Chapter 1

General Introduction and Literature Survey

1.1 Historical Overview of Nano

Nanotechnology could not have a specific determination era up till now. An early preoccupation history of nano and how nanoscience incorporated in the world around us started in 1959 when Richard P. Feynman (Nobel Prize in physics 1965) given his a popular talk Entitled, "*there is Plenty of Room at the Bottom*" at American Physical Society. This lecture described the controlling of particle and atom with its manipulating and dealing with small size problems [1, 2]. The first use of "Nanotechnology" invented in 1974 when Norio Taniguchi described the semiconductor processes in nanometer, "The nanotechnology concerned to separation, fusion, and reformation of the material by one atom or one molecule [2].

The implementation has begun with the National Nanotechnology Initiative (NNI) at California Institute of technology after President William J. Clinton gave a speech about the importance of nanoscale science and allotment in the first of the 21st century. Followed that, President George W. Bush said the 21st century is nanotechnology research and its improvement [1, 2].

Nowadays, the nanoscience revolution is getting progressively increase in modern centuries. Nanotechnology has variable research and studies about its concept, material fabrication, and application.

1.2 Definition of Nanometer Scale, Nanoscience, and Nanotechnology

Nanometer and Nanoscale: Word Nano is derived from the Greek Language nános (νάνος) that mean "dwarf" in English [3]. Nano is an SI prefix unit which used to denote a part of one-billionth of a meter, standard by multiplying 10^{-9} as a factor.

How big are one billion meters? It helps to put these numbers into perspective. The human hair width is approximately 40000-60000 nm, a diameter of human DNA is around 2-12 nm, and a single atom size is about several angstroms (0.1 nm) [4]. Therefore, one nanometer would be invisible to human eyes [5]. **Figure 1.1** illustrates the comparison between nanoscale with other scales.
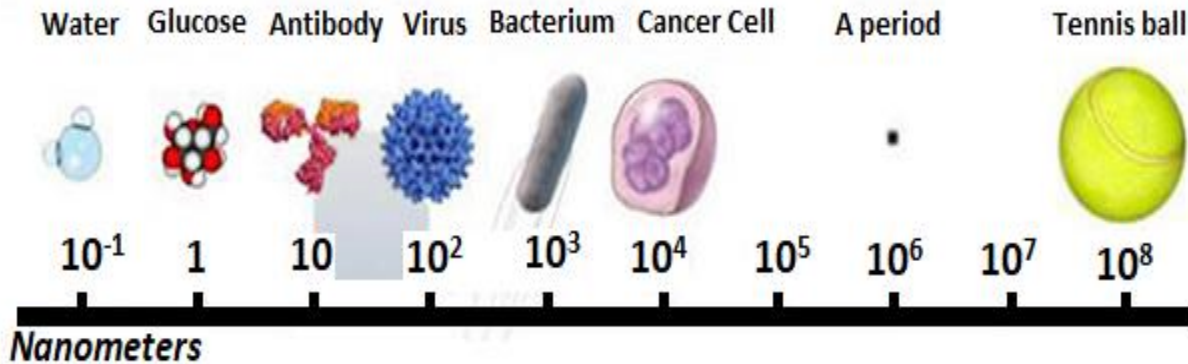
Figure 1.1: Comparison of the nanometer scale with other scales.

Nanoscience is a part of science that studies and deals with phenomena that occur at a small scale (nanometer) structure of atoms and molecules [4].

Nanotechnology is the technology that able to invent new material or instruments in the nanoscale range [6, 7] or enhance the ability of application or product [4]. The nano techniques have applied in the whole world from different fields such as physics, chemistry, biology, and engineering [7].

