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Nanomaterials (Properties and Uses)

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List of Abbreviations

Abbreviate	Meaning
NMs	Nanomaterials
EN	Engineered Nanomaterials
ZnO	zinc oxide
Au	Gold
Ag	Silver
nCHAP	Hydroxyapatite Nanoceramics
НАР	Hydroxyapatite
NPs	Nanoparticles
CVD	Chemical Vapor Deposition Method
SiO ₂	Silicon dioxide
PVD	physical vapor deposition
E-beam	Electron beam
BT	Barium titanate
Al_2O_3	Aluminum dioxide
Sno ₂	Tin dioxide
SEM	Scanning Electron Microscopy
EDX	energy-dispersive X-ray spectroscopy
FTIR	Fourier transform infrared spectroscopy
DLS	Dynamic light scattering
DFT	density functional theory
TGA	thermal gravimetric analysis
XRD	X-ray diffraction
ТЕМ	Transmission electron microscopy
AE	Auger electrons
BSE	Backscattered electrons
SE	Secondary electrons
HR	high-resolution
DF	Dark-field
BF	Dright- field
<i>CNT</i> _s	Carbone nanotubes
SWCNT ₂	Single – Walled Carbone nanotubes
AFM	Atomic Force Microscopy

<u>Aim of Work</u>

Nanomaterials (nanocrystalline materials) are substances possessing grain sizes on the order of a billionth of a meter. They manifest extraordinarily charming and beneficial properties, which can be exploited for a ramification of structural and nonstructural packages. Seeing that Nanomaterials own unique, beneficial chemical, bodily, and mechanical houses, they may be use for an extensive form of programs, like next era laptop chips, kinetic power (KE) penetrators with more advantageous lethality, better insulation materials, Phosphors for excessive-Defination TV, Low cost Flat-Panel displays, more and more difficult cutting tools, elimination of pollution, excessive strength density, Batteries, excessive power magnets, high sensitive sensors, motors with greater gas efficiency, Aerospace addititives with superior performance characteristics, higher and density weapons platforms, Longer-Lasting Satellites. Longer-Lasting medical implants, Ductile, Machinable ceramics, huge electro chromic show devices. Nanotechnology has the potential to be the key to a brand new world in the field of construction and building materials. Although replication of natural systems is one of the most promising areas of this technology, scientists are still trying to grasp their astonishing complexities. Furthermore, a nanotechnology is a rapidly expanding area of research where novel properties of materials manufactured on nanoscale can be utilized for the benefit of construction infrastructure, Therefore, the main objective of preparing this study is the importance of nanomaterials and their use in many modern industries due to their mechanical, electrical and chemical properties and for the purpose of identifying the most important methods of preparation, detection methods, types and applications of each type.

<u>Abstract</u>

gaining significance in technological Nanomaterials (NMs) are applications due to their tunable chemical, physical, and mechanical properties and enhanced performance when compared with their bulkier counterparts. This study presents a summary of the general types of NMs and provides an overview of the various synthesis methods of nanoparticles (NPs) and their functionalization via covalent or noncovalent interactions using different methods. It highlights the techniques used for the characterization of NPs and discusses their physical and chemical properties. Due to their unique properties, NMs have several applications and have become part of our daily lives. As a result, research is gaining attention since some NPs are not easily degraded by the environment. Thus, this study also highlights research efforts into the fate, behavior, of different classes of (NMs) in the environment.

<u>General Introduction</u>

Nanotechnology is an interdisciplinary study which allows us to develop new materials with new, interesting and useful properties. These new materials are nanomaterials made from nanoparticles. Nanoparticles are ultra-small particles with exceptional properties which can direct medicines straight to the place where the human body needs them, they can make materials stronger and they can convert solar energy more efficiently. Nanoparticles possess different properties and behave differently to the classical, larger building blocks of substances. From a scientific point of view, these interesting new properties are not so much the results from the fact that nanoparticles are small, but they result from the fact that a particle consisting of a relatively limited number of molecules behaves and interacts differently with its surroundings for fundamental physical reasons. Nanoparticles and nanomaterials have gained prominence in technological advancements due to their adjustable physicochemical characteristics such as melting point, wettability, electrical and thermal conductivity, catalytic activity, light absorption and scattering resulting in enhanced performance over their bulk counterparts. By controlling the shape, size and internal order of the nanostructures, properties (electrical conductivity, colour, chemical reactivity, elasticity, etc.) can be modified.

Some nanomaterials occur naturally, but of particular interest are engineered nanomaterials (EN), which are designed for, and already being used in many commercial products and processes. They can be found in such things as sunscreens, cosmetics, sporting goods, stainresistant clothing, tires, electronics, as well as many other everyday items, and are used in medicine for purposes of diagnosis, imaging and drug delivery. Engineered nanomaterials are resources designed at the molecular (nanometre) level to take advantage of their small size and novel properties which are generally not seen in their conventional, bulk counterparts. The two main reasons why materials at the nano scale can have different properties are increased relative surface area and new quantum effects. Nanomaterials have a much greater surface area to volume ratio than their conventional forms, which can lead to greater chemical reactivity and affect their strength. Also at the nano scale, quantum effects can become much more important in determining the materials properties and characteristics, leading to novel optical, electrical and magnetic behaviors.

Chapter One

Introduction of the Nanomaterials

<u>1.1 Definition of Nanomaterials</u>

Nanoscale materials are defined as a set of substances where at least one dimension is less than approximately 100 nanometers. A nanometer is one millionth of a millimeter - approximately 100,000 times smaller than the diameter of a human hair. Nanomaterials are of interest because at this scale unique optical, magnetic, electrical, and other properties emerge. These emergent properties have the potential for great impacts in electronics, medicine, and other fields [1].

<u>1.2 History of Nanomaterials</u>

Nanotechnology involves the synthesis and application of materials in dimensions of the order of a billionth of a meter (1×10^{-9}) . This categorizes them under ultrafine particles. (Figure 1.1) reveals the size comparison of the nanoparticles against different living and nonliving species [2]. The properties of nanoparticles vary from their bulk counterpart and their chemistry [2]. The electronic structure, reactivity, and thermal and mechanical properties tend to change when the particles reach the nanoscale. Through nanotechnology, we can build materials and devices with control down to the level of individual atoms and molecules. In the past two decades, there were reports of colloids and nanoparticles designed by nature [3, 4].

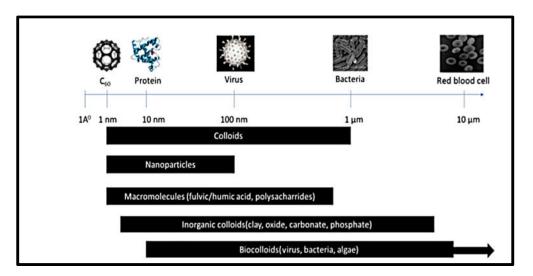


Figure (1.1): Size comparison of different structures (living and nonliving) [2].

The history of nanomaterials began immediately after the big bang when Nanostructures were formed in the early meteorites. Nature later evolved many other Nanostructures like seashells, skeletons etc. Nanoscaled smoke particles were formed during the use of fire by early humans. The scientific story of nanomaterials however began much later. One of the first scientific report is the colloidal gold particles synthesized by Michael Faraday as early as 1857. Nanostructured catalysts have also been investigated for over 70 years. By the early 1940's, precipitated and fumed silica nanoparticles were being manufactured and sold in USA and Germany as substitutes for ultrafine carbon black for rubber reinforcements [1].

Over the past few years, nanomaterials (NMs) have attracted the researchers because of their nanosize, physical, biological, and chemical properties compared to their bulk materials. These NMs are classified based on their size, chemical composition, shape, and sources. Different types of NMs have been synthetized from different sources and they are being classified accordingly. Many NMs have been produced in large quantities based on the requirements for many industrial applications. The two main sources through which NMs are being produced are synthetic source and naturally occurring

nanoparticles (NPs). In this chapter, we discuss the types and classifications of NMs and broadly discuss the different types of nanomaterials isolated from natural and synthetic sources [5].

1.3 Main differences between nanomaterials and bulk materials

Nanomaterials are particles that have their size in 1-100 nm range at least in one dimension. We cannot see their particles through the naked eye. Moreover, examples of these materials include nanozymes, titanium dioxide nanoparticles, graphene, etc. Bulk materials are particles that have their size above 100 nm in all dimensions. We can see their particles through the naked eye. The examples of these materials include plaster, sand, gravel, cement, ore, slag, salts, etc. The below infographic presents the difference between nanomaterials and bulk materials in tabular form. Figure (1.2) show the main different between nanomaterials and bulk materials and bulk materials [6].

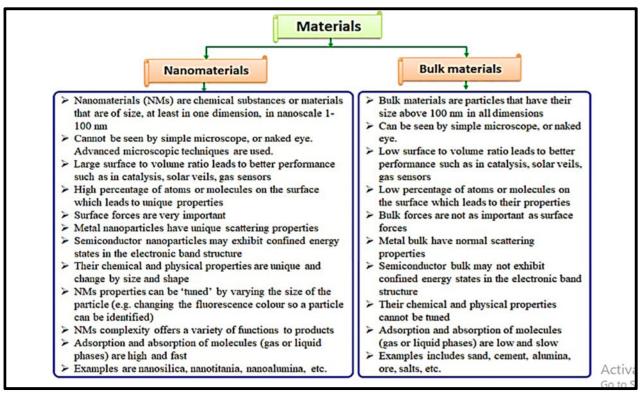


Figure (1.2): General Properties of NMs and Bulk Materials [6].

