered as the building blocks of nanotechnology. For instance, the length of a carbon-carbon bond is in the range of 0.12–0.15 nm, and the diameter of the DNA double helix is approximately 2 nm. Conversely, the length of the mycoplasma which is the smallest cellular forms of bacteria is nearly 200 nm. For instance, the human hair diameter is around 80,000 nm (Guo 2013). These nanostructured materials are characterized by extraordinary properties such as the controlled shape, size, crystallinity, and composition. Nanotechnology covers fields starting from biology to materials science and chemistry to physics. The controlled size, shape, composition, crystallinity, and structure-dependent properties of nanoparticles govern the unique properties of nanotechnology. However, physical and chemical methodologies used for nanoparticle synthesis such as sol-gel technique, chemical vapor deposition, precipitation, hydrothermal synthesis, and microemulsion proved to be toxic, hazardous, not eco-friendly, expensive, and harsh conditions are needed such as high temperature and/or pressure to complete the synthesis process. Thus, significant efforts were devoted for finding alternative techniques to guarantee the safe and clean synthesis of nanoparticles. This was successfully achieved by the progress of the nanobiotechnology field.

## 1.2 Fundamentals of Nanotechnology

### 1.2.1 *Definition and Concept of Nanotechnology*

The prefix “nano” is originated from the Greek word “*nanos*” which means “dwarf” or very small. Nanotechnology is defined as “the science that allows the manipulation of matter at atomic or molecular levels in the range of 1–100 nm” (Omran et al. 2018a, El-Gendy and Omran 2019). Thus, this would aid in producing innovative materials with extraordinary properties (Mohan Bhagyaraj and Oluwafemi 2018). Nanotechnology is a multidisciplinary science that combines several scientific fields including biotechnology, biology, chemistry, physics, medicine, pharmacy and engineering, etc. It is worth noting that the principles of quantum physics contributed in the revolutionary nature of nanotechnology (Basu 1997). The behavior of materials at the nanoscale is under the control of quantum laws rather than those of classical physics (Mohan Bhagyaraj and Oluwafemi 2018). These extraordinary features of nanoscaled materials offer new properties that make them superior and more favorable than those of bulk materials.

### 1.2.2 *Historical Arise of Nanotechnology*

Nanotechnology is the science which is concerned with the development and manipulation of materials at the nanoscale level. One nanometer is one billionth of a meter ( $10^{-9}$  m) which is extremely small (Ball et al. 2019). According to Balzani (2005), the U.S. National Nanotechnology Initiative (NNI) defined nanotechnology as the science that focuses on the research and the development of materials at the atomic or molecular levels to generate structures that can be employed in versatile applications. Paul and Chugh (2011) reported that the history of nanotechnology science began during the eras of the fourth and the fifth centuries BC in China and India. The traditional medical practitioners managed to synthesize gold colloids referred to as “Swarna Bhasma” which possessed potential therapeutic capabilities. Dykman and Khlebtsov (2012) demonstrated Paracelsus treated mental disorders and syphilis in Europe during the middle ages via colloidal gold. Ball et al. (2019) mentioned that in 1618, Doctor Francisco Antonii wrote a book on how colloidal gold can be prepared and the different applications in which it can be exploited. Furthermore, in 1857, Michael Faraday published the first scientific book on colloidal gold (Ball et al. 2019). In 1867, James Clerk Maxwell released his frontier observations about a technology that can manipulate individual molecules. In the early twentieth century, major advances were performed in ultramicroscopes. In 1914, Zsigmondy managed for the first time to observe and investigate nanostructures of a size of 10 nm (Zsigmondy 1914). Yet, the Nobel laureate Richard Feynman inspired the world in nanomaterials’ science by his lecture “There’s Plenty of Room at the Bottom” in 1959 at Caltech, USA (Feynman 1960). In his famous speech, he

clarified that there might be an ability to manipulate and control materials in a very small scale. The biggest popularization in nanomaterial science began when the American engineer Eric Drexler published his book in 1986 which was entitled *Engines of Creation: The Coming Era of Nanotechnology*. Engineer Eric Drexler was known as the “founding father of nanotechnology” (Drexler 1981). In 1991, Drexler established the molecular nanotechnology field by his doctoral dissertation which was entitled “Nanosystems, Molecular Machinery, Manufacturing, and Computation.” His work represented an inspiration for his scientific colleagues to further explore other manufacturing systems of nanotechnology which helped engineers and scientists in different disciplines to scale down the use of materials to the nanoscale levels. The term “nanotechnology” was first coined by the Japanese Professor Norio Taniguchi in Tokyo Science University in 1974. Two of his published works were related to nanotechnology, and they were *Nanotechnology: Integrated Processing Systems for Ultra-Precision and Ultra-Fine Products* and *On the Basic Concept of Nanotechnology* (Mohan Bhagyaraj and Oluwafemi 2018). Richard E. Smalley was another scientist whose work attributed majorly to the nanotechnology science. Smalley was a Nobel laureate, and he got the Nobel Prize in chemistry in 1996 for discovering Buckminsterfullerene. He worked in Rice University in Texas and was a professor of physics, chemistry, and astronomy and the founding director of a center for nanoscale science and technology since 1996 till 2002. His work focused mainly on different types of fullerenes for instance C60, C70, etc. He encouraged their use in various conducting applications based on his studies (Nelson and Strano 2006).

Certain developments aided in extensive progress in nanotechnology including the discovery of carbon nanotubes in 1991, the design of a nano-robotic system in 1997, and the design of the first nanochemical apparatus for DNA in 1998. The first industrial report on nanotech revolution and the first nanotech industrial conference were in 2001 and 2002, respectively (Mohan Bhagyaraj and Oluwafemi 2018). Currently, nanotechnology has become one of the most important technologies in all areas of science particularly modern materials science (Visweswara Rao and Hua Gan 2015).

### 1.3 History of Nanomaterials

Since thousands of years ago, humans started to use nanomaterials. Heiligtag and Niederberger (2013) reported that more than 4500 years ago, people reinforced ceramic matrixes by the inclusion of natural asbestos nanofibers. Also, Walter et al. (2006) demonstrated in his publication in 2006 that the Ancient Egyptians used nanomaterials for more than 4000 years ago. The Ancient Egyptians formulated a hair dye by a chemical process to synthesize PbS NPs with a size of approximately  $\approx 5$  nm diameter PbS NPs for hair dye. Likewise, the first synthetic pigment which was referred to as the “Egyptian blue” was fabricated and used by Egyptians near the third century BC (Johnson-McDaniel et al. 2013). Egyptian blue is a multifaceted

mixture of  $\text{SiO}_2$  and  $\text{CaCuSi}_4\text{O}_{10}$ . Different countries like Egypt, Greece, and Mesopotamia extensively used the Egyptian blue for decorative purposes which was then discovered during the archaeological explorations.

The chemically synthesized NPs occurred in centuries back to the thirteenth and fourteenth centuries BC. Schaming and Remita (2015) reported that both Egyptians and Mesopotamians made glass using metals which was considered as the starting era for the use of metallic nanoparticles. Afterwards, at the end of the Bronze Age (1200–1000 BC), red glass was explored in Frattesina di Rovigo (Italy) which was found to be colored by the incorporation of copper nanoparticles (CuNPs) (Artioli et al. 2008). Likewise, CuNPs in addition to cuprous oxide (cuprite  $\text{Cu}_2\text{O}$ ) were discovered in the Celtic red enamels which belonged to 400–100 BC period (Brun et al. 1991). Furthermore, a very popular Romanian work piece was discovered and was an evidence in using metallic NPs. The Lycurgus Cups which belong way back to the fourth century are Roman glass cups, and they are built up from a dichroic glass which exhibits different colors, for instance, green and red when the light passes from the front and behind, respectively, as was conducted by Leonhardt (2007). Nonetheless, recent studies discovered that the Lycurgus Cups contained Ag-Au alloy NPs, with a ratio of 7:3 along with 10% of CuNPs (Freestone et al. 2007).

Later, during the medieval period, churches' glass were found to be stained with yellow and red colors by the incorporation of colloidal AgNPs and AuNPs, respectively (Schaming and Remita 2015). Heiligtage and Niederberger (2013) reported that Mesopotamians began to use glazed ceramics for decoration purposes during the ninth century. These decorations were distinctive because they exhibited unique optical features because of the existence of Ag and/or CuNPs which were isolated within the outer ceramic layers. These decorations represented a perfect example of incorporating metal nanoparticles which would display exciting coloration, i.e., bright blue and green coloration, when exposed to reflection. A double layer of AgNPs with an approximate range of 5–10 nm was found in the outer layers, and larger particles of a size of 5–20 nm were found in the inner layers. Far ahead, the red glass was manufactured using that process worldwide.