1.3 Classification of Nanomaterials Based on Dimensions

Nano-objects mostly categorized into four parameters: nanoparticle geometry, morphology, uniformity, and agglomeration [8]. According to nanoparticle geometry, nanomaterials were classified as a zero dimension (0-D), one dimension (1-D), two dimensions (2-D), and three dimensions (3-D).
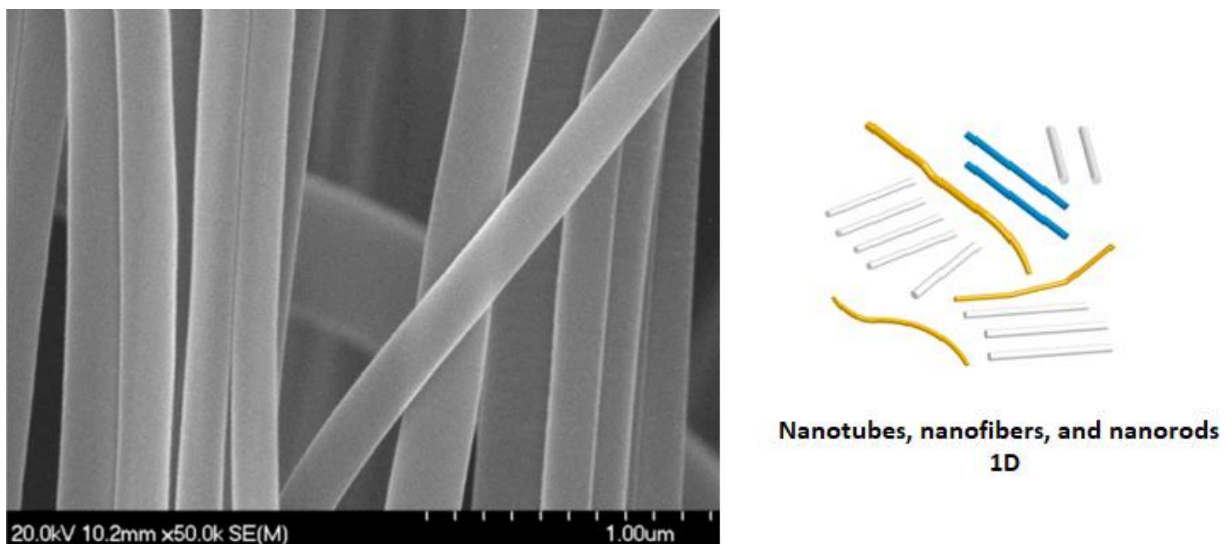
1.3.1 Zero-Dimension (0-D) Nanomaterials

The total particulate in 0-D is in the nanometer range, which generally referred to as nanoparticle cluster and quantum dots [8] **Figure 1.2**. 0-D nanomaterials have a large surface area, which leads up to chemical and physical affect properties [9]. Various physical and chemical preparation techniques could be performed to control the shape, size, and structure of the particles in zero-dimensional materials. Physical synthesized including sputtering process, flame pyrolysis, laser ablation, and so on, while chemical route includes sol-gel and hydrothermal technique. Most important to note, the 0-D fabricated materials could agglomerate due to high surface energy in a physical approach, not withstand chemical routes [9].
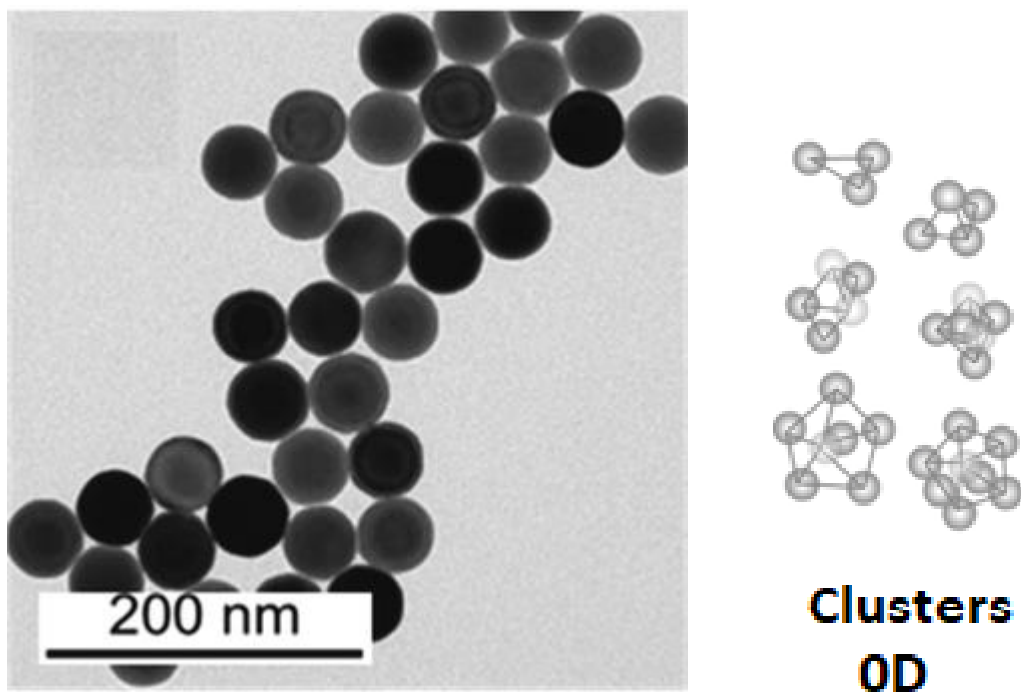
Figure 1.2: TEM of gold spherical nanoparticles and cluster in zero dimension [10].