1.4 Types and Classifications of the Nanomaterials

As the field of nanotechnology is growing rapidly, tremendous amount of NMs have been produced and all these NMs must be identified based on the structure, shapes, size, and chemical synthesis in order to differentiate from each other. Interestingly, NMs can be broadly typed into seven categories which are described below [7]:

1.4.1 Carbon Nanomaterials

The NMs which contain carbon are called carbon nanomaterials, and these carbon nanomaterials can be synthetized in different shapes such as (1) hollow tubes or (2) spheres. In addition, carbon nanofibers, graphene, fullerenes, carbon black, carbon nanotubes, and carbon onions are also classified as carbon nanomaterials (Figure 1.3) [7].

1.4.2 Metal and Metal Oxide Nanomaterials

The metal and metal oxide can also be used to produce NMs which are called as metal and metal oxide nanomaterials or inorganic nanomaterials. Some of these NMs are gold (Au), silver (Ag) nanomaterials and metal oxides-based nanomaterials are titanium dioxide (TiO₂) and zinc oxide (ZnO) nanomaterials [7].

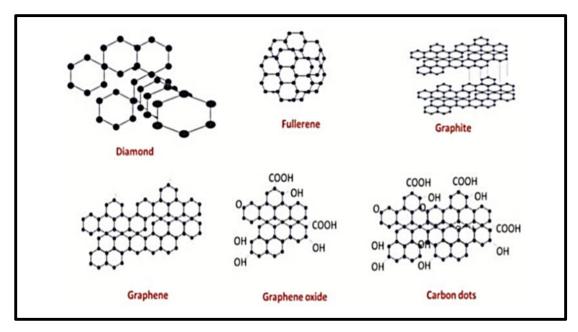


Figure (1.3) Different Carbon-base nanomaterials [7].

<u>1.4.3 Organic Nanomaterials</u>

This type of NMs mostly contains organic matter, without carbon or inorganic based nanomaterials. One of the characteristics of these organic nanomaterials is that they possess noncovalent bonds (weak in nature, which can be easily broken). These organic materials can be easily modified to produce different shapes of nanomaterials like liposomes, dendrimers, micelles, and polymers (Figure 1.4) [7].

1.4.4 Nanocomposites

The combination of one type of nanomaterials with another type of nanomaterials is called as nanocomposites. The nanomaterials either combine with other types of nanowires, nanofibers, or can be combined with larger size materials. These nanocomposites may be any combinations of metal-based, carbon-based, or organic- based nanowires, nanofibers, with any form of ceramic, metal, polymer bulk materials (Figure 1.5) [7].

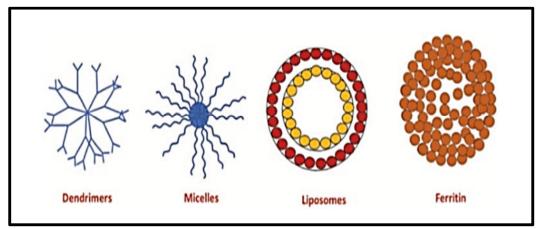


Figure (1.4): Different types of organic nanomaterials [7].

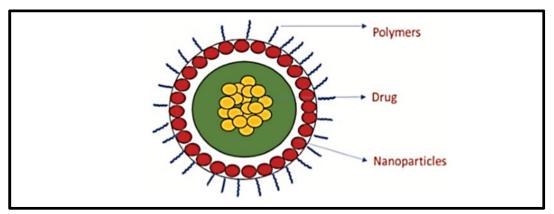


Figure (1.5) Structure of nanocomposites [7].

1.4.5 Ceramic Nanomaterials Nanoceramic

Is a type of NP material composed of ceramics and is further classified as heatresistant, inorganic, and nonmetallic solids made of nonmetal and metal compounds having dimensions smaller than 100 nm [8]. Many chemical and physical methods for the preparation of ceramic NMs have been explored and reported. It was found that these materials exhibited enhanced structural, electro-optical, superconductive, ferromagnetic, and ferroelectric properties. Similarly, the structural and physical properties of Ti-doped BiFeO₃ nanoceramics can be changed by changing the doping concentration, which could induce the structural distortion of materials and the elimination of oxygen vacancies [9]. Sobierajska et al. reported the preparation of porous hydroxyapatite nanoceramics and its applications due to its antimicrobial activity [10]. The calcium hydroxyapatite porous nanoceramics (ncHAP) were prepared by the co-precipitation of high purity hydroxyapatite (HAP) and methylcellulose. The specific surface area and the porosity of ncHAP depend on the sintering temperatures. The interactions between its surface charges and the bacteria influence its ability in antimicrobial activity. The synthesis of nanoceramics under pressure-less and low-temperature conditions produce Al_2O_3 – ZrO_2 nanoceramics. The study's results revealed that amorphous materials were successfully formed at low temperatures with the homogeneous mixture and the grain size of NPs [11].

<u>1.4.6 Semiconductor Nanomaterials</u>

Semiconductor NMs have low bandgap energy of less than 4 eV. Examples of known semiconductors are silicon, germanium, gallium arsenide, and elements near the so-called "metalloid staircase" on the periodic table. These NMs are composed of different compounds from various groups, such as II-VI (ZnO), IV (SiO₂), and III–V (GaAs). The modification of the structure of these materials into the nanoscale can alter the chemical and physical properties of the materials due to the quantum size effect or by increasing the surface area. The C/ZnO semiconductor, with its high porosity, showed that the high electrical conductivity of the materials depends on the nanostructure formed. The semiconductor NMs can be divided into two types: (1) intrinsic semiconductors, composed of pure compounds or elements without doping that are present from other metals in the structure. The main characteristic of intrinsic semiconductors is that they have negative temperature coefficients of resistance. This means that by increasing the temperature, the resistivity of the material will decrease and the conductivity will increase; (2) extrinsic semiconductors, which are a type of material added to other metals by doping in its structure, which aims to increase their conductivity, for example, type-n and type-p semiconductors [12].

<u>1.4.7 Polymeric nanomaterials</u>

Polymeric NMs are solid particles that are nanosized and consist of natural or synthetic polymers. These materials are widely used in pharmaceutical and medical applications as drug release controllers used to sense the body [13]. Polymer-based NMs include the following: (i) polymeric micelles formed by the self-assembly of amphiphilic block copolymers in a specified solvent. Chitosan polymeric micelles can be used for drug delivery due to their unique characteristics, such as their nanosize, stability, biocompatibility, micellar association, and low toxicity [13]; (ii) polymeric NPs, which are generally composed of biocompatible and biodegradable polymers with an average size of 10-1000 nm. These materials are widely used to deliver drugs to specific targets [14]. The preparation methods to produce polymer NPs affect the specific characteristics of the material produced [15]. Generally, the preparation methods are classified as polymerization of monomers, the ionic gelation of hydrophilic polymers, and the dispersion of polymers; (iii) dendrimers, which have a size of less than 15 nm with 3D-shaped macromolecules. These materials are a new type of polymeric NMs that are widely used in pharmaceutical and medical applications due to characteristics such as their structure, size, and multivalence [16]; and (iv) polymeric nanocomposites, which are a combination of other nanofillers and polymers used to provide superior properties and characteristics [17].

<u>1.5 Classification of Nanomaterials</u>

<u>1.5.1 Dimensions and Sizes</u>

As different types of nanomaterials are produced for a variety of applications, it becomes necessary to categorize these nanomaterials for proper applications. The nanomaterials are mostly solid particles, and their size and dimensions can be easily measured by using different methods. The idea for classification of nanomaterials was proposed by a scientist in the year 2000 [8], he classified the nanomaterials based on their crystalline forms and chemical compositions. Still, this method of measuring was not fully complete as it did not measure dimensions of the nanomaterials [18]. In another study, different groups of researchers have made a new classification which was primarily based on 0 Dimension, 1 Dimension, 2 Dimension, and 3 Dimension nanomaterial [19]. The classification of nanomaterial is basically dependent on the movement of electrons in the nanomaterial. The presence of electrons is generally fixed in "0" dimension nanomaterials, whereas for "1" dimension nanomaterials, electrons can move freely along the x-axis, which is commonly less than 100 nm. Similarly, "2" dimension and "3" dimension nanomaterials have better electron movements along the x- to y-axis or x-, y-, z-axis, respectively. It has been found that the ability to predict the properties of nanomaterials determines the classification of the nanomaterials. Moreover, the characteristics of nanomaterials are basically dependent on the grain boundaries as per the Gleiter's classification, whereas the classification by Pokropivny and Skorokhod suggested that the characteristics of nanomaterials are ascribed to the nanoparticle shapes and dimensionalities [19].

<u>1.5.2 Origin of Nanomaterials</u>

The nanomaterials can be classified based on their source of origin, which means, the source materials to produce nanomaterials. They can be classified as naturally origin nanomaterials or synthetically produced nanomaterials.

1.5.2.1 Natural Nanomaterials

Natural nanomaterials can be formed in biological species such as microbes, or plants and also through anthropogenic actions. The creation of natural nanomaterials is an accessible process as they are present in the hydrosphere, atmosphere, lithosphere, and biosphere. Interestingly, our planet is comprised of nanomaterials that are naturally formed and are present in the rivers, groundwater oceans, lakes, rocks, soils, magma, or lava as well as in the microbial organisms and also in humans [20, 21]

1.5.2.2 Synthetic Nanomaterials

The most widely used method to make nanomaterials is the synthetic method, which allows the production of nanomaterials by biological, physical, chemical, or hybrid methods. One of the advantages of the synthetically produced nanomaterials is that it is possible to produce large quantity of nanomaterials with different shapes and sizes. Another important aspect of the synthetic method is that different chemicals or reagents can be linked or conjugated with nanomaterials accurately and precisely. The major concern among synthetically designed nanomaterials is whether present knowledge is sufficient to envisage their performance. In addition, they display a different environment behavior, which is different from natural nanomaterials. Presently, diverse sources of nanomaterials are produced for various biological applications [22].