In the middle of the nineteenth century, a similar technique was employed to generate the popular Satsuma glass in Japan (Nakai et al. 2004). The Satsuma glass was colored by the absorption properties of CuNPs that were helpful in producing the ruby color. It was reported by Rytwo (2008) that in 5000 BC, cloths and wools were bleached in Cyprus by clay. In 1857, Michael Faraday described the process of synthesizing colloidal AuNPs, and from that time the scientific arena of nanomaterial synthesis was initiated. Moreover, he postulated that there was a major difference between the optical features of Au colloids and their bulk counterparts. This might be considered as one of the earliest reports illustrating the effect of quantum size. Later, the reason behind the color variation of metal colloids was further described and explained by Mie (1908). During 1940s, silicon oxide nanoparticles ( $\text{SiO}_2$  NPs) were produced to be used as an alternative for carbon black for rubber reinforcement purposes (Rittner and Abraham 1998).

Today, manufactured nanomaterials possess significant advantages over their bulk counterparts involving improvement of conductivity strength, durability, lightness, as well as providing beneficial properties (e.g., self-healing, self-cleaning, anti-freezing, and antibacterial). They can also reinforce materials for construction purposes or for safety issues (Jeevanandam et al. 2018). In 2003, Samsung company started to release electronic devices with the advantage of employing antibacterial technology which was given the trade name of Silver Nano™. Such devices involved air conditioners, air purifiers, refrigerators, washing machines, and vacuum cleaners, which used ionic AgNPs (Jeevanandam et al. 2018). Additionally, nanostructured materials are widely employed in auto production, for instance, as fillers in tires to enhance adhesion to the road, as fillers in the car body to increase the stiffness, and also as transparent layers used for constructing heated, mist- and ice-free window panes (Jeevanandam et al. 2018).

At the end of 2003, Mercedes-Benz managed to exploit metal and nonmetal NPs for paint finishing for their car series. This coating had the advantage of increasing scratch resistance and enhancing the appearance by increasing the car gloss. Kreuter (2007) reported that in 2005, a human serum albumin material composed of paclitaxel was synthesized, commercialized, and released in the market and was given the trade name of Abraxane™. Vance et al. (2015) reported that in 2014, approximately 1814 nanotechnology-based consumer products were commercially available in markets of over than 20 countries around the world. Yet, this number is in huge increase.

## 1.4 Classification of Nanomaterials

Nanomaterials are characterized by their extraordinary properties which can be tailored to be applied in different disciplines. Among these characteristic features are the reduction in spatial dimensions as well as their small surface-area-to-volume ratio. Basically, nanomaterials are classified into three main categories including zero-dimensional, one-dimensional, and two-dimensional structures as described in Table 1.1.

## 1.5 Types of Nanomaterials

Recently, most nanomaterials produced are categorized into four categories, namely, carbon-based nanomaterials, inorganic-based nanomaterials, organic-based nanomaterials, and composite-based nanomaterials as listed in Table 1.2 (Jeevanandam et al. 2018).

**Table 1.1** Classification of nanomaterials

Structure of nanomaterial	Definition	Examples	Description	Application	References
Zero-dimensional structures	Structures that are confined in three dimensions	Nanoparticles, nanograins, nanoshells, nanocapsules, nanorings, fullerenes, colloidal particles	Particles which range in size from a few tens to a few hundreds of nanometers	Aid in fabricating novel composite materials, for example, synthesis of plastics with high resistance to UV light, synthesis of more effective drugs, and catalysts	Tiwari et al. (2018)
One-dimensional structures	Structures that are confined in two dimensions	Carbon nanotubes (CNTs)	Nanotubes are referred to as hollow cylinders with either single or multilayered walls with a diameter in the range of few nanometers. Nanotubes are characterized by high tensile strength, elasticity, high electrical conductivity, flexibility, thermal conductivity, good electron field emitting properties, low thermal expansion coefficient, and high aspect ratio	Nanotubes are used to construct enormously strong materials with different applications including vehicle manufacturing, nanocircuits, mechanical gears for nanomachines, and display screens	Chen et al. (2006)
Two-dimensional structures	Structures that are confined in one dimension	Nanowires (quantum wires) Nano-membranes, nanofilms, nanolayers, graphene	They differ from the nanotubes in that they are not hollow They possess a variety of optical, chemical, mechanical, biodegradable, and biocompatible properties	Nanowires are more favorable in making electronic chips and devices Tissue engineering and in drug delivery	Lalwani et al. (2013), Wan et al. (2016)

**Table 1.2** Categories of nanomaterials

Classification	Examples	Description
Carbon-based nanomaterials	Fullerenes (C60), carbon nanotubes (CNTs), carbon nanofibers, carbon black, graphene, and carbon onions	Nanomaterials which contain carbon exhibit different morphological structures like hollow tubes, spheres, and ellipsoids
Inorganic-based nanomaterials	Metal, metal oxide nanoparticles such as AuNPs, AgNPs, ZnO NPs, TiO <sub>2</sub> NPs	They exhibit versatile shapes, i.e., rod, spherical, hexagonal, cuboid
Organic-based nanomaterials	Dendrimers, micelles, liposomes and polymer NPs.	Nanomaterials made up of organic matter
Composite-based nanomaterials	Metal organic frameworks (MOFs)	They are multiphase NPs in which NPs combine with other NPs or combine with larger or with bulk-type materials. The composites are constructed by the combination of carbon-based, metal-based, or organic-based NMs with any type of metal, ceramic, or polymer bulk materials

## 1.6 Characteristic Features of Nanomaterials

Nanomaterials possess unique physical and chemical features including shape, size, aspect ratio, surface area, size distribution, crystallinity, agglomeration state, and surface morphology/topography. Discussed below are some of the exceptional properties of nanomaterials.

### 1.6.1 Optical Properties

Nanomaterials are characterized by unique optical properties which can be easily identified via different spectroscopic techniques. Electron transition between the two states of emission and adsorption results in determining the optical properties of the prepared nanomaterial (Mohan Bhagyaraj and Oluwafemi 2018). Different metal nanoparticles exhibit a great difference in their optical features based on their particle size. For instance, the color of the dispersed nanoparticles can be totally variable based on the prepared size and shape; for example, silver nanoparticles (AgNPs) might exhibit a blue and a yellow color at sizes 40 and 100 nm, respectively. Moreover, if the prepared AgNPs possess a prism shape, the visible color becomes red. Raza et al. (2016) performed a study in 2016, in which he and his coauthors managed to synthesize AgNPs with different sizes and shapes by solution-based chemical reduction methodology. Silver nitrate (AgNO<sub>3</sub>) was used as a precursor for silver ions, sodium borohydride and tri-sodium citrate (TSC) were used as reductants, while polyvinyl pyrrolidone (PVP) was employed as a stabilizing agent. Different colors were obtained including faint yellow, dark yellow, faint brown, dark brown, and a greenish color as well. Additionally, it has been noticed

that as the size of gold nanoparticles (AuNPs) increases, the color of the colloidal suspension of gold turns from red to yellow. For instance, AuNPs exhibit a yellow, red, and purple colors at sizes 2–5, 10–20, and > 20 nm, respectively (Mohan Bhagyaraj and Oluwafemi 2018).

The manifestation of nanoparticles' color is mainly dependent upon the surface plasmon resonance (SPR) effect. SPR effect is a resonance which takes place because of the interaction between the outer electron bands of the prepared nanoparticles along with the light wavelength. Light photons cause excitation to the particles' outer electrons, and consequently the outer electrons on the metal particles vibrate at a certain wavelength and absorb light which corresponds to that resonance. The scattering mathematic theory of both Mies and Rayleigh scattering clarified the link between particle size and color (González et al. 2014).

### ***1.6.2 Magnetic Properties***

The interaction between the magnetic spins of the constituent material with the electron charges results in the confinement of the unique magnetic properties of a nanomaterial (Mohan Bhagyaraj and Oluwafemi 2018). The fabricated nanomaterials exhibit different magnetic features owing to the large surface-area-to-volume ratio which characterize the majority of nanostructures. Moreover, the constituent atoms undergo different magnetic interactions with the neighboring atoms, resulting in various magnetic features. Super-paramagnetism may result because of the fluctuation in the energy of magnetic anisotropy. Super-paramagnetic materials are free of coercivity and remanence. They can be very useful in a wide range of disciplines, for instance, bioprocessing, magnetic resonance imaging, and bioprocessing in addition to refrigeration. Interestingly, both bulk platinum and gold display no magnetic properties, while at the nano-sized scale, they possess magnetic features.

### ***1.6.3 Electronic Properties***

The increase in the wave-like quantum mechanical properties and the lack of scattering centers majorly affect the electronic properties of nanoscaled materials. The discrete nature of the energy states becomes apparent when the size of the system becomes comparable with the de Broglie wavelength of the electrons. But a fully discrete energy spectrum is only observed in three-dimensional structures. In some cases, below a critical length scale, the conducting materials become insulators as the energy bands cease to overlap. The intrinsic wave-like nature of the nanostructures makes the electrons tunnel quantum mechanically between two closely adjacent nanostructures. Applying a voltage between the aligned discrete energy levels



of two nanostructures, causes the occurrence of resonant tunneling, which results in an abrupt increase in tunneling current. Highly confined structures like quantum dots are very sensitive to the presence of other charge carriers and the charge of the dot. These Coulomb blockade effects result in conduction processes involving single electrons, and as a result, they require only a small amount of energy to operate a switch, transistor, or memory element. All these phenomena can be utilized to produce radically different types of components for electronic, optoelectronic, and information- processing applications, such as resonant tunneling transistors and single-electron transistors.