1.3.2 One-Dimension (1-D) Nanomaterials

One-dimension nanoparticles have two-dimensions at the nanometer scale while the third dimension could exist at the microscale; this means that the confinements were done in two dimensions only. Nanotubes, nanowires, and nanofibers are an example of two-dimension nanomaterials [9, 11] **Figure 1.3**. One-dimensions have specified properties such as high tensile strength, magnificent adsorption, and a high degree contrast of displays [9]. Many physical and chemical methods can be used to prepare 1-D nanomaterials as thermal evaporation, sputtering techniques electrospinning, electrochemical deposition, electrochemical anodization, and lithographic, etc.[9].


Figure 1.3: SEM of carbon nanofibers as an example of a 1-dimension of nanomaterials [12].

1.3.3 Two-Dimension (2-D) Nanomaterials

Two-dimension nanomaterials defined as a one-dimension of particulate at the nanoscale range; however, the other two dimensions in the microscale. These mean that the confinements were applied in one dimension. Thin-film coating,

nanosheet, and nanolayer are an example of two-dimension nanomaterials as [8, 9] **Figure 1.4**. A typical representation of the 2D fabricated method includes physical vapor deposition (PVD), chemical vapor deposition (CVD), dip-coating [9].
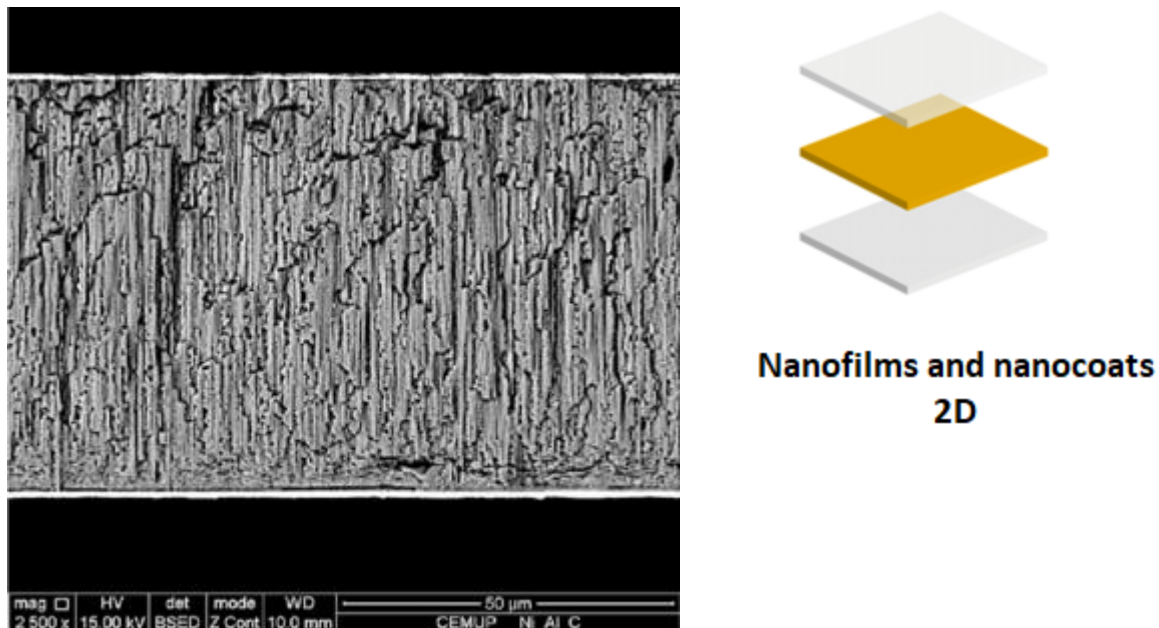
Figure 1.4: SEM of Ni/Al nanolayers as an example of 2-dimension nanomaterials [13].