Chapter Two

Synthesis of Nanomaterials: Methods & Characterizations

2.1 Introduction

Over the past couple of decades, various methods of preparation and synthesis of nanomaterials have been developed. The main objectives of the synthesis of nanomaterials are to ensure that for what purpose these nanomaterials are being synthesized. The researchers should know the applications of the nanomaterials so that they can synthesize them accordingly. The method of production of nanomaterials to be used in the industrial application for the development of various products will be different than the method of production to be used in biological or medical applications. Other objectives of the researchers to synthetize nanomaterials are better functionality and lower cost. Over the past few years, several physical and chemical methods have been used to improve the performance of nanomaterials demonstrating enhanced properties.

2.2 Methods to Synthesize Nanomaterials

The "top-down" and "bottom-up" are the two major methods which have been used to successfully synthesize nanomaterials. We have described these methods in further detail (Figure 2.1) [23].

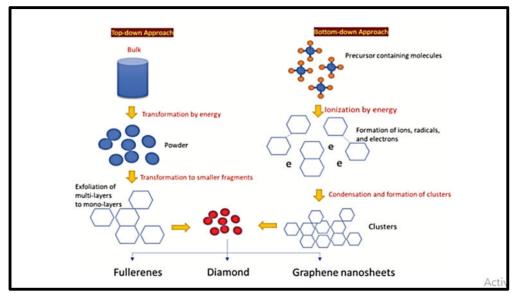


Figure (2.1) Diagrammatic representation of top-down approach and bottom-down approach of making of nanomaterials [23].

2.2.1 Production of Nanomaterials by Top-Down Method

In this method, solid and state processing of the materials are mostly used and this method involves breaking of the bulk material into smaller particles using physical processes such as crushing, milling, and grinding methods. Generally, this method is not appropriate for formulating evenly shaped nanomaterials, and it is very difficult to get very small size nanoparticles even with high energy usages. The major difficulty of this method is the shortage of the surface structure as it has significant impact on physical properties and surface chemistry of nanomaterials. In addition, this method also causes substantial crystallographic loss to the processed shapes [23].

2.2.2 Production of Nanomaterials by Bottom-Up Method

In this method, materials are prepared by atom-by-atom or molecule-bymolecule to make large amount of materials. This method is more frequently used for producing most of the nanomaterials. This method has an ability to produce a uniform size, shape, and well- distributed nanomaterials. It basically control the chemical synthesis process in a precisely manner to prevent undesirable particle growth. This method plays an important role in the production and processing of nanomaterials with better particle size distribution and better morphology. Another important feature is that its an environment friendly and economical processes for the nanoparticle production [24]. There are many approaches for synthesizing nanomaterials like hydrothermal, combustion synthesis, gas-phase methods, microwave synthesis, and sol-gel processing [25], which we have described below.

2.2.2.1 Hydrothermal Method

The hydrothermal method is normally done in a pressurized container which is called as an "Autoclave" where temperature and pressure can be controlled and regulated. During nanomaterial synthesis, the temperature can be increased at the boiling point of water, which allows the vapor to get saturated. This method (Figure 2.2) has been extensively used in the production of different nanoparticles [26]. The advantage of this method is that this can be useful to control material size, particle morphology, crystalline phase, and surface chemistry through regulation of the reaction temperature, pressure, solvent properties, solution composition, and additives [27].

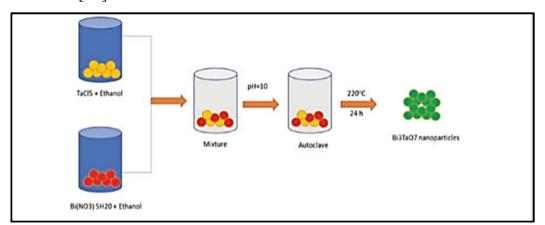


Figure (2.2) Diagrammatic representation of hydrothermal process nanoparticle production [26].

2.2.2.2 Solvothermal Method

The solvothermal method (Figur 2.3) is like hydrothermal method, the only difference is that it uses different solvents other than water. Interestingly, this method is more effective in synthesis of nanomaterials with good distribution, especially when organic solvents or chemicals with high boiling points are selected. Moreover, this method provides better controlling method to produce better size and shapes of the materials than the hydrothermal method. This method synthetizes nanomaterials or nanorods with or without the addition of surfactants [28].

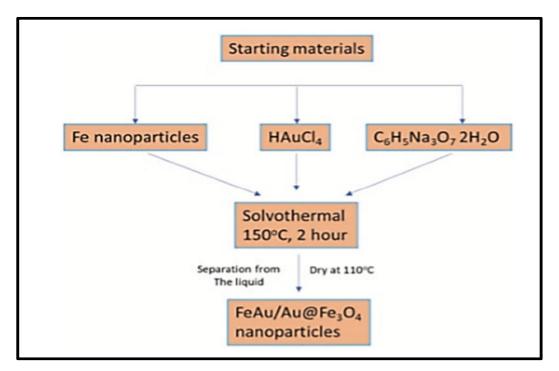


Figure (2.3) Diagrammatic representation of solvothermal process of nanoparticle production [28].

2.2.2.3 Chemical Vapor Deposition Method

The chemical vapor deposition (CVD) method is used to manufacture high performance thin nano-films. In this method, substrate is basically treated with volatile precursors which act on the substrate surface to produce the desirable films. Usually, volatile by-products are eliminated by gas flow through the reaction chamber. The quality of the deposited materials on the surface is greatly dependent on several factors like temperature, rate of reaction, and the amount of the precursors [29]. It has been reported that Sn_4 +doped TiO₂ nanoparticle films were produced by CVD method [30]. Another doped TiO₂ nanoparticle was synthesized by CVD method where TiO₂ is crystallized into the rutile structures depending on the type and number of cations present in the chemical reactions. The advantage of this method is getting consistent glaze of the nano film, but this method has many limitations including higher temperatures required for chemical reactions, and secondly it is difficult to scale up [31].

2.2.2.4 Method of Thermal Decomposition and Pulsed Laser Ablation

The doped metals can be produced by using decomposing metal alkoxides, salts, heat or electricity. Moreover, the properties of nanomaterials strongly depend on the flow rate of the precursor's concentrations in the reactions and its environment. It has been reported that TiO₂ nanoparticles with a diameter < 30 nm can be synthetized by using the thermal decomposition of titanium alkoxide at 1200°Celsius temperature [32]. In another study, TiO₂ nanoparticles with a diameter (3–8 nm) were produced by pulsed laser ablation technique [33]. In addition, doped anatase TiO₂ nanoparticles were produced by the solution combustion method [34]. Nevertheless, the disadvantages of this method are the high cost, low yield, and difficulty in managing the structure and morphology of the nanomaterials.

2.2.2.5 Templating Method

The process to construct materials with a similar morphology is known as templating method. The production of nanomaterials which uses the templating method has become exceptionally popular recently. This method uses the morphological characteristics with reactive deposition, so it is possible to prepare numerous new materials with a regular and controlled morphology by simply changing the morphology of the template materials. Over the past few years, a variety of templates have been developed to synthesize different nanomaterials [35]. This method has some shortcomings, like complicated synthetic procedures where templates must be removed, normally by calcination technique, which causes an increase in the manufacturing costs and also chances of contamination.

2.2.2.6 Combustion Method

The combustion method includes a quick heating of a solution comprising redox groups. This method leads to production of highly crystalline nanoparticles with large surface areas. During production, the temperature reaches to roughly 650°Celisus for 1–2 min to make the crystalline materials [36].

2.2.2.7 Gas Phase Method

This method is good to produce thin film because it can be performed chemically or physically. Nanomaterials are formed because of chemical reaction or decomposition of a precursor in the gas phase [37]. Moreover, physical vapor deposition (PVD) is another technique which can be used to produce thin film deposition. Interestingly, films are formed from the gas phase method without using chemical transition. To produce TiO_2 thin films, a beam of electrons heats the TiO_2 material and the electrons are produced and this process is recognized as Electron beam (E-beam) evaporation. There are many benefits of making of TiO_2 deposited with E-beam evaporation than CVD method such as smoothness and better conductivity [38].

2.2.2.8 Microwave Radiation Method

Nanomaterials can also be produced by using microwave radiation and there are several benefits of this method, like this method does not use high temperature calcination for extended period of time and also is a quick method of making crystalline nanomaterials. Moreover, high quality of rutile rods can be created by joining hydrothermal and microwave methods, while TiO_2 hollow open- ended nanotubes can be manufactured through reacting anatase and rutile crystals in the NaOH solution [39].

2.2.2.9 Conventional Sol-Gel Method

This method has numerous advantages, for example, this method allows impregnation or co-precipitation of nanomaterials, which can be used to introduce dopants. To synthesize various oxide materials, sol-gel method has been used, and this method allows better control for the texture formation, the chemical reaction, and the morphological properties of the solid materials. The major benefit of the Sol-Gel technique is the ability to scale up with a high purity of nanomaterials. In Sol-Gel technique process, a colloidal suspension is formed from the hydrolysis and polymerization reactions of the precursors. These precursors are usually inorganic metal salts or metal organic compounds. In addition, any factor that effects either or both reactions are likely to impact the properties of the gel formation and these factors are generally described as Sol-Gel technique factors. These factors include type of solvent, water content, acid or base content, and different type of precursor, precursor concentration, and temperature. These factors affect the structure of the initial gel formation. After this step, the wet gel can be mature in another solvent. The time between the formation of a gel and its drying is known as aging [40].