### ***1.6.4 Mechanical Properties***

The mechanical features of nanoparticles such as hardness and elasticity contribute to the proper employment of the prepared nanoparticles and aid in evaluating their roles and mechanism of action. Hardness can be measured by applying a technique which is called nano-indentation technique. Additionally, it can be applied to determine the elastic properties of particles. However, different factors might affect the measurement of the mechanical properties of nanomaterials such as the uniform dispersion of nanoparticles on a hard substrate, the appropriate use of loads onto the particle, the accurate position of the particle, the measurement of particle deformation, etc. (Wagner et al. 2011). Also, instrumental errors with the instrument calibration and the calculation models might be also taken into account while measuring the mechanical features of the prepared nanomaterials.

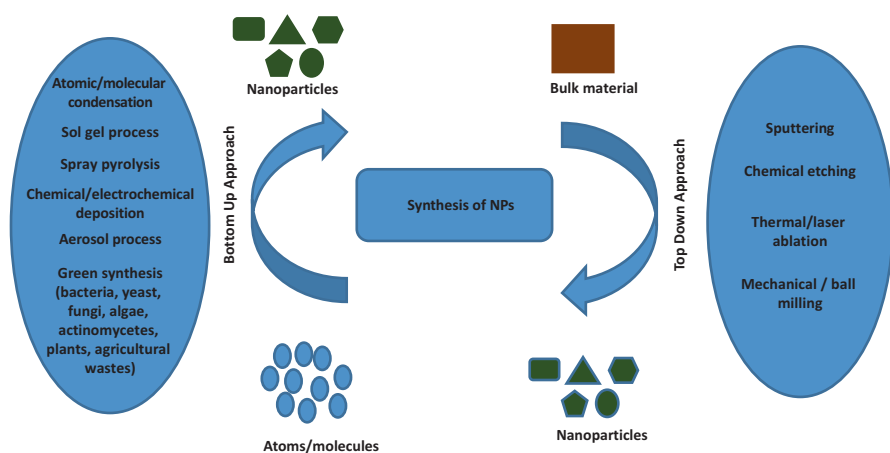
### ***1.6.5 Catalytic Properties***

Nano-catalysts possess unique catalytic properties such as high selectivity and reactivity when compared with their counterparts. Interestingly, several experimental studies on nano-catalysts showed the relationship between particle size and the catalytic activity of the prepared nano-catalyst. Furthermore, other factors play an important role in determining the catalytic reactivity and selectivity of nanostructures such as geometry, oxidation state, composition, and the surrounding chemical/physical environment. For instance, nanoparticles synthesized from different transition element oxides possess awesome catalytic properties because of the large surface area. Mori and Shitara (1994) suggested that there is a relation between materials' catalytic activity and the roughness of its surface. Moreover, in a study conducted by Häkkinen et al. (2003), another factor affects the catalytic activity of nanomaterials which was the ability of small clusters to jiggle between favorable isomers with different energies within a chemical reaction.

## 1.7 Synthesis Approaches of Nanomaterials

In order to expand the application of nanomaterials in different disciplines, it is vital that such materials become available with the preferred shape, size, morphology, crystallinity, and chemical composition. To date, numerous techniques are available for synthesizing nanomaterials. However, they can be fabricated via two main approaches referred to as “top-down” and “bottom-up” approaches (Fig. 1.1) (Birnbbaum and Pique 2011). The first approach is the top to down in which bigger particles are broken down into smaller and smaller dimensions with different shapes (Balasooriya et al. 2017). This approach involves different techniques such as mechanical milling, lithography, laser ablation, electrochemical explosion, attrition, chemical etching, etc. However, the top-down approach has certain disadvantages like the formation of imperfect surface structure. Sometimes the prepared nanomaterials exhibit somehow broad size distribution. Furthermore, in the prepared nanomaterials, certain impurities might exist.

The second approach is the bottom-up approach in which nanoparticles are built up via the smaller building blocks (i.e., atoms, monomers, molecules, etc.). In the bottom-up approach, the individual building blocks of atoms and molecules fit together and become self-assembled accurately and placed where they are desired. Different techniques such as pyrolysis, spinning, plasma or fire sparing, sol-gel process, biological method, chemical vapor deposition, atomic condensation, etc. follow the bottom-up approach. Bottom-up approach possesses more advantages than the top-down approach including decrease in the dimension of the prepared nanoparticles, large surface area, large surface energy, spatial confinement, and reduced imperfections.



**Fig. 1.1** Nanoparticle synthesis approaches

## 1.8 Synthesis Routes of Nanomaterials

### 1.8.1 *Physical Routes for Synthesis of Nanomaterials*

#### 1.8.1.1 Physical Vapor Deposition (PVD)

Physical vapor deposition (PVD) is a vaporization coating procedure which involves the transfer of material to atomic levels (Tulinski and Jurczyk 2017). PVD is somehow like the chemical vapor deposition (CVD) method. They differ only in the state of the precursor starting material, as it has to be in a solid form in the case of PVD and in a gaseous form in the case of CVD. PVD processes involve the techniques of both pulsed laser deposition (PLD) and sputtering. PVD is performed under vacuum conditions and involves the four following stages which are evaporation, transportation, reaction, and deposition. During the first stage, i.e., evaporation, the starting material is targeted by a high-energy source, for instance, a beam of ions or electrons. This results in vaporizing the materials' surface atoms. The following stage involves the transportation of vaporized atoms from the targeted material to the substrate in order to be coated. This coating is comprised of metal oxides, carbides, nitrides, etc. Additionally, during the transportation stage, the vaporized atoms react with the suitable type of gas. Such gases may be nitrogen, oxygen, or methane. PVD coatings are essential as they provide better hardness, wear resistance, and minimized friction and are enriched with oxidation resistance. Hence, nanomaterials prepared by PVD are substantially applied in optical, magnetic, optoelectronic, and microelectronic devices. Other applications may include disciplines of tribology, corrosion resistance, decorative coatings, and thermal protection.

Thermal evaporation is one of the most applied techniques of PVD. In this technique, the substance is first heated in order to be evaporated by the effect of energy either in the form of laser, electrical current, arc discharger, electron beam, etc. till reaching the required temperature. It is worthy to note that in order to obtain definite film properties, the temperature must be higher than 100 °C. The thermally unconfined molecules or atoms attach around the coating substrate (Vossen et al. 1991). The main difference between thermal evaporation and sputtering techniques is that evaporation relies on thermal excitation in order to transfer the coating material to the gas phase, while sputtering technique transfers the coating material into the gas phase via impulse transfer.

#### 1.8.1.2 Pulsed Laser Deposition (PLD)

Pulsed laser deposition (PLD) is considered one of the easiest physical routes for depositing thin films like metals, oxides, semiconductors, nitrides, organic compounds, etc. This technique is derived from PVD processes which imply a high-power with short-pulsed laser radiation on solid substrates (Tulinski and Jurczyk 2017). In this technique, a laser beam passes through the vacuum chamber and

strikes the target material. Atoms are cleaved from the bulk material by vaporizing the bulk material at the non-equilibrium state. PLD has versatile applications, for instance, synthesizing thin films of nanoscaled metal oxides and manufacturing multilayered superconducting materials, nitride films, as well as ceramic oxides (Zhang et al. 2014).

### 1.8.1.3 Ion Beam Implantation or Ion Implantation Technique

Ion implantation is a physical technique in which ions with high energy strike into the surface of a solid sample. An ion source is responsible for generating these ions. Additionally, these ions can be produced via a secondary energy source which aids in ionizing the existing gases, e.g., nitrogen or methane. The device is comprised of six major components involving vacuum system, ion source, accelerator, magnetic analyzer, beam scanning, as well as target chamber (Tulinski and Jurczyk 2017). An important portion is the ultrahigh vacuum (UHV) which usually accompanies the apparatus of ion beam implantation in order to prevent ion scattering as well as ion beam contamination.

For ions to be selectively chosen, a magnetic analyzer is employed to speed up ion selection via a flight tube. At the flight tube, ions are divided based on their mass ratio as well as their ionic charge. Afterwards, the mass-selected ions are speeded up under the effect of high energy in an acceleration tube with an acceleration voltage ranging between 30 and 300 Kv. Then, they become concentrated into a beam and directed to the target surface. The capability of the ion implantation technique to deal with the microstructures at the atomic levels is attributed to its high quenching rate. Ion implantation is characterized by its accuracy, its elasticity, and its ability to manufacture nanocrystalline materials.