1.3.4 Three-Dimension (3-D) Nanomaterials

The particulate is defined as all dimensions on the microscale range and no dimension in the nanoscale range, 3D nanomaterials are classified as material are not confined to the nanoscale level [9, 14]. The movement of electrons in this dimension is delocalized; in this case the electron moves within all dimensions [14]. Moreover, 3D nanomaterials can be containing the dispersion of 0D, 1D, or 2D [9]. The most common representation of three-dimension nanosystem is (bulk) polycrystals material [11] **Figure 1.5**.
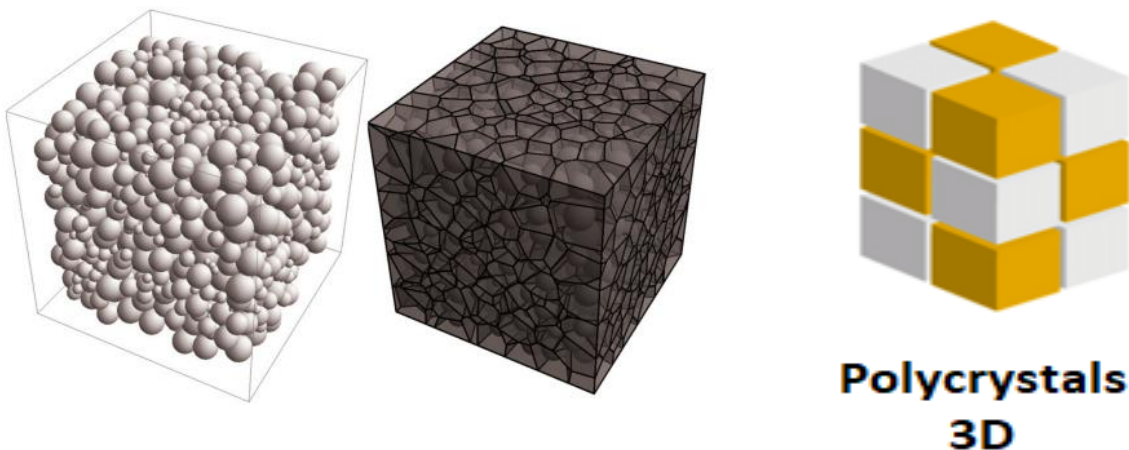
Figure 1.5: *Bulk polycrystal structure as an example of 3-dimension nanomaterials [15].*
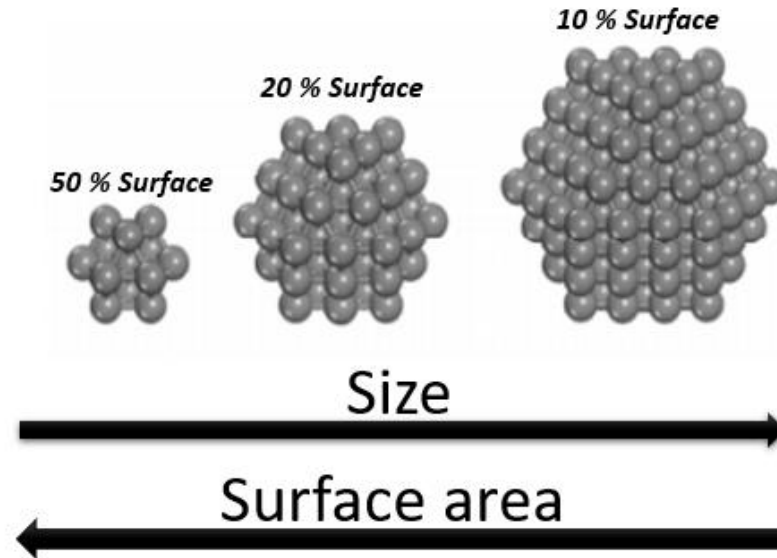
1.4 Properties of Nanomaterials

1.4.1 Surface Energy of Nanomaterials

One of the main parameters of high interest with respect to nanoscale materials is that the massive variation of other larger-scale materials is a surface area to volume ratio. Surface area to volume ratio in nanosized material has a significant effect on in their catalytic properties because of the increase in the surface area allowed to molecules or atoms to overpopulated on the surface, and thus the energy of the surface will be growth [16]. A primary concern, the nanocrystal has a large surface area, which leads to performing more chemical reactions [16].

The surface area to volume ratio of the sphere nanoparticle with radius (r) which equivalent to the ratio $\frac{s}{v} = \frac{3}{r}$ mean, the surface energy was affected by the radius of the nanoparticle [6]. For instance, about 50 % of molecules located at the surface when the spherical nanoparticles have a size 3 nm while 20 % of atoms expressed the surface for the spherical nanoparticles have a 10 nm approximately.

Moreover, around 10% of molecules would be at the surface of the nanoparticle has 30 nm [16] **Figure 1.6**.

Figure 1.6: *Schematic image explains the relation between surface area and particle size.*

1.4.2 Quantum Size Effect of Nanomaterials

The optical properties of the semiconductor structure could make exciting differences in the same nanomaterial with different sizes because of its effect on the bandgap. These optical properties are related to electronic properties that depend on the number of atoms on the particle. The change occurs in electronic properties related to quantum mechanics effects [6].

There is no confinement for electrons and holes in a bulk semiconductor due to its continuous energy, where the energy level state is convergent. Highest occupied band (valence band) and lowest unoccupied band (conduction band) separated by the energy gap (E_g) [17] **Figure 1.7**.