2.3. Characterization of Nanoparticles

Nanoparticles occupy various application domains that are relevant to our lives. According to the type of application, it is essential to characterize NPs for their chemical, physical, and other properties. Different tools that can be used to obtain these properties are in the next chapter. The significant physical and chemical properties of NPs include their composition, size and shape, and surface area as well as distribution, stability, surface chemistry, roughness, and topography.

<u>2.3.1 Electronic properties</u>

The electronic properties of NPs depend on their size, surface area, chemical composition, and modification. Modification of Al_2O_3 with organic ligands can control the size of the materials produced through the aggregation process. The presence of organic compounds such as ligands can improve the different surface characteristics of NMs. Different types of ligand monomers used can also have an effect on the structural characteristics of the material produced, as seen in the modification of Al_2O_3 with organic ligands, which control the size of the materials produced through the aggregation process. This kind of modification also provides different electrical characteristics. As such, the electric properties of the polymer nanocomposites were increased by the addition of inorganic compounds to the polymer systems. Electrical properties, such as electrical conductivity and the dielectric constant, could be improved by the addition of barium titanate (BT) due to its perovskite nanostructures and piezoelectric properties [6].

2.3.2 Optical properties

The optical properties of NPs, especially semiconductor materials, are important for several applications, such as photocatalysts and photovoltaics. The optical properties can be determined by basic light principles and the Beer–Lambert law. The increased absorption of wavelengths in semiconductor NPs are influenced by several factors, such as size distribution, shape, sizes, and the type of modifiers. The optical properties of Nd-doped NiO have been studied using UV–Vis spectroscopy. Nd-doped NiO NPs could shift to a lower energy value than pure NiO due to the exchange of electrons in the energy band and the localized electron of Nd3+. Optical properties are influenced by the composition of nanostructures, such as metal ion doping and surface modification. Optical properties, especially the reflectance and scattering phenomena, are affected by the particle size of NMs. The reflectance increases with increasing particle size can affect scattering particle patterns when exposed to light, resulting in different spectral reflectance [6].

2.3.3 Magnetic properties

Magnetic NPs are used for applications in the medical and environmental fields. Magnetic properties are influenced by the particle size of NPs with the best performance showing a particle size of less than 35 nm. In single compound NPs, the magnetic moment value of a molecule is represented directly by the number of magnetic atoms, whereas for multicomponent NPs, the magnetic value is determined by the number of lone pair electrons according to the valence-shell electron-pair repulsion (VSEPR) theory. Generally, the change in particle size is quite small and does not change the lattice parameters of the metals. However, for metals that contain metal oxides on the surface, the lattice parameters of metals may change with changing particle size due to mismatches between the lattice parameters of the metal oxides, which further causes interfacial stress on the surface. Therefore, the magnetization value will

change with the change in particle size. Also, the magnetic properties are influenced by other factors, such as the composition of the nanostructure and the synthesis methods [6].

2.3.4 Mechanical properties

Nanoparticles have different mechanical properties compared to microparticles or bulk materials. NMs provide a large surface area and are easy to modify, resulting in an increase in mechanical properties such as hardness, adhesion, stress and strain, and the elastic modulus. NPs from a group of inorganic compounds show mechanical properties, while organic compounds generally have low mechanical properties. Therefore, increasing the mechanical properties of organic compounds is commonly done by the addition of inorganic compounds. Bui et al. investigated the mechanical properties of acrylic polyurethane by the addition of the metal oxide SnO_2 . The presence of SnO_2 in the polymer matrix improved the mechanical properties, especially the hardness, impact and abrasion resistance, and adhesion. However, the addition of more metal oxides to the polymer matrix may reduce mechanical properties because the presence of metal oxides can decrease the polymer–polymer interactions, the polymer to metal-oxide interactions, and possible agglomeration processes. Other studies have also reported that mechanical properties depend on the size of the NPs [41].

2.3.5 Thermal properties

The thermal properties of NPs are better than their fluid form because they have a large surface area and so heat transfers occur directly on the surface of the material. The thermal properties of materials gradually increased by increasing the metal oxide (SiO₂) contents added to the polycarbonate. The presence of metal oxides such as SiO₂ can increase interactions between NPs and polymers, along with restrictions in polymer chain formation. The addition of a nanofiller, with a high intrinsic thermal conductivity, influenced the thermal properties of NMs. Overall, the thermal properties of NPs depend on the large surface area, mass concentration, the ratio of energic atoms in NPs, and the fraction of NP volume dispersed [42].

Chapter Three

<u>Methods of detection of Nanomaterials: Techniques and Tool</u> <u>3.1 Introduction</u>

Nanomaterials have shown excellent physical, electrical, and chemical properties compared to when they are in the bulk phase. Nanotechnology/biotechnology is dealing with synthesis, characterization, and applications of nanomaterials. The nanoscale materials contained tiny particles, often known as nanoparticles and they require special instrumentations and tools for their successful characterization and analysis. In this chapter, we will describe briefly the tools and techniques which are widely used for the characterization of nanomaterials. These techniques include but not limited to scanning electron microscopy (SEM), transmission electron microscopy (TEM), Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), energy-dispersive X-ray (EDX) spectroscopy, thermal gravimetric analysis (TGA), dynamic light scattering (DLS) analysis, density functional theory (DFT), zeta sizer, etc. The illustration of each technique and some cases with graphics is provided.

3.2 Scanning Electron Microscopy (SEM)

From the name, it is clear that the electron microscopes use electrons for the formation of images instead of light as the case for optical microscopes. The electronic image has often better image quality in terms of resolution than optical microscopy, thanks to their small wavelengths. Scanning electron microscope (SEM). SEM is a very useful technique to obtain the surface topography and chemical composition of the specimens with a wide view [43]. SEM instrument along with a schematic of basic signals produced in SEM are shown in (Figure 3.1).

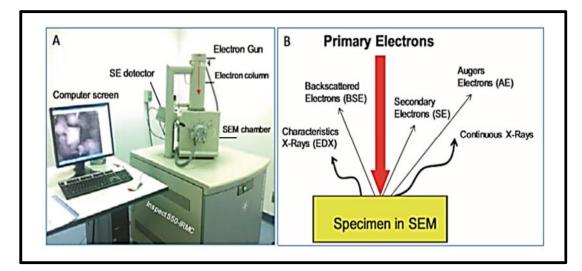


Figure (3.1): (a) Photograph of SEM instrument, showing its different parts (b) basic signals produced in the SEM after interaction of primary electrons with the specimen [43].

SEM instrument has the following basic parts: electron gun (top), electron column (where electromagnetic lenses and coils are attached), chamber (for specimen), detectors, and vacuum pumps (not shown in this figure). In SEM, electrons are generated by an electron gun situated at the top of the column and accelerated towards the specimen by applying a high voltage (typically 20–30 kV). The gun electrons (called primary electrons) are then focused by electromagnetic lenses while traveling through the column and scan the specimen using electrical coils. Different kinds of signals such as secondary electrons (SE), backscattered electrons (BSE), Auger electrons (AE), X-rays, etc. are generated as energetic beam of electrons is subjected to the specimen. These signals are then detected by the dedicated detectors and produce electronic images or spectra as shown on the computer screen. The SE signals are utilized to generate surface morphological images while BSE and EDX signals are used to obtain chemical and structural information of the specimen (see Figure 3.2) [43].

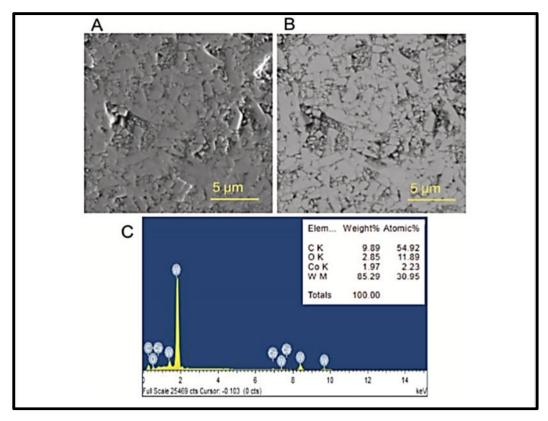


Figure (3.2): (a) SE image, (b) BSE image, and (c) EDX spectra of tungsten carbide doped cobalt specimen (SEM working voltage: 15 kV). EDX spectrum shows the contents of the specimen, e.g. C, O, Co, and W. W is found to be a major constituent (~85 wt.%) of this compound. The scale bars are 5 μ m [43].