### 1.8.1.4 Plasma Synthesis

One of the physical routes which are employed in order to synthesize, activate, and functionalize materials is the low-temperature plasma. It is employed for synthesizing nanomaterials through a thermal reaction in which material is heated till being evaporated within induction plasma (Tulinski and Jurczyk 2017). Then, the resultant vapors are exposed to a very rapid quenching reaction zone. The quenching gases can be either inert gases, for instance, nitrogen (N) or argon (Ar), or reactive gases as ammonia ( $\text{NH}_3$ ) or methane ( $\text{CH}_4$ ) based on the type of nanomaterial being fabricated (Tulinski and Jurczyk 2017). The produced nanopowder is collected via a porous filter located far from the plasma reaction. The manufactured nanoparticles are in the range of 20 to 100 nm based on the employed quenching atmosphere. It is worth noting that the production rate may reach few hundred grams per hour to 3–4 kg per hour, but this differs from one material to another depending upon its

physical properties. Different methods such as alloying of surface plasma help to upgrade the surface properties of the targeted materials (Miklaszewski et al. 2011).

#### **1.8.1.5 Laser Evaporation Method**

Laser evaporation is considered a very promising bottom-up technique which facilitates the synthesis of magnetic nanopowders. The employed laser is responsible for evaporating the precursor metal oxides which are the main sources for the required metals. The produced nanoparticles are generated by the effect of rapid condensation and nucleation because of the applied temperature gradient (Kurland et al. 2007, 2009). The particle size as well as its magnetic phase can be easily controlled by adjusting the laser power as well as atmosphere composition (Stötzel et al. 2013).

### ***1.8.2 Chemical Methodologies for Synthesis of Nanomaterials***

Nanomaterials synthesized via chemical-based methodologies depend on the interaction between different ion solutions in specific quantities under controlled circumstances such as pressure, temperature, pH, and stirring rate. Chemical-based methodologies offer a high confinement over the particle structure, shape, and size. They include chemical vapor deposition, epitaxial growth, colloidal dispersion, sol-gel, hydrothermal route, microemulsions, polymer route, precipitation processes, etc. (Tulinski and Jurczyk 2017).

#### **1.8.2.1 Chemical Vapor Deposition (CVD)**

Chemical vapor deposition (CVD) is a chemical procedure which can be applied to synthesis of solid thin film coatings, production of highly pure powders and bulk materials, as well as fabrication of composite materials (Dobkin and Zuraw 2003). CVD depends on flowing gases within a chamber containing the heated objects which need to be coated. Chemical reactions take place close to the hot surface leading to the manufacture of thin films on the surface. Usually, chemical byproducts are released out of the chamber along with the remaining unreacted gases. There are many kinds of CVD. They may be designed in either hot wall or cold wall reactors. Also, some upgraded CVD processes have been introduced by the involvement of photons, lasers, plasma, ions, and hot filaments.

CVD possess several advantages in depositing thin films: (i) CVD films are accurate, and (ii) the deposited materials are highly pure and are deposited fairly rapid. On the contrary, the disadvantage of CVD involves the hazardous materials that are employed during deposition as some precursors may be hazardous, corrosive, and flammable.

### 1.8.2.2 Epitaxial Growth

Epitaxy refers to the organized growth of single film material above a certain substrate (Foord et al. 1997). Epitaxy is a linking procedure that combines the scientific art of crystal growth and manufacturing of devices and circuits with applications in microelectronics, optoelectronics, and photonics. Versatile techniques of epitaxy exist including liquid phase epitaxy (LPE), hydride vapor phase epitaxy (HVPE), ultrahigh vacuum chemical vapor deposition (UHV-CVD), chemical beam epitaxy, metal organic vapor phase epitaxy (MOVPE), and molecular beam epitaxy (MBE) (Tulinski and Jurczyk 2017). Homoepitaxy describes the process when the material grown has the same composition of the substrate, while heteroepitaxy describes the process when the material's structure differs from that of the substrate.

### 1.8.2.3 Sol-Gel Technique

In this technique, first, the concentrated suspension of a metallic oxide or hydroxide is formed (sol). The sol is then dehydrated by evaporation or solvent extraction, resulting in the formation of colloidal suspension (gel) (Liu et al. 2018). Controlled heating in autoclave or in vacuum converts the gel to finely divided powder, with particle size in the range of 0.03–0.1  $\mu\text{m}$ . This method can produce extremely homogeneous mixtures of two or more components because the mixing of ingredients takes place at the atomic level in a liquid rather than in the solid state. A wide range of pure and mixed oxides can be produced with controlled size and composition, high surface area and high purity due to the absence of grinding and pressing steps. However, the sol-gel method possesses some disadvantages also such as relatively high cost of precursors, long processing time, large shrinkage during processing, and the possibility of the formation of hard agglomerates (Ullattil et al. 2017).

### 1.8.2.4 Coprecipitation Technique

The most commonly used method for the synthesis of multicomponent oxide is coprecipitation method, which produces a “mixed” precipitate comprising two or more insoluble species that are simultaneously removed from the solution. The precursors used in this method are mostly inorganic salts (nitrate, chloride, sulfate, etc.) that are dissolved in water or any other suitable medium to form a homogeneous solution with clusters of ions (Shinde et al. 2017). The crystal growth and their aggregation are influenced by the concentration of salt, temperature, the actual pH, and the rate of pH change that force the dissolved inorganic salts to precipitate as hydroxides, hydrous oxides, or oxalates. Generally, a calcination step is necessary to transform the hydroxide into crystalline oxides. In most of the binary, ternary, and quaternary systems, a crystallization step is necessary, which is generally achieved by thermal treatment or, more elegantly, by a hydrothermal procedure in high-pressure autoclaves. A large number of reports are available on the synthesis of ultrafine oxide powders (Bumb et al. 2008), oxide-oxide composites, and biomaterial by

coprecipitation reactions (Liang et al. 2011; Kalam et al. 2018). The advantages of coprecipitation reactions are (i) the homogeneity of component distribution, (ii) the relatively low reaction temperature, (iii) the fine and uniform particle size with weakly agglomerated particles, and (iv) the low cost. However, these reactions are highly susceptible to the reaction conditions, and because of incomplete precipitation of the metal ions, control over the stoichiometry of the precursors is rather difficult to achieve. In addition, the coprecipitation reactions are not suited for certain oxides/hydroxides, for instance, in the case of amphoteric systems.

### 1.8.2.5 Flame Spray Pyrolysis Technique (FSP)

FSP is a process of a gas phase combustion synthesis method which enables the production of a broad range of materials in the form of nanostructured powders with high specific surface area and primary particle size in the range of nanometers. There are two main routes for injection of the precursor in this method including; (1) in homogenous phase, through an evaporation system at controlled temperature, or (2) through a spray system, in liquid phase. This last methodology offers a greater flexibility in terms of type of precursors to be used and flow control to determine the amount of produced material (Solero 2017). The advantage of FSP is the use of a wide variety of possible low-cost precursors (mainly in the field of metal oxides such as  $\text{TiO}_2$ ,  $\text{Al}_2\text{O}_3$ ), obtaining a final product with high purity and relatively narrow size distribution (Tok et al. 2006). FSP seems to be a versatile process allowing a strict control of the produced nanomaterial; particularly product size and morphology which strictly depend on precursor concentration and dispersion gas flow rate (Height et al. 2006).

### 1.8.2.6 $\text{CO}_2$ Laser Pyrolysis Technique

Laser pyrolysis method is a technique used to synthesize ultrafine powders by heating a mixture of reactant vapor and inert gas with a laser. Laser pyrolysis is a very suitable gas phase process for the synthesis of a wide range of nanoparticles at laboratory scale. The principle of the method is based on the decomposition of gaseous or liquid reactants by a high-power  $\text{CO}_2$  laser, followed by a quenching effect. The literature reports the possibility to produce carbides, nitrides, oxides, metals, and composite nanoparticles by this process (Borsella et al. 2011).

## 1.8.3 *Mechanical Methodologies for Synthesis of Nanomaterials*

Various mechanical methodologies are usually employed to obtain small-sized nanostructures. The main working principle of such mechanical methods is dependent upon the generation of very fine-grained powders (at the nanometer scale) and

then consolidated through hot isostatic pressing (HIP) (Groza 1999). Mechanical processes include mechanical grinding (Prasad Yadav et al. 2012), high-energy ball milling (Arulmani et al. 2018; Rane et al. 2018), mechanical alloying (MA) (Wang et al. 2019), and reactive milling (Kirti et al. 2018). The mechanical techniques possess several advantages as they are cost-effective, simple procedures and a large feedstock powder of the desired material can be generated. However, certain disadvantages may arise as aggregation of the prepared nanopowders, and contamination may take place from the process equipment (Tulinski and Jurczyk 2017). It is worth mentioning that these mechanical synthesis methods are employed to synthesize inorganic compounds as well as metals or alloys.

### 1.8.3.1 Milling Processes

Milling processes have the ability to manufacture nanomaterials, bio-nanomaterials, and/or bio-nanocomposites (Niespodziana et al. 2010; Tulinski and Jurczyk 2012; Balcerzak et al. 2015). Different types of ball mills have been developed involving tumbler, attrition, shaker, vibratory, and planetary mills. Dense materials such as tungsten carbide or steel are much preferred since the kinetic energy of the balls is a function of both their velocity and mass (Tulinski and Jurczyk 2017). Moreover, by applying vibration with small amplitude and high frequency, high-energy milling forces can be attained.