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The quantum size could be distinguished when the energy level between the two bands becomes excellent. The bands have discrete nature, and the wave function of nanostructure semiconductor of an electron is localized, e.g., quantum dot the entire bulk in semiconductor its electronic wave function is delocalized [6].
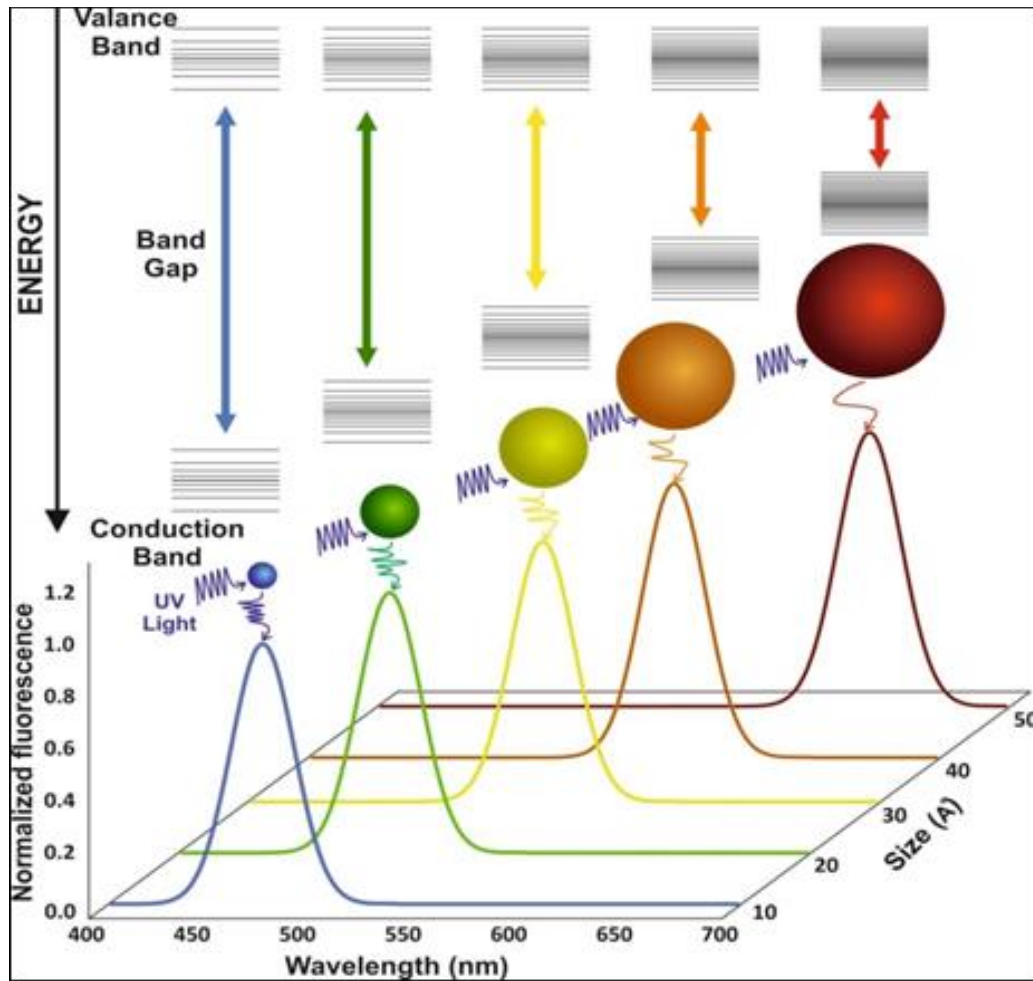
Figure 1.7: The comparison between particle size and energy gab [18].

Exciton in Nanoparticle is a consequence interaction between the promoted electron in the conduction band and left a hole behind in the valance band [19] **Figure 1.8**. A couple of electron-hole bond form attraction reaction such as a hydrogen atom, which has a separation in the middle denoted a Bohr's radius [17].
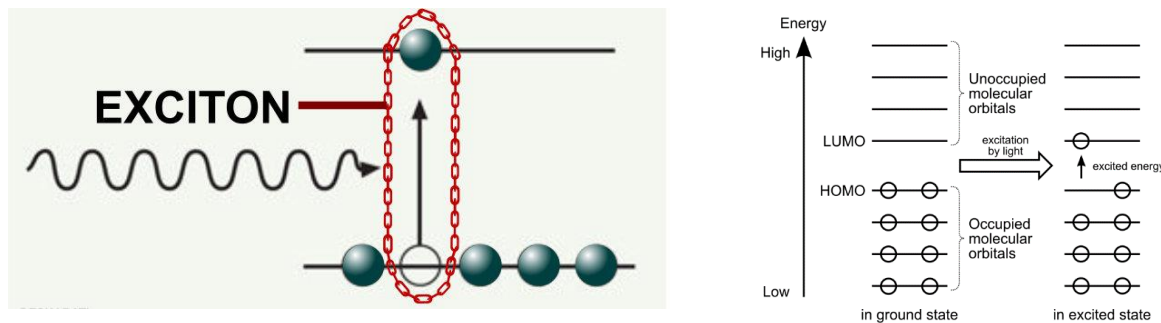
Figure 1.8: *Schematic illustrate the exciton between (HOMO-LUMO) band gab.*