3.3 Transmission Electron Microscopy (TEM)

Transmission electron microscopy (TEM) is a powerful tool to attain a high-quality data of the nanomaterials. The microscope that performs this job is known as TEM instrument. In general, TEM is performed to obtain a detailed morphology and structure of the specimen which is beyond the limit of SEM. The main difference in SEM and TEM is that in TEM, the electron beam is transmitted through a thin specimen, while in SEM, the beam of electrons scans the surface of the sample instead of passing through. Another important difference is the power of the microscope (accelerating voltage; V). Typically, TEM is operated at 80–300 kV, this power is much higher than SEM (maximum: 30 kV). Thus, TEM can

produce better images than SEM in terms of resolution. It is a worthy to note that the wavelength (λ) of the electrons is related to V that can be varied according to the following relation ($\lambda = h/((2m0eV)1/2)$); h is a Planck's constant, m0 is the rest mass, and eV is the energy of the electrons provided by V. The reciprocal relationship between λ and V introduces a very important concept: by increasing V, we can shorten the λ of the electrons and hence improve the resolution. The λ of electrons in TEM is comparable or smaller ($\lambda = 0.00197$ nm at 300 kV) than the size of the atom (~ 0.1 nm) that helps TEM to reveal the finest details of the internal structure of the specimen as small as individual atoms and molecules. The main unit of TEM along with the basic interaction of electrons and specimen is shown in Figure (3.3). TEM has the following basic parts: electron gun (at the top), electron column, electromagnetic lenses, apertures, sample holder, fluorescence screen (camera), vacuum pumps, and high-tension tank (not shown in this figure). TEM has several modes to collect the data but important imaging modes are bright-field (BF), darkfield (DF), and high-resolution (HR) imaging, known as BF-TEM, DF-TEM, and HR-TEM, respectively. Direct electrons are used to form the BF imaging after blocking the scattered electrons by objective aperture and vice versa for DF-TEM. HR-TEM is performed using the phase of the electrons and acquired a detailed structure of the specimens down to the atomic level. The working principle of TEM is based on the interaction between incident electrons and specimen. In TEM, high energy electrons are accelerated towards the specimen by applying a high voltage (80-300 kV). These electrons are focused by a system of condenser lenses. A fine focused beam of electrons is then transmitted through the thin sample. Typically, the suitable thickness of the specimen is about 100 nm for material science samples and 200 nm for biological specimens. The transmitted electrons are generally of two types: direct electrons (do not

change their direction) and scattered electrons that changed their trajectory after passing through the sample. Either type of electrons can be utilized to make the image. If the image is made by direct electrons, then it is known as BF image (see Figure 3.3). On the other hand, if the scattered electrons are allowed to pass through the objective aperture for the purpose of the image and blocked the direct electrons, then it is called DF image [44].

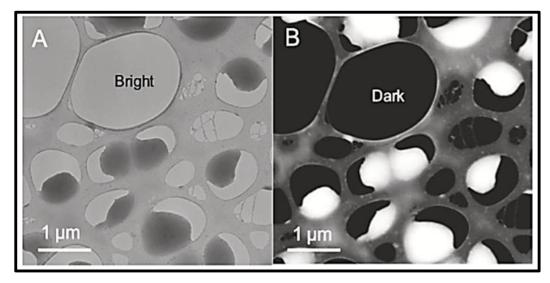


Figure (3.3): Two imaging modes of TEM: (a) BF and (b) DF imaging. The carbon hole that has bright contrast in BF turned to dark (inverse) in DF (working voltage: 200 kV). The scale bars are $1 \mu m$ [44].

The important difference between the two images is the contrast that is opposite; for example, the bright features of BF image (such as holes of carbon support film) will appear dark in DF image and vice versa. TEM image (either made by direct or scattered electrons) can be viewed on the fluorescence screen or recorded by a computer using a digital camera. Notably, images formed by TEM have proven better resolution than SEM due to the basic principle of TEM (transmission of electrons) and because of the high energy of electrons.

3.4 Fourier Transform Infrared (FTIR) Spectroscopy

Fourier transform infrared (FTIR) is an infrared spectroscopy technique to study the molecular bonding of the organic/inorganic materials. IR is a region of electromagnetic radiations between the red edges of the visible spectrum at a wavelength of 700 nm to 1 mm, i.e. IR waves are longer than visible light while shorter than radio waves (see Figure 3.4 a). During FTIR, a specimen is exposed to IR radiations in order to create a spectrum of the specimen [45]. A portion of the radiations is transmitted, while the rest of the radiations are absorbed by the specimen depending on the nature of bonding in the material. A molecular fingerprint of the specimen is created as a result of transmission and absorption at a molecular level. A wide range of information, such as identifying the material properties, quality of the specimen, and number/ratio of the individual ingredients in a mixture can be extracted by FTIR spectra [45].

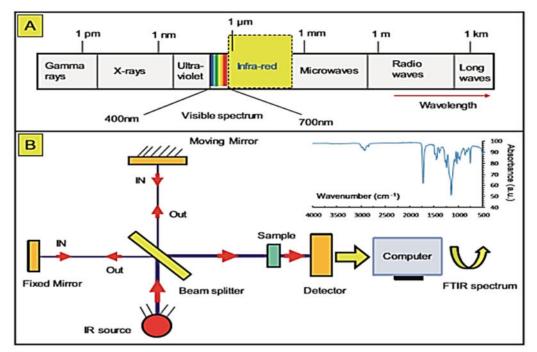


Figure (3.4): (a) Electromagnetic radiation spectrum where wavelengths range for IR region is from about 700 nm to 1 mm. (b) Schematic of working of FTIR instrument along with FTIR spectrum [45].

3.4.1 Main Components of FTIR Instrument

The following are the main parts of the FTIR instrument:

1. Source: The source to emit the IR energy in the form of a beam.

2. Interferometer: A distinctive signal (interferogram) containing all the IR frequencies is produced by the interferometer. The interferogram signal is created as a result of the interference of two beams and contains the information of each IR frequency. Measuring the interferogram means a simultaneous measurement of all IR frequencies.

3. Sample Chamber: The sample is mounted into the specimen chamber. The IR beam goes into the chamber for specimen interaction. Only specific frequencies of the IR signal are absorbed/transmitted depending on the nature of the specimen.

4. The Detector: A special-purpose detector is designed to gauge the interferogram signal.

5. The Computer: To analyze the signal for identification purposes, a plot of each IR frequency is required. Therefore, the interferogram is decoded into the individual frequencies in a computer using a mathematical formulation, known as Fourier transform [45].

3.4.2 Working of FTIR Instrument

In FTIR instrument, radiations are produced by an IR light source in the form of a beam. The beam of energy then travels through the interferometer for spectral encoding. The interferogram is created as a result of spectral encoding. The working of interferometer and creation of FTIR plot is described as follows (see Figure 3.4 b). Firstly, the beam splitter (a partially reflecting mirror) of the interferometer divides the incoming radiations into two beams. These two beams are then reflected from two separate mirrors, one of the mirrors is fixed and the other is moveable. After reflecting from respective mirrors, both beams are merged back at the beam splitter. Now, the IR beam goes into the specimen chamber. The signal from the interferometer is the result of interferogram contains the

information of each IR frequency that is falling on a specimen from the source. The beam is either passed through or bounces off the specimen surface, depending on the analysis requirement. A desired range of IR frequencies representing a distinctive property of the specimen is absorbed. The interferogram signal is detected by a special purpose detector and decoded in the computer to transform into a meaning data using a mathematical tool known as Fourier transformation. After the signal transformation, FTIR signal in the form of spectrum is available for manipulation and expositions. FTIR spectrocopic characterization can be used to analyze several kinds of materials [46].

<u>3.5 X-Ray Diffraction (XRD)</u>

X-ray diffraction (XRD) is a non-destructive method to study the material's structure at the molecular and atomic level. XRD is the best method to investigate the crystalline, polycrystalline, and non-crystalline (amorphous) materials. The wavelengths (λ) of the X-rays (used in the XRD) are in the range of nanometers. XRD is the elastic scattering (noloss of energy during a collision) of X-rays by atoms of the materials. The principle of XRD is based on the interference of scattered waves. The resultant amplitude (intensity) of the scattered waves depends on the difference in the distance traveled by the waves, i.e. path difference (phase or angle). If the two waves superimpose in such a way that they are in phase (same crusts and troughs), then the resultant intensity is the sum of the two intensities, the phenomenon is known as constructive interference. On the other hand, in the destructive interference, two out of phase waves merged and the resultant intensity is the difference of two intensities. XRD analyzer plotted the x-y plot (XRD pattern) between intensity (in arbitrary units) and scattering angle, 2θ (degrees). The XRD pattern is analyzed by a mathematical formulation, known as Bragg's law and the following information can be obtained such as nature of material, atomic arrangement, crystallite size, chemical composition, etc. The XRD line patterns of more than 60,000 different crystallographic phases are available in the electronic database: JCPDS (Joint Committee on Powder Diffraction Standards). The PDF file (example: JCPDS No. 19-0628) consists of three most strong characteristics lines of the existing phase. The XRD technique applies to specimens of powders, thin films and solids.

3.5.1 Main Components of XRD Instrument

1- X-Rays Tube: A beam of fast-moving electrons is collided with atoms of a metallic target (copper) to produce X-rays in the tube.

2- Collimator: A collimator is used to make the rays parallel before they hit the specimen.

3- Sample Stage: Specimens are placed in the sample stage.

4- Detector: The diffracted beam of X-rays is detected by a counter.

5- Computer: The collected data is later plotted in the form of XRD pattern (2θ versus reflection intensity) on a computer.

3.5.2 Working of XRD Instrument

In XRD, a collimated beam (thin and parallel beam) of X-rays is directed towards a sample. The incoming beam of rays interacts with atoms of the specimen and scattered outward direction. Angle made by an incoming beam with the surface of the specimen is θ , then the angle of the diffracted beam is 2θ ; 2θ is dependent on arrangement of the atoms and type of atoms, etc. The diffracted beam is then detected by a detector and sent to a computer for making an XRD pattern (see Figure 3.5 a). Now, for a given specimen consider several periodic lattice planes (atomic layers) where each layer is separated by d (inter-plane spacing). According to Bragg's Law, constructive interference occurs when the path difference is an integral number of wavelengths. We can describe this law as follows: $AB = d \sin \theta$, and $BC = d \sin \theta$, then path difference is $(AB + BC) = 2d \sin \theta$. According to the Bragg's laws, a constructive interface occurs when 2d $\sin \theta = n \lambda$ is satisfied (Figure 3.5 b), where n is an integer, λ is the wavelength of the X-ray beam, and θ is the angle between the incident beam and the normal to the sample planes.