High-energy ball milling (HEBM) is a top-down approach. HEBM is an effective, simple type of a ball milling process in which the powder mixture is placed in a ball mill, and then it becomes exposed to collisions with high energy from the balls. High-energy ball milling is sometimes referred to as [mechanical alloying](#) (Rane et al. 2018). In 1970, Benjamin proposed a pioneering development on the ball milling technique (Benjamin 1970). Then, it was successfully applied to manufacture oxide dispersion strengthened (ODS) iron- and nickel-based alloys which were heavily employed in aerospace industry (Bhadeshia 1997). In 1983, Koch managed for the first time to prepare successfully by applying the mechanical alloying technique (Koch et al. 1983). Till now, mechanical alloying has been used to synthesize ODS materials like highly thermal-resistant materials, magnetic materials, hydrogen storage materials, amorphous materials, superconducting materials, and nanocrystalline materials (Bidabadi et al. 2013). During the process of HBEM, coarse grained structures are subjected to disassociation due to the intensive cyclic deformation which is done by the milling of the stiff balls within a high-energy mill shaker (Koch et al. 1983). HBEM can produce nanoparticles within the range of 4–26 nm. Three main types of HBEM exist including the shaker mill, the planetary mill, and the attritor mill (Wang et al. 2019). Another advantage of this process is that it is characterized by its simplicity and can manufacture massive amounts of the desired materials reaching to tons (Rane et al. 2018). Yet, contamination from the surrounding environment may occur (e.g., balls and vials) and from the surrounding atmosphere. Consequently, a number of actions have been performed such as usage of [surfactants](#), alloy-coated milling media, and protective atmospheres to lessen the contamination problem.



Cryomilling is also referred to as low-temperature mechanical alloying. It is somehow similar to HEBM, but it differs from HEBM in that the metallic powders become severely milled in conditions containing a cryogen (e.g., liquid argon or liquid nitrogen) or under low temperature (Wang et al. 2019). During the 1980s, cryomilling was extensively applied to manufacture ODS materials, intermetallic compounds, nanocrystalline materials, etc. (Kumar and Biswas 2019). Cryomilling mainly depends upon solid-state reactions as well as atomic diffusion to produce alloys. But it has been noted that extreme cold welding of particles may lead to particles' aggregation. Hence, a balance between cold welding and fracturing should be taken into account during cryomilling.

### 1.8.3.2 Severe Plastic Deformation (SPD)

Severe plastic deformation (SPD) is a metal forming process in which ultrafine metals are generated by the introduction of an ultra-large plastic strain to a bulk metal (Rosochowski 2005). The basic purpose of a SPD process is the manufacturing of highly strengthened parts. The traditional metal forming processes like forging, rolling, and extrusion form structures which have low thickness with a very thin diameter thus becoming not preferable during structure manufacturing. Hence, various processes have been explored like equal-channel angular pressing (ECAP) (Lapovok 2005), accumulative roll bonding (ARB) (Toth and Gu 2014), high-pressure torsion (HPT), repetitive corrugation and straightening (RCS) (Sunil and Sunil 2015; Langdon 2016), and cyclic extrusion compression (CEC) (Pardis et al. 2011).

### 1.8.3.3 Lithography

Lithography is the most applicable mechanical route for synthesizing a number of ordered nanoparticles in an array (Gentili et al. 2005). In 1796, the Bavarian researcher Alois Senefelder invented the process of lithography where the desired materials were patterned onto a base substrate using masks (Nayfeh 2018). Lithography is the process in which one- and two-dimensional structures are fabricated and at least one of the lateral dimensions is in the nanoscale. Lithography is subcategorized into electron beam lithography, photolithography, X-ray and extreme UV lithography, soft lithography, colloidal lithography, nanoimprint lithography, focused ion beam and neutral atomic beam lithography, scanning probe lithography, and atomic force microscope nanolithography (Kumar et al. 2018). As mentioned, different lithographic processes are widely employed in the industry, among which is the **optical lithography**. Optical lithography is a top-down approach which is an effective technique in fabricating materials for **microelectronic** and **nanoelectronic** devices. Additionally, it is further applied to synthesize integrated circuits (Nalamalpu et al. 2015).

### 1.8.3.4 Etching

Etching is used in either nanofabrication or microfabrication in which chemical layers are removed from the wafer's surface during manufacturing (Kolasinski 2005). In each etching step, parts of the tested wafer are protected from the etchant by the help of a "masking" material which governs resistance against etching. These masking materials may be photoresist materials which are formulated using photolithography. In some cases, these masking materials may be composed of silicon nitride which is characterized by its long-term validity.

## 1.9 Techniques Employed for Nanomaterials' Characterization

For further exploration of the unique and extraordinary features of nanomaterials, accurate and detailed characterization of the material has to be performed. This can be done by the help of different characterization techniques which provide optical, morphological, electrical, and magnetic information about the prepared nanomaterial. A great progress concerning the technologies and the characterization instruments has been devoted. Such techniques possess the advantage of characterizing materials without causing any significant modification or any damage to the nanomaterials under study (Omran et al. 2019a, b).

### 1.9.1 *Spectroscopic Characterization Techniques*

The interaction between the matter and the electromagnetic radiation is referred to as spectroscopy (Bumrah and Sharma 2016). The main principles of the spectroscopic techniques are dependent upon absorption, emission, fluorescence, or scattering (Skoog et al. 2017). Different spectroscopic techniques are employed to determine the optical properties of nanostructures. Some of the main optical characterization techniques include UV/visible spectroscopy (UV/Vis), photoluminescence spectroscopy (PL), surface-enhanced Raman spectroscopy (SERS), Brillouin spectroscopy, etc.

#### 1.9.1.1 Ultraviolet-Visible Spectroscopy (UV/Vis)

UV/Vis spectroscopy is a kind of a spectroscopic technique in which light in the UV range (200–400 nm) is absorbed by the molecule. Electrons become excited from the ground state to a higher energy state (Chirayil et al. 2017). The energy difference between both that of the ground state and that of the higher energy state becomes equal to the amount of energy being absorbed. The apparatus of the UV/Vis spec-

trophotometer includes the following parts: reference and sample beams and deuterium or tungsten lamp for the wavelengths of the ultraviolet and the visible regions, respectively, monochromator and a detector. The UV spectrum is the spectrum which appears when a sample is exposed to UV light (Chirayil et al. 2017). Samples are placed inside glass, quartz, silica, or plastic cuvettes within the apparatus in front of the light path to be ready for measurement. It is worth noting that both the plastic and the glass cuvettes absorb wavelengths at 310 nm, so they should not be used for studying absorbance lower than that wavelength. Hence, quartz cuvettes are much preferred as they can be used for measuring absorption in the ultraviolet range (above 180 nm). Two types of beams exist; one is the reference beam, and the other one is the sample beam. The reference beam is emitted from the light source to the detector with no interactions with the sample. On the contrary, the sample beam interacts with the sample. Usually, the ratio between the intensities of the reference and the sample beams is determined by the help of the detector (Marvin et al. 2003). When a difference is found in the intensities, that means the reference beam's intensity is higher than that of the sample. Another important term is transmittance which takes place when the light beam passes through a solution, part of the light becomes absorbed, and the rest becomes transmitted via the solution. Therefore, the ratio between the light entering the sample to the light which exits the sample at a certain wavelength is referred to as "transmittance." Absorbance is referred to as the negative logarithm of transmittance.

UV/Vis spectroscopy follows the Beer-Lambert law. The Beer-Lambert law states that when a beam of a monochromatic light passes through a solution of an absorbing material, the rate of reduction in the intensity of the radiation in addition to the thickness of the absorbing solution is directly proportional to the incident radiation and to the concentration of the solution (Chirayil et al. 2017; Titus et al. 2019). The expression of the Beer-Lambert law is

$$A = \log\left(\frac{I_0}{I}\right) = ECL$$

where A is the absorbance,  $I_0$  is the light intensity that leaves the sample cell, I is the light intensity that is incident upon the sample cell, E is the molar absorptivity, C is the molar concentration of the solute, and L is the length of the sample cell (cm). From the Beer-Lambert law, it can be concluded that as the number of molecules which are capable of absorbing light becomes greater at a certain wavelength, the greater will be the magnitude of light absorption, and this is the basic working principle of UV/Vis spectrophotometer. UV/Vis spectrophotometer is majorly employed in the discipline of analytical chemistry to provide quantitative determination of analytes like transition metal ions, biological macromolecules, and highly conjugated organic compounds. Additionally, it helps to determine the size and concentration of the prepared nanoparticles. It also gives an indication concerning nanoparticles' aggregation/agglomeration. Moreover, it is a quite simple and effective technique to predict the stability of the prepared nanoparticles. Simply, as particles become destabilized, the original absorption peak decreases in intensity

(because of the reduction of stable nanoparticles), and frequently the peak becomes broadened, and sometimes a secondary peak will occur at longer wavelengths (due to the formation of aggregates) (Chirayil et al. 2017).