1.4.3 Mechanical Properties of Nanomaterials

The mechanical properties aid a lot in the proper design of nanomaterials; hence of particle size decreases, the nanomaterial distinctive with large surface area to volume ratio [20]. The influence of increasing surface per volume, cause enormous alteration in crystal mechanical properties such as stress, strain, elastic modulus, hardness, adhesion, and friction [20, 21].

Stress is defined as the force per unit area of material, its expressed as

$$\sigma = F/A \tag{1.1}$$

Where the Greek litter sigma σ represents stress, F is the applied force, and A is a cross-section area of the object [14]. The unit of stress N/m^2.

Strain the material responding to the acting force (tension or compression) alter length or volume. In other words, the rate change in length dimension to original length [14] is defined as the following equation

$$\varepsilon = \Delta L/L_\circ \tag{1.2}$$

$$\varepsilon = \Delta V/V_\circ \tag{1.3}$$

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Where **Eq. (1.2)** act as a linear strain and **Eq. (1.3)** is volume strain Greek letter epsilon ε represents strain, L is the length, and V refers to volume [14].

Elasticity is the ability of materials to resist a distorting impact attempting to returns its original shape and size when the influence force removed. The relation between stress and strain denoted as elastic modulus [14]. Its shown in **Eq. (1.4)**

$$E = \sigma/\varepsilon \quad\quad\quad\quad\quad (1.4)$$

Where E refers to elastic modulus, and Greek letters σ and ε represent stress and strain, respectively. Moreover, stress is proportional to strain.

Hardness is the ability of materials to resist penetration or indentation in its shape and size [22].

Adhesion is the tendency of different particles or surfaces to bond or stick together. It also defined as the attraction force between substances that bring them into contact [23, 24].

Friction is the attractive force between two adhesive particles or surfaces, caused difficult movement to each other [24].

When the nanomaterial distinctive as hardness and strength, its flexibility will be decreasing follow that lowering in nano robustness comparing with conventional grain size. Briefly, the material's strength correspondingly increases with minimizing particle size [14].

An example in term of mechanical behavior would be changed in nanomaterial properties, the bulk material of copper element is ductile while the copper particles which have 50 nm are strength [25]. As a consequence of maximizing strengths and minimize ductility, copper nanoparticles with size ($<$ 20

nm) are brittle. Through variation of stress and strain, the material could be classified into either brittle or ductile [14].

1.4.4 Magnetic Properties of Nanomaterials

Magnetism is a physical phenomenon that leads material to exchanges its behavior responding to the external magnetic field [14, 26]. The magnetic phenomenon is produced from particle movement by an effect on both electric charge and mass. A particle is referring to electrons, holes, and protons. In addition to its charge might be positive or negative ions. A magnetic dipole arises from the movement of the electric charge and separated by a small distance [27].

Magnetic nanoparticle could be classified into paramagnetic and diamagnetic due to its electron pair state [14].

Diamagnetic materials that have no unpaired electrons and the net of magnetic moment is zero in case no external field applied **Figure 1.9** while in case of an external magnetic field exist; it showed a very weak response it might repel magnetic field. Also, when the external magnetic field removed, the magnetization domain will lose; hence that, the diamagnetic materials could be classified as temporary magnetization [14, 26].

Figure 1.9: Schematic diagram illustrates the diamagnetic materials.

Paramagnetic, the material has unpair electrons and has permanent magnetization domain, as shown in **Figure 1.10**. It has zero magnetic fields in the absence of an

external field, while in the exhibit of the external magnetic field, the net of the magnetic field increase, and it could be attractive [14, 26].
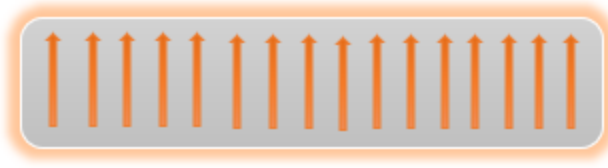

Figure 1.10: Schematic diagram illustrates the paramagnetic materials.