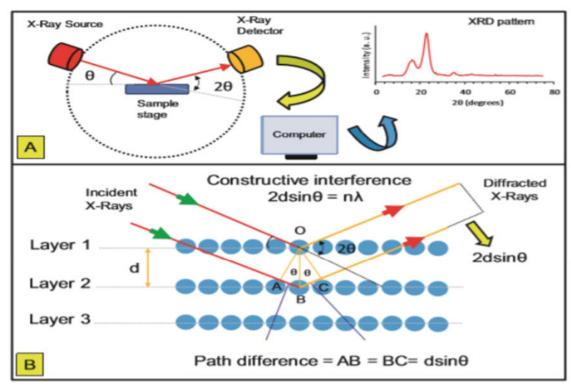


Figure (3.5): (a) Schematic representation of working of XRD instrument along with XRD pattern. (b) A 2-D crystal lattice and a set of imaginary planes. Constructive interference occurs when the path difference (AB + BC = 2d sin θ) is equal to integral multiple of wavelength (n λ) (Bragg's law of diffraction) [47].

In general, for wider interparticle distance d, the scattering angle 2 θ is lower. This means that the planes with wider d appeared earlier in the XRD patterns where scattering angle is low. In XRD, the angle of the incident beam is varied to obtain all the possible reflections for a given sample. By measuring θ , d of every single crystallographic phase can be determined by comparing the data with the standard line patterns available in the Powder Diffraction File (PDF) database [47].

<u>Chapter Four</u> <u>Applications, Advantages and Disadvantages</u> <u>Of the Nanomaterials</u>

4.1 Introduction

In this chapter we will outline several of the many applications of nanomaterials, both current and anticipated. To our knowledge, there is no comprehensive review of nanotechnology applications, likely due to the rapid development of this field. We feel that this chapter is necessary in order to broaden understanding of the importance that nanomaterials have and will play in our future, improving the quality of life through nanomedicine, electronics, and other nano-fields. Among established applications of nanomaterials, we give as examples: the microelectronics, synthetic rubber, catalytic compounds, photographic supplies, inks and pigments, coatings and adhesives, ultrafine polishing compounds, UV absorbers for sun screens, synthetic bone, ferrofluids, optical fiber cladding, and cosmetics. Applications currently entering widespread use include: fabrics and their treatments, filtration, dental materials, surface disinfectants, diesel and fuel additives, hazardous chemical neutralizers, automotive components, electronics, scientific instruments, sports equipment, flat panel displays, drug delivery systems, and pharmaceutics. The unique properties of nanomaterials encourage belief that they can be applied in a wide range of fields, from medical applications to environmental sciences. Studies conducted by nanotechnology experts mapping the risks and opportunities of nanotechnology have revealed enormous prospects for progress in both life sciences and information technology [48]. Medical applications are expected to increase our quality of life through early diagnosis and treatment of diseases, and prosthetics, among others. Ecological applications include removal of persistent pollutants from soil and water supplies. Nanotechnology has become a top research priority in most of the industrialized world, including the USA, the EU and Japan. In the U.S.A. nanotechnology is now at the level of a federal program [49]. Since 2000, around 60 countries have initiated nanotechnology based initiatives at a national level [49].

4.2 Electronics

4.2.1 *Microelectronics*: Many of the current microelectronics applications are already at a nanoscale. During the last four decades, the smallest feature of a transistor shrunk from 10 μ m down to 30 nm. The ultimate objective of microelectronics fabrication is to make electronic circuit elements that are nanoscopic. For example, by achieving a significant reduction in the size of circuit elements, the microprocessors (or better said, nanoprocessors) that contain these components could run faster and incorporate more logic gates, thereby enabling computations at far higher speeds. CNTs are exciting alternatives to conventional doped semiconductor crystals due to their varied electronic properties, ranging from metallic, to semiconducting, to superconducting [49].

4.2.2 Displays: The resolution of a television or a monitor improves with reduction of pixel size. The use of nanocrystalline materials can greatly enhance resolution and may significantly reduce cost. Also, flat-panel displays constructed with nanomaterials may possess much higher brightness and contrast than conventional displays owing to the enhanced electrical and optical properties of the new materials. CNTs are being investigated for low voltage field-emission displays. Their combination of mechanical and electrical properties makes them potentially very attractive for longlife emitters [49].

<u>4.2.3 Data storage:</u> Devices, such as computer hard-disks function based on their ability to magnetize a small area of a spinning disk to record information, are established nano-applications. Discs and tapes containing engineered nanomaterials can store large amounts of information. Future avenues for magnetic recording that will drastically increase the capability of data storage include spintronics and nanowires [49].

<u>4.2.4 High energy density batteries.</u> New nanomaterials show promising properties as anode and cathode materials in lithium-ion batteries, having higher capacity and better cycle life than their larger-particle equivalents. Among them are: aerogel intercalation electrode materials, nanocrystalline alloys, nanosized composite materials, carbon nanotubes, and nanosized transitionmetal oxides [49].

<u>4.2.5 High-sensitivity sensors</u>: Due to their high surface area and increased reactivity, nanomaterials could be employed as sensors for detecting various parameters, such as electrical resistivity, chemical activity, magnetic permeability, thermal conductivity, and capacitance [49].

4.3 Transportation and telecommunication

<u>4.3.1 Car tires:</u> Nanoparticles of carbon black ranging between 10 nm - 500 nm act as a filler in the polymer matrix of tires, and are used for mechanical reinforcement [49].

<u>4.3.2 Car bumpers:</u> Clay particle based composites containing plastics and nanosized clay are used to make car exteriors that are lighter and twice as resistant to scratches as usual materials [49].

4.4 Imaging

<u>4.4.1 Scanning microscope imaging</u>: SWCNTs have been used as probe tips for atomic-force microscopy imaging of antibodies, DNA, etc. Nanotubes are ideal probe tips for scanning microscopy due to their small diameter (which maximizes resolution), high aspect ratio, and stiffness [49].

<u>4.4.2 Molecular-recognition AFM tips:</u> SWCNTs with attached biomolecules are attached to AFM tips, and used for "molecular-recognition" in order to study chemical forces between molecules [49].

4.5 Biomedical applications

<u>4.5.1 Nanoscaffolds</u>: Nanofiber scaffolds can be used to regenerate central nervous system cells and possible other organs. Experiments performed on a hamster with severed optic tract demonstrated the regeneration of axonal tissue initiated by a peptide nanofibers scaffold [49].

<u>4.5.2 Antimicrobial nanopowders and coatings</u>: Certain nanopowders, possess antimicrobial properties. When these powders contact cells of E. coli, or other bacteria species and viruses, over 90% are killed within a few minutes. Due to their antimicrobial effect, nanoparticle of silver and titanium dioxide (<100nm) are assessed as coatings for surgical masks [49].

<u>4.5.3 Bioseparation</u>: Nanotube membranes can act as channels for highly selective transport of molecules and ions between solutions that are present on both side of the membrane. For example, membranes containing nanotubes with inside diameters of molecular dimensions (less than 1 nm) separate small molecules on the basis of molecular size, while nanotubes with larger inside diameters (20–60 nm) can be used to separate proteins [49].

4.5.4 Drug delivery: The ability of nanoparticles to target and penetrate specific organs and cells contributes to their toxicity, however, this ability may be exploited in nanomedicine. Nanospheres composed of biodegradable polymers can incorporated drugs, allowing the timed release of the drug as the polymer degrades. When particles are set to degrade in an acid microenvironment, such as tumor cells or around inflammation sites, this allows site-specific or targeted drug delivery [49].

<u>4.5.6 Gene transfection</u>: Surface-functionalized nanoparticles can be used to permeate cell membranes at a much higher level than nanoparticles without a functionalized surface. This property can be used to deliver genetic material into living cells, a process called transfection. For example, silica nanospheres labeled on their outer surfaces with cationic ammonium groups can bind DNA (a

polyanion) through electrostatic interactions. Then nanoparticles deliver the DNA into cells [49].

<u>4.5.7 Medical imaging</u>: A variety of techniques currently called "non-invasive" have been used for more than a quarter of a century in medical imaging, for example superparamagnetic magnetite particles coated with dextran are used as image-enhancement agents in magnetic resonance imaging. Intracellular imaging is also possible through attachment of quantum dots to selected molecules, which allows intracellular processes to be observed directly [49].

<u>4.5.8 Nasal vaccination</u>: Nanospheres carriers for vaccines are in development. Antigen-coated polystyrene nanospheres, used as vaccine carriers targeting human dendritic cells, have been researched for nasal vaccination. Nanospheres had a direct effect on human dendritic cells, inducing transcription of genes important for, e.g., phagocytosis as well as an immune response [49].

4.5.9 Nucleic acid sequence and protein detection: Targeting and identifying various diseases could be made possible by detecting nucleic acid sequences unique to specific bacteria and viruses, or to specific diseases, or abnormal concentration of certain proteins that signal the presence of various cancers and diseases [49]. Nanomaterials-based assays are currently evaluated as well as more sensitive proteins detections methods. Nucleic acid sequences are currently detected with polymerase chain reaction (PCR) coupled with molecular fluorophore assays. Despite high sensitivity, PCR has significant drawbacks, such as: complexity, sensitivity to contamination, cost, and lack of portability [49]. Current protein detection methods, such as enzyme-linked immunoabsorbent assay (ELISA), allow the detection of proteins concentrations at which the disease is often advanced. More sensitive methods based on nanomaterials would revolutionize physical treatment of many cancer types and diseases [49].

Smart nanophase extractors. Differentially functionalized nanotubes are used as smart nanophase extractors, with molecular-recognition capabilities, to remove specific molecules from solutions [49].

4.5.10 Treatment for local anesthetic toxicity: Local anesthetic can be sometimes very toxic, ranging from local neurotoxicity to cardiovascular collapse and coma. In addition to conventional therapies, drug-scavenging nanoparticles have shown to increase survival rate from no animals in the control group to all animals in the treated group [49].