### 1.9.1.2 Raman Spectroscopy (RS)

In 1928, C.V. Raman along with K.S. Krishnan published together the first article applying the Raman technique (Raman and Krishnan 1928). Raman spectroscopy was named after its inventor C.V. Raman. Raman spectroscopy (RS) is a multipurpose technique in which a variety of samples can be analyzed. It provides qualitative and quantitative analyses. By evaluating the frequency of the scattered radiation, qualitative analysis can be carried out, while quantitative analysis is performed via the measurement of the intensity of the scattered radiation (Bumrah and Sharma 2016).

In RS, a beam of monochromatic light illuminates the molecules of a tested sample and originates a scattered light. The scattered light has a frequency which is different from that of the incident or the inelastic light collision and is used to display the Raman spectrum. When a monochromatic radiation hits the sample molecules, it scatters in every direction. Much of this scattered radiation has a frequency which is equal to the frequency of incident radiation and makes up the Rayleigh scattering. However, only a small fraction of the scattered radiation possesses a frequency that is different from that of the incident radiation and constitutes the Raman scattering. Raman Stokes in Raman spectrum appear when the frequency of the incident radiation is higher than that of the scattered radiation. Contrary, the Raman anti-stokes lines appear when the frequency of the incident radiation is lower than that of the scattered radiation (Dent and Smith 2005). Raman Stokes bands are more intensive than Raman anti-Stokes and thus are easily to be measured in conventional Raman spectroscopy, while anti-Stokes bands are measured with fluorescing samples.

Raman spectra are recorded over a range of  $4000\text{--}10\text{ cm}^{-1}$ . Nonetheless, Raman active modes for organic molecules vibrations occur in the range of  $4000\text{--}400\text{ cm}^{-1}$ . Raman spectrophotometers can be either dispersive or nondispersive. A prism or grating are usually used in dispersive Raman spectrophotometer, while nondispersive Raman spectrophotometer depends on an interferometer like Michelson interferometer (Bumrah and Sharma 2016). Raman spectroscopy is a spectroscopic technique which helps in studying the vibrational and rotational modes of a specimen by the help of Raman scattering or by the scattering of monochromatic laser light (Bumrah and Sharma 2016; Pilot et al. 2019). Typically, the sample is hit by a laser beam. A lens is responsible for collecting the electromagnetic radiation from the laser hit and then passes through a collimator. Stokes of Raman scattering are initiated because of the molecular excitation from the ground state to a vibrational excited state. Changes in polarizability affect Raman scattering, whereas the Raman shift is dependent upon the involved vibrational level. Advanced versions of Raman spectroscopy involve stimulated Raman spectroscopy, surface-enhanced Raman spectroscopy (SERS), and resonance Raman spectroscopy (Titus et al. 2019).

### 1.9.1.3 Photoelectron Spectroscopy (PES)

Photoelectron spectroscopy (PES) is a technique in which electron energy from solids, liquids, and gases is evaluated by the photoelectric effect (Ghosh 1983). The photoelectric effect is the main principle of physics behind the PES technique. PES is categorized into two main types based upon the source of exciting radiation, namely, ultraviolet PES (UPS) and X-ray PES (XPS). In UPS, the photon energy ranges from 10 to 50 eV which is greater than the traditional energy range (i.e., 2–5). Consequently, electrons are released from the sample surface under the photoelectric effect. UPS is a helpful technique which aids in studying chemical bonding, valence energy levels, and particularly, the bonding of molecular orbitals. Furthermore, UPS facilitates the observation of fine structures with high resolution due to the vibrational motion of molecular ions. On the other hand, XPS is a quantitative spectroscopic technique which determines the elemental composition of a sample at parts per thousand (Matsushima and Yamauchi 2019). Irradiation of a material results in obtaining the X-ray photoelectron spectra. XPS is also referred to as electron spectroscopy. XPS gives information about the local bonding of atoms.

### 1.9.1.4 Infrared Spectroscopy (IR)

Infrared spectroscopy (IR) spectroscopy is a technique which provides data by the interaction of infrared radiation with the tested sample. The resultant scanned spectrum ranges from 4000 to 400  $\text{cm}^{-1}$ . Changes in the electric dipole moment of a specific molecular functional group are the keys behind generation of an IR spectrum (Dominguez et al. 2014; Chaber et al. 2017). Infrared active molecules are the molecules whose dipole moments are altered during vibration. IR spectroscopy basically aids in identifying the type of chemical bonds in a sample which are revealed by absorbing the characteristic wavelength of infrared radiation due to the presence of particular functional groups (Kumar et al. 2019). Any form of samples can be analyzed via IR spectroscopy, whether it is liquid, solid, powder, or film.

IR spectroscopy provides qualitative in addition to quantitative data. By employing IR spectroscopy, getting deeper insight of materials' structural analysis and interactions at molecular level has touched the ground. In short, IR spectroscopy is a very promising analyzing technique in getting more information regarding the chemical structure of small molecules, nanomaterials, natural products, and other biomolecules. Also, it provides easiness in identifying the functional groups in a tested sample. Additionally, determination and characterization of supramolecular interactions is attainable (Sondhi et al. 2009; Ellis and Goodacre 2006). Hence, IR spectroscopy offers several applications in different disciplines like organic chemistry, drug discovery, and drug design and provides precious information regarding the morphological transitions within the phase(s) of metal/metal oxide nanoparticles, carbon nanoparticles, and graphene quantum dots (GQDs) and their interactions with biomolecules (Bayda et al. 2017).

Fourier transform infrared spectroscopy (FTIR) is a very common technique employing the working principle of IR. It has been used for more than 50 years. FTIR provides information about the molecular interactions as well as the molecular structure of a specific material via absorbing the infrared light. Absorption takes place because of the excitation from the ground energy level to a higher energy level. FTIR spectroscopy can be used for the characterization of nanomaterials, biomolecules, and organic molecules and has the capability to clarify the structure of proteins. Each band which appears in the FTIR spectrum represents a fingerprint to a certain functional group (Hambardzumyan et al. 2011). FTIR introduces a rapid, accurate, and a non-destroying technique to confine the different ligands which are attached to NPs depending on their vibrational signature (López-Lorente and Mizaikoff 2016). Another apparatus applying the working principles of IR spectroscopy is called attenuated total reflection (ATR)-FTIR spectroscopy. It has the ability to determine the adsorbed molecular species structure. Additional advantages of ATR-FTIR spectroscopy are the minimization of the required steps needed for sample preparation as well as the absence of spectral reproducibility which are present in traditional IR mode (Beasley et al. 2014).

### 1.9.1.5 Mass Spectrometry (MS)

Mass spectrometry (MS) provides data regarding the elemental/ molecular composition and structure. It is very helpful in providing data concerning the physiochemical features of nanomaterials like mass, composition, and structure. Moreover, it is a very important characterization technique especially in toxicological, environmental, and nanotechnological studies. The main principle of MS upon which it can differentiate between charged particles is their mass-to-charge ratio. The combination of MS and inductively coupled plasma (ICP) aids in atomizing and ionizing the elements with high accuracy as well a provision of elemental chemical quantification analysis. Yet, the equipment is somehow costly and lacks databases while identifying certain species (Lavigne et al. 2013).

### 1.9.2 Morphological Characterization Techniques

Different microscopic techniques are employed to observe the morphological structure of nanomaterials including scanning electron microscope (SEM), field emission scanning electron microscopy (FESEM), scanning tunneling microscope (STM), high-resolution transmission electron microscope (HRTEM), atomic force microscope (AFM), etc.

### 1.9.2.1 Scanning Electron Microscope (SEM)

In scanning electron microscope (SEM), an electron beam is usually directed towards the specimen rather than a light beam, as in the case of optical microscopes (Joshi et al. 2008). SEM differs from the conventional light microscopes as the images are magnified by light in the case of the light microscope. An electron gun is responsible for emitting the electron beam, and it is located at the top of the microscope. Generally, there are two main kinds of electron guns: (i) field emission guns, which release a strong electric field that splits electrons from the atom, and (ii) thermionic guns in which the filament is heated till the electrons get away. The tested samples are subjected to scanning by high-energy electron beams (Titus et al. 2019). When the emitted beam of electrons hits the specimen surface, three kinds of electrons are released, and they are the backscattered (or primary) electrons, secondary electrons, and Auger electrons. Both of the secondary and the backscattered electrons are very important for SEM. High-resolution images generated by SEM demonstrate details of approximately 1–5 nm via the secondary electrons. Additionally, the energy dispersive X-ray part is usually equipped with SEM in order to identify the elemental composition of the tested sample. The backscattered electrons are also used to form the image in this technique.