Superparamagnetic are the materials that have a magnetic form and appear insufficiently small domain number and particle size of ferromagnetic materials; it caused by the thermal energy of multi-domain particles under Curie temperature (the temperature above ferromagnetic substance loses its ferromagnetism and becomes paramagnetic) **Figure 1.11** [28, 29].

Figure 1.11: Schematic diagram illustrates the superparamagnetic materials.

Ferromagnetic the intrinsic materials that have natural magnetization properties even if the external magnetic field was absent. Moreover, the atomic magnetic moment configured in parallel domain **Figure 1.12** [14].
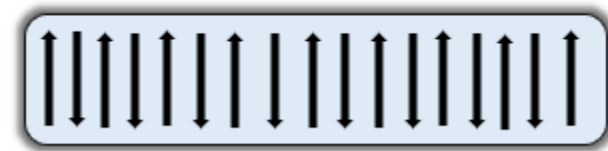
Figure 1.12: Schematic diagram illustrates the ferromagnetic materials.

Ferrimagnetic materials whose atoms or ions arranged as an antiparallel magnetic moment in the presence of external magnetic fields while in the absence case, the magnetization domain will be rearranged randomly and cancel out their magnetic field **Figure 1.13** [27].

*Figure 1.13: Schematic diagram illustrates the ferrimagnetic materials.*

Antiferromagnetic materials that have two different atoms, these atoms are equal in magnitude and configured in antiparallel direction. Due to that, it has zero magnetic moment **Figure 1.14** [26].

Figure 1.14: Schematic diagram illustrates the antiferromagnetic materials.

The magnetic behavior size specified by the structure domain of magnetic materials. To be more specified, the single domain appears at ferromagnetic material by decreasing size under critical point. Especially important, a small ferromagnetic particle has uniform magnetization at a lower state of free energy. In contrast, the large particles have non-uniform magnetization [27]. The critical size of the single domain might affect various parameters such as saturation value, surface value, surface energy, crystal anisotropy, and particle shape [27].

As the size of the magnetic nanoparticle decrease, the coercivity increase to a maximum value, thereby it would be drastically lower to zeroth **Figure 1.15**. Consequently, the particles become superparamagnetic. Magnetic nanoparticles are almost superparamagnetic because of their nanoscale size [27].
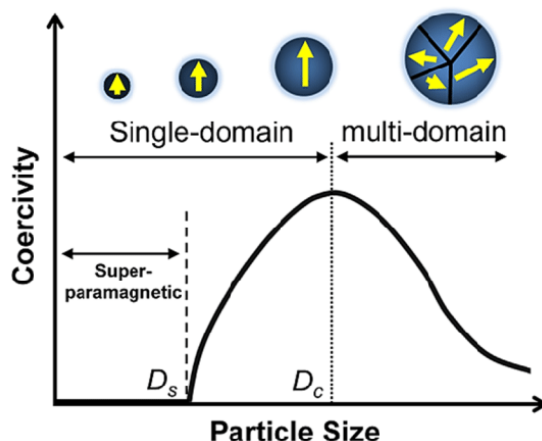
**Figure 1.15:** *The size-dependent coercivity in a magnetic nanoparticle [30].*

1.4.5 Optical Properties of Nanomaterials

The differences in energy between the highest occupied molecular orbital HOMO (valance band) and lowest unoccupied molecular orbital LUMO (conduction band) (HOMO-LUMO) the bandgap changed with changing the nanoparticle size in nanomaterials. These lead to a change in optical properties such as absorption,

emission transitions, and strength line between two bands. All physical and chemical properties in nanoscale materials could also affected by changing its particle size [14, 25]. For instance, the gold element has a yellowish-brown color; however, this color could be change at the nanoscale size; it has a deep red color when its crystal size has 20 nm. Otherwise, pure silver in bulk state is metallic gray, contrasting to yellowish-gray in nanoparticle [25].