4.6 Pollution remediation

Although research on environmental applications of nanoparticles is still a new area, it is growing rapidly. The potential of nanoparticles to react with pollutants in the air, soil, and water and transform them into harmless compounds is currently being researched. Nanotechnology could be applied at both ends of the environmental spectrum, to clean up existing pollution and to decrease or prevent its generation (see below) [49].

4.6.1 Elimination of pollutants: Due to their enhanced chemical activity, nanomaterials can be used as catalysts to react with toxic gases (such as carbon monoxide and nitrogen oxide) in automobile catalytic converters and power generation equipment. This could prevent gaseous environmental pollution arising from burning gasoline and coal. Paints that absorb noxious gases from vehicle exhaust have already been developed. They contain 30 nm spherical nanoparticles of titanium oxide and calcium carbonate mixed in a silicon-based polymer, polysiloxane, and absorb nitrogen oxide gases from vehicle exhausts, a pollution source that can cause smog and respiratory problems. The porous polysiloxane lets the nitrogen oxide gases diffuse and adhere to the titanium dioxide particles. UV radiation from sunlight converts nitrogen oxide to nitric acid, which is then neutralized by the calcium carbonate. The lifetime of the paint is said to be up to 5 years.

<u>**4.6.2** Water Remediation:</u> Iron nanoparticles with a small content of palladium are tested to transform harmful products in groundwater into less harmful end products. The nanoparticles are able to remove organic chlorine (a carcinogen) from water and soil contaminated with the chlorine-based organic solvents (used in dry cleaners) and convert the solvents to benign hydrocarbons.

4.7 Cosmetics

Titanium dioxide and zinc oxide become transparent to visible light when formed at the nanoscale, however are able to absorb and reflect UV light, being currently used in sunscreens and in the cosmetic industry. More cosmetics products containing nanoparticles [49].

4.8 Coatings

Nanomaterials have been used for very thin coatings for decades, if not centuries. Today thin coatings are used in a vast range of applications, including architectural glass, microelectronics, anticounterfeit devices, optoelectronic devices, and catalytically active surfaces. Structured coatings with nanometerscale features in more than one dimension promise to be an important foundational technology for the future [49].

<u>4.8.1 Self-cleaning windows:</u> Self-cleaning windows have been demonstrated that are coated in highly hydrophobic titanium dioxide. The titanium dioxide nanoparticles speed up, in the presence of water and sunlight, the breakdown of dirt and bacteria that can then be washed off the glass more easily [49].

<u>4.8.2 Scratch resistant materials</u>: Nanoscale intermediate layers between the hard outer layer and the substrate material significantly improve wear and scratch resistant coatings. The intermediate layers are designed to give a good bonding and graded matching of mechanical and thermal properties, leading to improved adhesion [49].

<u>4.8.3 Textiles:</u> Nanoparticles have already been used in coating textiles such as nylon, to provide antimicrobial characteristics, also the control of porosity at the nanoscale and surface roughness in a variety of polymers and inorganic materials led to ultrahydrophobic - waterproof and stain resistant fabrics [49].

4.9 Materials

<u>4.9.1 Insulation materials:</u> Nanocrystalline materials synthesized by the sol-gel technique exhibit a foam-like structure called an "aerogel". Aerogels are composed of three-dimensional, continuous networks of particles and voids. Aerogels are porous, extremely lightweight, and have low thermal conductivity [49].

4.9.2 Nanocomposites: Composites are materials that combine two or more components and are designed to exhibit overall the best properties of each component (mechanical, biological, optical, electric, or magnetic). Nanocomposites containing CNT and polymers used to control their conductivity are interesting for a wide range of applications, such as supercapacitors, sensors, solar cells, etc. [49].

<u>4.9.3 Paints</u>: Nanoparticles confer enhanced desired mechanical properties to composites, such as scratch resistant paints based on encapsulated nanoparticles. The wear resistance of the coatings is claimed to be ten times greater than that for conventional acrylic paints [49].

4.10 Mechanical engineering

<u>4.10.1 Cutting tools</u>: made of nanocrystalline materials (such as tungsten carbide, WC) are much harder than their conventional due to the fact that the microhardness of nanosized composites is increased compared to that of microsized composites [49].

<u>4.10.2 Lubricants:</u> Nanospheres of inorganic materials could be used as lubricants, acting as nanosized ball bearings [49].

4.11 Advantages and Disadvantages of Nanotechnology

While nanotechnology is seen as the way of the future and is a technology that a lot of people think will bring a lot of benefit for all who will be using it, nothing is ever perfect and there will always be pros and cons to everything. The **advantages and disadvantages of nanotechnology** can be easily enumerated, and here are some of them [50]:

4.11.1 Advantages of Nanotechnology

To enumerate the advantages and disadvantages of nanotechnology, let us first run through the good things this technology brings:

- Nanotechnology can actually revolutionize a lot of electronic products, procedures, and applications. The areas that benefit from the continued development of nanotechnology when it comes to electronic products include nano transistors, nano diodes, OLED, plasma displays, quantum computers, and many more.
- Nanotechnology can also benefit the energy sector. The development of more effective energy-producing, energy-absorbing, and energy storage products in smaller and more efficient devices is possible with this technology. Such items like batteries, fuel cells, and solar cells can be built smaller but can be made to be more effective with this technology.
- Another industry that can benefit from nanotechnology is the manufacturing sector that will need materials like nanotubes, aerogels, nano particles, and other similar items to produce their products with. These materials are often stronger, more durable, and lighter than those that are not produced with the help of nanotechnology.
- In the medical world, nanotechnology is also seen as a boon since these can help with creating what is called **smart drugs**. These help cure people faster and without the side effects that other traditional drugs have. You will also

find that the research of nanotechnology in medicine is now focusing on areas like tissue regeneration, bone repair, immunity and even cures for such ailments like cancer, diabetes, and other life threatening diseases.

4.11.2 Disadvantages of Nanotechnology

When tackling the advantages and disadvantages of nanotechnology, you will also need to point out what can be seen as the negative side of this technology:

- Included in the list of disadvantages of this science and its development is the possible loss of jobs in the traditional farming and manufacturing industry.
- You will also find that the development of nanotechnology can also bring about the crash of certain markets due to the lowering of the value of oil and diamonds due to the possibility of developing alternative sources of energy that are more efficient and won't require the use of fossil fuels. This can also mean that since people can now develop products at the molecular level, diamonds will also lose its value since it can now be mass produced.
- Atomic weapons can now be more accessible and made to be more powerful and more destructive. These can also become more accessible with nanotechnology.
- Since these particles are very small, problems can actually arise from the inhalation of these minute particles, much like the problems a person gets from inhaling minute asbestos particles.
- Presently, nanotechnology is very expensive and developing it can cost you a lot of money. It is also pretty difficult to manufacture, which is probably why products made with nanotechnology are more expensive.

Conclusions & Recommendations

5.1 Conclusions

- 1- Nanomaterials are modern materials that are used in many engineering, medical and electronic applications.
- 2- Nanomaterials are distinguished from other materials that give them an increase in mechanical properties as a result of the uniform distribution of their molecules and the absence of agglomerations.
- 3- Nanomaterials are prepared in two methods are: Top-Down Method and Bottom-Up Method.
- 4- Nanomaterials are detected by several methods are (SEM, TEM, EDX, FTIR, TGA and XRD).

5.2 Recommendations

Nanotechnology is at the forefront of the most important and exciting fields of physics, chemistry, biology, engineering and many other fields. It has given great hope for scientific revolutions in the near future that will change the direction of technology in many applications. Therefore, it is necessary to establish a special laboratory for the tests of nanomaterials, including devices and equipment that fall within the scope of their preparation, detection methods and measurement of their granular size.

References

[1] Alagarasi, A, "INTRODUCTION TO NANOMATERIALS", D. G. Vaishnav college, Department of Chemistry, Ph.D. (Chemistry), November 2016.

[2] N.S. Wigginton, K.L. Haus, M.F. Hochella Jr, Aquatic environmental nanoparticles, J. Environ. Monit. 9 (12) (2007) 1306-1316.

[3] Y. Shao, H.P. Zhao, X.Q. Feng, Optimal characteristic nanosizes of mineral bridges in mollusk nacre, RSC Adv. 4 (61) (2014) 32451-32456.

[4] S. Keten, M.J. Buehler, Atomistic model of the spider silk nanostructure, Appl. Phys. Lett. 96 (15) (2010) 153701.

[5] Firdos Alam Khan, "Applications of Nanomaterials in Human Health", Department of Stem Cell Biology, Imam Abdulrahman Bin Faisal, University Dammam, Saudi Arabia.

[6] Tawfik A. Saleh, "Nanomaterials: Classification, Properties, and Environmental toxicities", Journal "Environmental Technology & Innovation", 20 (2020) 101067.

[7] Kumar N, Kumbhat S. Essentials in Nanoscience and Nanotechnology. Hoboken, NJ, U.S.A.: John Wiley & Sons, Inc.; 2016. Carbon-Based Nanomaterials; pp. 189–236.

[8] Gleiter, H., 2000. Nanostructured materials: basic concepts and microstructure. Acta Mater. 48, 1–29.

[9] Tian, Y., Xue, F., Zhou, "Structural and Physical Properties of Ti-doped BiFeO₃ nanoceramics. Ceram. Int., 44, 4287-4291, 2018.

[10] Sobierajska, P., Dorotkewicz-Jack, "Preparation and Antimicrobial Activity of the Porous Hydroxyapatite Nanoceramics. Journal Alloys Compd. 748, 179-187, 2018.

[11] Xu, X., Yang, Y., Wang et al., "Low-Temperature Preparation of $Al_2O_3 - ZrO_2$ via Pressure less Sintering Assisted by Amorphous Powders. Journal Alloys Compd. 783, 806-812, 2019.