The electron beam is passed through a scanning coil and then to a final lens. This results in beam deflection in horizontal and vertical directions so that the performance becomes more efficient and faster. Then, signals become detected and enlarged by the aid of electronic devices, which display the signals into images on a cathode ray tube. The resultant displayed image is considered a distribution map of the signal intensity which is emitted from the specimen scanned area. It is important to note that proper sample preparation is very essential as this analysis will not work properly if the samples are not well prepared. Nonmetal samples need prepping with a sputter coater (Nixon 1971). Specimens are usually conducted with gold as a thin conducting layer. Coating the specimen with gold takes place via argon gas and an electric field. Electrons are removed from the argon by exerting an electrical field, thus releasing positively charged ions. These positively charged ions become attracted to the negatively charged gold. The argon ions separate gold atoms, which in turn fall onto the specimen which then becomes covered with a thin conductive coating. Water removal is important in traditional SEM, because of the vacuum vaporization of water molecules which causes reduction in the clarity of the resultant image. Interestingly, new versions of SEM do no longer need a full vacuum (Titus et al. 2019).

### 1.9.2.2 Transmission Electron Microscopy (TEM)

A transmission electron microscope (TEM) gives details concerning the morphological structure, crystallinity, size, shape, and the compositional data of the tested sample by the help of an electron beam. TEM can reveal the finest details of the specimen under study, and in some cases it can reveal internal structures like indi-



vidual atoms. TEM differs from the light microscope in that it uses electrons rather than light. Additionally, the glass lenses in the light microscope are replaced with electromagnetic lenses, and images are displayed on a screen instead of being viewed via an eye piece. TEM uses electrons instead of light. As electrons' wavelength is far smaller than that of the light, the image resolution obtained from TEM images is way better than that of the light microscope (Chirayil et al. 2017). Specimens are introduced onto grids in order to be imaged. However, certain samples are cut into very thin films by an ultramicrotome using a diamond knife under freezing conditions (Cheville and Stasko 2014). The images are displayed in black and white by TEM. Operating the imaging process requires special training, and samples must have the ability to withstand vacuum. High-resolution transmission electron microscope (HRTEM) is a very powerful microscopic technique to study the atomic features of materials (Chirayil et al. 2017). It is very helpful in imaging semiconductors, metals,  $sp^2$ -bonded carbon (e.g., graphene, carbon nanotubes), etc., and particularly it is very useful in the field of nanotechnology.

### 1.9.2.3 Scanning Transmission Electron Microscopy (STEM)

Scanning transmission electron microscope (STEM) combines the main principles of both TEM and SEM. It helps in imaging nanostructures with different modes and gives data concerning the elemental composition of the tested specimen. Samples must be very thin in order to be imaged by STEM by the help of an electron beam. Numerous types of electrons and electromagnetic signals are generated by the interaction between the electron nanoprobe and the specimen. The prementioned signals are then gathered together to produce the required images or to obtain diffraction patterns which can in turn be analyzed to reveal some spectroscopic information. For instance, high-angle annular dark-field (HAADF) or Z-contrast images provide information concerning the structural composition of the sample by collecting high-angle scattered electrons (Chirayil et al. 2017). The presence of subangstrom or subnanometer electron probes helps in providing details concerning shape, size, surface and crystal structures, and any emerging defects.

### 1.9.2.4 Scanning Probe Microscope (SPM)

Scanning probe microscopes (SPM) are extremely beneficial for imaging and characterizing materials at the nanoscale levels as well as imaging atoms. SPM depends on light waves to image the samples. A very fine probe referred to as a "tip" is responsible for sample scanning. The surface is scanned via an atomically sharp probe. It provides a three-dimensional topographic image of the specimen being imaged at the atomic scale. SPM is a very powerful microscope which has a resolution of less than 1 nm. Generally, two types of modes are usually employed by



researchers, and they are the contact mode and non-contact mode. In contact mode, the force is remained constant between the tip and the surface, thus giving the ability for quick imaging of the specimen surface. In tapping non-contact mode, the cantilever oscillates by touching the specimen surface. And it is very beneficial in imaging a soft surface.

There exist numerous types of scanning probe microscopes involving atomic force microscope (AFM) which measures the electrostatic forces between the tested sample and the cantilever tip, magnetic force microscopes which measure the magnetic forces, and scanning tunneling microscopes (STM) which measure the electrical current that flows between the sample and the cantilever tip (Chirayil et al. 2017). Thus, electrical, magnetic properties as well as the sample topography can be easily attained.

### 1.9.2.5 Atomic Force Microscopy (AFM)

The atomic force microscope (AFM) is a powerful microscope that aids in studying materials at the nanoscale levels (Binnig et al. 1987). It displays three-dimensional images with plenty of surface measurements, and at an atomic resolution, it meets the requirements of researchers in different scientific fields. Sample preparation is not hard when it is being imaged by AFM. Moreover, it helps in estimating the surface roughness of polymer nanocomposites and has the ability to define the surface texture of several types of materials. It is worth noting that this microscopic technique does not cause any damage to the tested sample. The sample surface is scanned via a sharp tip. When the sample surface approaches the tip, a small deflection takes place due to the attractive forces between the tip and surface which can be detected by a laser beam. A photosensitive diode is an important part of AFM which helps in tracking the reflected beam's direction which might occur due to the cantilever deflection. AFM produces a morphological image of the scanned surface by maintaining the laser position constant via controlling the tip height (Titus et al. 2019).

Three kinds of scanning modes for AFM exist, and they are the contact mode, noncontact mode, and the tapping mode. In contact mode, the tip scans the sample's surface, and then by pushing the cantilever against the tested sample by a piezoelectric positioning element, the repulsive forces on the tip is generated. Afterwards, evaluation of the cantilever deflection takes place and the images are displayed. In noncontact mode, the tip flutters over the sample surface, and then the attraction forces between the tip and the specimen are estimated, and hence the images are produced. In the tapping mode, a piezoelectric crystal is responsible for generating a high-resolution image. The cantilever oscillates because of the piezo motion. Oscillation is reduced as the cantilever begins to touch the sample surface, and this reduction aids in measuring the different characteristics of the tested specimen.

### 1.9.2.6 Confocal Laser Scanning Microscopy (CLSM)

Confocal laser scanning microscopy (CLSM) is a potent technique to generate sharp images of a sample that might be blurred when examined under a conventional microscope. This technique became very popular between the scientific and industrial communities. Different scientific fields favor the use of CLSM like life, biological, and materials science disciplines, cell biology, microbiology, genetics as well as in semiconductor examination. Furthermore, it is very useful in quantum optics and imaging of nanocrystals (Fellers and Davidson 2007). This technique enables taking a high number of images with different depths, a process referred to as optical sectioning. The light beam becomes focused by the help of an objective lens, and afterwards the object is subjected to scanning by a computerized scanning device. The light points emitted from the tested specimen are then detected by a photomultiplier tube (PMT), and the output from PMT is turned into an image and demonstrated by the computer screen (Fellers and Davidson 2007).

### 1.9.2.7 Scanning Tunneling Microscopy (STM)

Scanning tunneling microscope (STM) produces images with an atomic scale. The main principle of AFM depends upon quantum tunneling (Titus et al. 2019). The sample surface is imaged by a fine probe equipped with a tip with the aid of a piezoelectric crystal, and the resultant tunneling current is measured. When the conducting tip gets into contact with the specimen surface, electrons flow through the vacuum. The piezoelectric crystal creates images by adjusting the sample surface with the tip distance, and hence the current between them maintains constant. Topography of the sample surface is determined by plotting the tip height as a function with its lateral position over the specimen (Titus et al. 2019). STM can be used at different conditions either in vacuum or in air, liquid, or gas and at a wide range of temperatures. It is worth noting that the tip should be entirely clean and sharp in order to work properly. Carbon nanotube tips are used in STM (Pasquini et al. 2005). It is a potential tool that provides facility to characterize materials.

### 1.9.2.8 Scanning Near-Field Optical Microscopy (SNOM)

Scanning near-field optical microscopy (SNOM) is a microscopic technique which provides a description of the topographic structure as well as the optical fluorescence features of the studied material (Chirayil et al. 2017). Images are created by SNOM through sample scanning with a small aperture at a certain distance, which is illuminated from the back side and is responsible for recording optical information and expressing the transmitted fluorescent light into an image. The obtained optical image is a result of scanning each point and each line in the sample. The reflected or transmitted light becomes restricted when sample scanning is done from a small distance. Among the advantages of SNOM is that no sample preparation is required and it is used in imaging different kinds of samples, i.e., transparent, con-

ductive, and non-conductive ones. It can be applied in different types of research such as nanotechnology, nano-optics and nano-photonics.

### ***1.9.3 Other Important Characterization Techniques***

#### **1.9.3.1 Dynamic Light Scattering (DLS) and Zeta Potential**

Dynamic light scattering (DLS) is a powerful technique to tailor the average size particle of nanoparticles. In DLS, light is scattered from laser source and goes through the tested colloidal solution. The intensity of the scattered light is then analyzed as a function of time, and hence the average particle size can be estimated. It is worth noting that nanoparticles' diffusion rate strongly influences the time delay (Meulendijks et al. 2018). Brownian motion is the main working principle behind DLS (Mailer et al. 2015). Small-sized particles move faster than the large-sized ones and hence less light is scattered. An important term is the hydrodynamic diameter which is defined as the diameter of a solid sphere which would be the same as the hydrodynamic friction of the molecule of interest. Additionally, DLS provides information about the state of agglomeration of nanoparticles.

When particles are charged with opposite charges, a thin layer is created which is referred to as "stem layer," and the outer layer becomes diffusive and contains the weekly associated ions. Electric double layers are generated because of both the stem and the outer layers (Sapsford et al. 2011). Zeta potential refers to the shear surface electric potential. It is estimated by effect of charged species velocity towards the electrode under the effect of an external electric field within the sample solution (Clogston and Patri 2011). Usually, nanoparticles possess a negative or positive charge on their surface. For instance, particles with a negative zeta potential value bind to the positively charged surfaces and vice versa. When an electric field is applied under the control of DLS, particles start moving due to the interaction between the charged particle and the electric field. Zeta potential measures the effective electric charge on the tested nanoparticle's surface and provides a calculated charge stability of the colloidal particles. The magnitude of the zeta potential provides information about the particle stability. High stability of the prepared nanoparticles can be detected via the higher magnitude of zeta potential. For more clarification, particles tend to agglomerate in zeta potential range of 0–5 mV; minimally, moderately, and highly stable particles are usually determined at the ranges of 5–20, 20–40, and >40 mV, respectively (Titus et al. 2019).

#### **1.9.3.2 Energy Dispersive X-Ray Analysis (EDX)**

Energy dispersive X-ray analysis (EDX) is an elemental analysis which is equipped along with electron microscopes. It basically depends on the emission of X-rays that demonstrates the type of elements present in the tested specimen. EDX is a power-

ful analytical technique to detect nanoparticles. It provides quantitative and qualitative information. EDX has the advantage of sample overall mapping by the accurate analysis of the near-surface elements and also has the capability to evaluate the elemental percentage in the tested sample. EDX is used in conjunction with SEM or TEM. Usually, an electron beam with an energy of 10–20 keV hits the sample's surface which in turn leads to emission of X-rays from the tested material (Joshi et al. 2008). The composition and quantity of nanoparticles can be evaluated using EDX. For example, nanoparticles like silver, gold, palladium, etc. can be easily identified using EDX. It is worth mentioning that elements with low atomic number are hard to be detected by EDX (Titus et al. 2019).

### 1.9.3.3 X-Ray Diffraction (XRD)

To obtain information regarding the phase identification, quantification, average size particle, lattice distortion, deviation of a specific element from the ideal composition, and nanocrystalline orientation, X-ray diffraction is always employed (Titus et al. 2019). The desired material that is being analyzed is mounted on the goniometer and then bombarded via the emitted X-rays with gradual rotation. The atomic planes interact with the X-ray beam, and then the rest of the beam is absorbed, scattered, refracted, or diffracted by the tested sample. Usually, X-rays are diffracted by each element in a totally different way, relying on the type and the arrangement of the atoms. X-rays are known to be short-wavelength electromagnetic radiation. A high voltage is kept steady between the electrodes; thus attraction between the electrons and the metal target occurs. At the striking point, X-rays are generated and radiated in every path. Afterwards, the generated X-rays are collimated and concentrated towards the tested sample which is finely grounded. X-rays are detected by a detector, and signal processing takes place via a microprocessor or electronically performed. X-ray scan or a spectrograph is obtained by the applied angle variation between the source, sample, and the detector. Scattering takes place when the X-ray impacts the crystal lattice. Diffraction occurs when scattering comes in phase with other plane scatterings. It is worth noting that each crystalline material has its unique atomic structure and hence diffracts the X-rays in a totally distinctive pattern (Titus et al. 2019).

In 1913, Bragg formulated Bragg's equation (Bragg 1913) which measures the diffraction angle. The Bragg equation is

$$2d\sin\theta = n\lambda$$

where  $d$  denotes to the spacing between the planes,  $\theta$  denotes to incidence angle,  $n$  denotes to an integer, and  $\lambda$  denotes to beam wavelength.

#### 1.9.3.4 Thermogravimetric Technique

Thermogravimetric technique enables to track the mass changes of a nanomaterial. This technique enables to provide information like desorption, absorption, adsorption, sublimation, decomposition, oxidation, and reduction in cases of nanomaterials. Different materials can be analyzed using this technique such as paints, films, and so on. The equipment is made up of different parts involving electronic microbalance, sample holder, furnace, temperature programmer, and recorder. The main task of the microbalance is to record any changes of sample mass. Two types of microbalance exist, the deflection type and the null-point type. The sample holder is the place where the sample is located and is referred to as a crucible. It is attached to the weighing arm of the microbalance. Different types of crucible are available including deep, retort cup, loosely covered, and shallow pan types. Furnaces are responsible in providing a specific heat rate. Temperature measurement is achieved via thermocouples, and the temperature programmer controls the temperature rate during analysis.

#### 1.9.3.5 Nuclear Magnetic Resonance (NMR)

Nuclear magnetic resonance (NMR) is a characterization technique which handles atomic nuclei containing both angular momentum and magnetic moments when exposed to an external magnetic field (MacArthur 2016). NMR provides detailed information concerning the chemical environment structure, possible reactions, and expected dynamics of tested atomic nuclei (Kumar et al. 2019). NMR detects each spectral line of the tested nuclei with high sensitivity. The main principle of NMR is to get the most use of the magnetic properties of specific nuclei and translate them into chemical data output. NMR provides data regarding the physiochemical features involving structure, functionality, and purity. Recently, a pulsed field gradient NMR has been developed to estimate the diffusion capability of nanomaterials, and under which the species interaction and the size can be analyzed (Deshayes et al. 2010). Among the main advantages of using NMR is that small amounts of the samples are required, but the main drawbacks are represented in time consumption as well as the low detection sensitivity (Mullen et al. 2010).

### 1.10 Arising Era of Nanobiotechnology

In nanobiotechnology, the term begins with the prefix “nano” and the word “biotechnology” which refers to the employment and self-assembly of biologically oriented molecules towards different technological applications (El-Gendy and Omran 2019). Nanobiotechnology represents the fusion point between the disciplines of biotechnology and nanotechnology (Manju and Sreenivasan 2010). It is a multidis-

ciplinary field of science which deals with the biomimetic synthesis, manipulation, and controlled bio-functionalization of structures at the nanoscale level (Mogoşanu et al. 2016; Omran et al. 2018a). It covers a wide range of scientific disciplines including chemistry, physics, engineering, biology, etc. Nanobiotechnology was initiated by the development of the atomic force microscope (AFM) which facilitated atomic imaging in the 1980s. Hess and Jaeger (2010) demonstrated that nanobiotechnology was fully involved as an important scientific discipline since the year 2000. Christopher Lowe was the pioneer scientist in introducing nanobiotechnology by his publication in the journal *Current Opinion in Structural Biology* in 2000 in which he introduced this emerging discipline to the scientific communities (Lowe 2000). Afterwards, in 2004, two books were edited by Christof Niemeyer and Chad Mirkin. These two books provided a reference to various researchers in the community of nanobiotechnology worldwide (Hess and Jaeger 2010). Briefly, nanobiotechnology continues to be the science of the hour. As a result of the outstanding properties of nanomaterials, the number of engineers and scientists who keep working on and exploring materials at the nanoscale is enormously increasing (Guo 2013). As mentioned earlier, when materials are in the nanoscale level, their fundamental chemical, physical, and mechanical properties differ from their bulk counterparts.

Since many years ago, green-based technologies have been the focus point of the whole world to protect human health as well as the surrounding environment from any hazardous issues that may arise. The beginning of green technology took place in purifying the water system; afterwards other green techniques were introduced involving the provision of catalytic converters for cars, treatment plants recycling, solar panels, and many others (Guo 2013). Green chemistry and engineering arise as an important branch that would help the science of nanotechnology to imitate natural processes to lessen any hazardous effect which may result from the conventional chemical and physical synthesis methodologies. The main target of green chemistry/engineering is to enhance industries to act somehow similar to ecosystems or like living cells, in which benign constituents are employed, biogenic wastes are recycled, and energy can be effectively monitored.

Not surprisingly, cells may act as green nano-factories. Natural components are utilized by cells at room temperature to assemble nanostructures. These reactions are carried out without using any toxic solvents, hence the combination between nanotechnology and green chemistry facilitates the manufacture of environmentally sustainable nanomaterials. Such combination is worthy to be kept on and be developed for many reasons, among which is that this combination helps to synthesize clean nanomaterials from the beginning without causing any environmental problems. Applying a green nano-approach to nanotechnology ultimately helps the environment to boost environmental performance by waste detoxification. Additionally, more green products are manufactured to replace the old wasteful and hazardous ones.

Using biological components to produce nanoscaled materials is the basic simple principle of nanobiotechnology (Omran et al. 2018b; El-Aswar et al. 2019; Omran et al. 2019a). Therefore, green nanotechnology helps to achieve the main tasks of

nanotechnology as they may be applied in electronic, computing, biological and clinical applications. The target of the upcoming chapters is to show by several selected examples how these biological approaches tend to introduce a great contribution to nanoscience.

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