[12] Yan, Joharian, M., Naghloo, et al., "Metal- Organic Framework Derived Porous 2D Semiconductor C/ZnO Nanocomposite with High Electrical Conductivity. Mater- Lett. 252, 325-328, 2019.

[13] Yang, X., Lian, et al., "Selective Uptake of Chitosan Polymeric Micelles by Circulating Monocytes for Enhanced Tumor Targeting. Carbohydr. Polymers 229, 115435, 2020.

[14] Sur, S., Rathore, A., et al., "Recent Developments in functionalized Polymer Nanoparticles for Efficient drug Delivery system"., Nano-struct. Nano- Object. 20, 100397, 2019.

[15] Gharieh, A., Khoee, S., "Emulsion and miniemulison techniques in preparation of polymer nanoparticles with versatile characteristics"., Adv. Colloid Interface Sci. 269, 152-186, 2019.

[16] Okrugin, B.M., Neelov, I.M., Borisov, "Structure of asymmetrical peptide dendrimers: Insights given by self- consistent field theory"., Polymer 152, 292-302, 2017.

[17] Fu, S., Sun, Huang, Z., "Some Basic aspects of Polymer nanocomposites": A critical review, Nano Mater. Sci. 1, 2-30, 2019.

[18] Tiwari JN, Tiwari RN, Kim KS, "Zero-dimensional, one-dimensional two-dimensional and three-dimensional nanostructured materials for advanced electrochemical energy device. Prog Mater Sci 57:724–803, 2012.

[19] Pokropivny VV, Skorokhod VV, "Classification of nanostructures by dimensionality and concept of surface forms engineering in nanomaterial", science. Mater Sci Eng C 27:990–993, 2007.

[20] Hochella MF Jr, Spencer MG, Jones KL, "Nanotechnology: nature's gift or scientists' brainchild", Environ Sci Nano 2:114–119, 2015.

[21] Sharma VK, Filip J, Zboril R, Varma RS, "Natural inorganic nanoparticles–formation, fate, and toxicity in the environment", Chem Soc Rev 44:8410–8423, 2015.

[22] Wagner S, Gondikas A, Neubauer E, Hofmann T, von der Kammer F, "Spot the difference: engineered and natural nanoparticles in the environment—release, behavior, and fat". Angew Chem Int Ed 53:12398– 12419, 2014. [23] Shibata S, Aoki K, Yano T, Yamane M, "Preparation of silica microspheres containing Ag nanoparticles", J Solgel Sci Technol 11:279, 1998.

[24] Hahn H, "Gas phase synthesis of nanocrystalline materials", Nanostruct Mater 9:3, 1997.

[25] Watson S, Beydoun D, Scott J, Amal R, "Studies on the preparation of magnetic photocatalysts", J Nanopart Res 6, 2004.

[26] Yang J, Mei S, Ferreira JMF, "The effect of F–doping and temperature on the structural and textural evolution of mesoporous TiO_2 powders", Mater Sci Eng B C15, 2001.

[27] Carp O, Huisman CL, Reller A, "Photoinduced reactivity of titanium dioxide", Prog Solid State Chem 32:33, 2004.

[28] Yin H, Wada Y, Kitamura T, Kambe S, Murasawa S, Mori H, Sakata T, Yanagida S, "Hydrothermal synthesis of nanosized anatase and rutile TiO₂ using amorphous phase TiO₂", J Mater Chem 11:1694–1703, 2001.

[29] Kim CS, Okuyama K, Nakaso K, Shimada M, "Direct measurement of nucleation and growth modes in titania nanoparticles generation by a CVD method", J Chem Eng Jpn 37(11):1379, 2004.

[30] Cao Y, Yang W, Zhang W, Liub G, Yue P, "Improved photocatalytic activity of Sn4b doped TiO₂ nanoparticulate films prepared by plasmaenhanced chemical vapor deposition", New J Chem 2(8):218–222, 2004.

[31] Gracia F, Holgado JP, Caballero A, Gonzalez-Elipe AR, "Structural, optical, and photoelectrochemical properties of Mn+-TiO₂ model thin film photocatalysts", J Phys Chem B 108(45):17466–17476, 2004.

[32] Kim C, Nakaso K, Xia B, Okuyama K, Shimada M, "A new observation on the phase transformation of TiO₂ nanoparticles produced by a CVD method", Aerosol Sci Technol 39(2):104–112, 2005.

[33] Liang C, Shimizu Y, Sasaki T, Koshizaki N, "Synthesis, characterization, and phase stability of ultrafine TiO_2 nanoparticles by pulsed laser ablation in liquid media", J Mater Res 19(5):1551–1557, 2004.

[34] Nagaveni K, Hegde MS, Madras G, "Structure and photocatalytic activity of Ti1-x MxO₂; (M = W, V, Ce, Zr, Fe, and Cu) synthesized by

solution combustion method", J Phys Chem B 108(52):20204–20212, 2004.

[35] Jinsoo K, Jae Won L, Tai Gyu L, Suk Woo N, Jonghee H, "Nanostructured titania membranes with improved thermal stability", J Mater Sci 40(7):1797–1799, 2005.

[36] Nagaveni K, Hedge MS, Ravishankar N, Subbanna GN, Madras G, "Synthesis and structure of nanocrystalline TiO₂ with lower band gap showing high photocatalytic activity", Langmuir 20:2900–2907, 2004.

[37] Lee EJ, Huh BK, Kim SN, Lee JY, Park CG, Mikos AG, Choy YB, "Application of materials as medical devices with localized drug delivery capabilities for enhanced wound repair", Prog Mater Sci 89:392–410, 2017.

[38] Van de Krol R, Goossens A, Schoonman J, "In situ X-ray diffraction of lithium intercalation in nanostructured and thin film anatase TiO₂", J Electrochem Soc 144, 1997.

[39] Wu X, Jiang QZ, Ma ZF, Fu M, Shangguan WF, "Synthesis of titania nanotubes by microwave irradiation", Sol State Comm 136:513–517, 2005.

[40] Chen X, Mao SS, "Titanium dioxide nanomaterials: synthesis, properties, modifications, and applications", Chem Rev 107:2891, 2007.

[41] Bui, T.M.A, Nguyen, "Investigation of crosslinking, mechanical properties and weathering stability of acrylic polyurethane coating reinforced by SiO₂ nanoparticles", issued from rice husk ash. Mater. Chem. Phys. 241, 122445, 2020.

[42] Jeon, H., Lee, K., "Effect of gold nanoparticle morphology on thermal properties of polyimide nanocomposite film. Colloids surf. A579, 123651, 2019.

[43] Akhtar S, Rehman S, Almessiere MA, Khan FA, Slimani Y, Baykal A., "Synthesis of Mn0.5Zn0.5SmxEuxFe1.8-2xO4 nanoparticles via the hydrothermal approach induced anticancer and anti-bacterial activities", Nanomat (Basel) 9(11):1635, 2019.

[44] Akhtar S., "Transmission electron microscopy of graphene and hydrated biomaterial nanostructures: novel techniques and analysis", Uppsala University [urn:nbn:se:uu:diva:171991], 2012.

[45] Winter M., "FTIR and DEMS investigations on the electroreduction of chloroethylene carbonate-based electrolyte solutions for lithium-ion cells", J Power Sources 81-82:818–823, 1999.

[46] Vizintin, "Poly(phenanthrene quinone)/graphene cathode material and investigation of its redox mechanism through operando ATR-IR spectroscopy in Li- and Mg- batteries", Chem Sus Chem 13, 2020.

[47] Misture ST, Snyder RL, "X-ray Diffraction. In: Buschow KHJ et al (eds) Encyclopedia of materials: science and technology", Elsevier, Oxford, pp 9799–9808, 2001.

[48] K. Donaldson, V. Stone, C. Tran, W. Kreyling, and P. J. A. Borm, Occup. Environ. Med. 61, 727, 2004.

[49] Cristina B., Ivan I., Kevin R., "Nanomaterials and nanoparticles: Sources and toxicity", Biointerphases, Vol. 2, No. 4, December 2007.

[50] Ruslan Valiev, "Nanomaterial advantage", Nature Publishing Group, Vol 419, 31 October 2002.

الخلاصة

تكتسب المواد النانوية أهمية في التطبيقات التكنولوجية نظرًا لخصائصها الكيميائية والفيزيائية والميكانيكية القابلة للضبط والأداء المحسن نتيجة لانها تمتاز بمساحة سطحية كبيرة عند مقارنتها بنظير اتها الأكبر حجمًا .تقدم هذه الدراسة ملخصًا للأنواع العامة من المواد النانوية وتقدم لمحة عامة عن طرق التحضير للدقائق النانوية وتوظيفها عبر التفاعلات التساهمية أو غير التساهمية عامة عن طرق التحضير للدقائق النانوية وتوظيفها عبر التفاعلات التساهمية أو غير التساهمية معامة من المواد النانوية ويقدم لمحة عامة عن طرق التحضير للدقائق النانوية وتوظيفها عبر التفاعلات التساهمية أو غير التساهمية باستخدام طرق مختلفة و يسلط الضوء على التقنيات المستخدمة لتوصيف الدقائق النانوية ويناقش خصائصها الفيزيائية والكيميائية .نظرًا لخصائصها الفريدة ، تمتلك المواد النانوية العديد من التطبيقات وأصبحت جزءًا من حياتنا اليومية .نتيجة لذلك ، تكتسب هذه الدراسة اهتمامًا نظرًا لأن بعض الدقائق النانوية لا تتدهور بسهولة بسبب البيئة .وبالتالي ، فإن هذه الدراسة تسلط الضوء ألغن



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