The free particle movement determines via dimension of bulk material. Generally, the electronic density state can be affected by one or more-dimension material through that it could be confined. Hence, the quantum wells, quantum wires, and quantum dots would be obtained **Figure 1.16**. As an example of three-dimension materials is a bulk semiconductor where the density state is proportional to $(E - E_{C/_V})^{1/2}$. Quantum well is to dimension material confined the electron movement in 1D while quantum wire system is one dimension where the electrons confined in 2D then pass density of state it is proportional to $(E - E_{C/_V})^{-1/2}$. Eventually, an example of a zero-dimension domain is a quantum dot, where the motion of the electron is confined in 3D [17]. All the above can be affected by energy gap value, which directly changes in optical properties.
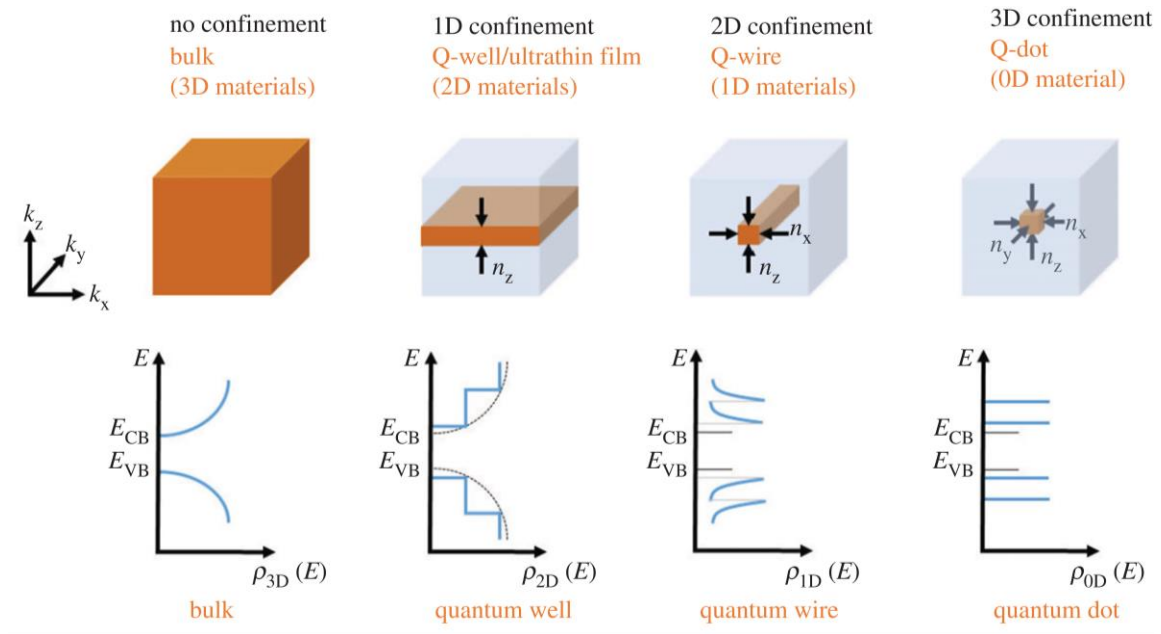
Figure 1.16: *Schematic illustration of broken symmetry and functional form of the density of states in 1D, 2D, and 3D confined materials [31].*

1.5 Preparation of Nanomaterials

The conventional fabrication method of nanostructures building material relies upon two types; the top-down approach and bottom-up approach **Figure 1.17** [1, 32].
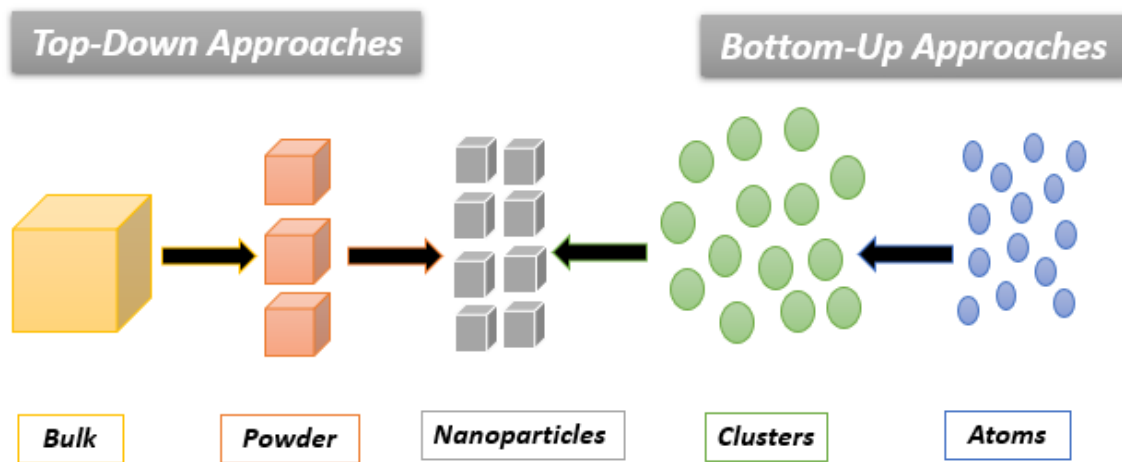

Figure 1.17: *Schematic of nanoparticle Top-Down and Bottom-up approaches [33].*

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1.5.1 Top-Down Method

It is a physical approach that begins engineer bulk material structure to be tiny and extremely nanoscale, e.g., mechanical grinding (ball milling) technique [1, 34].

Ball Milling Technique is a cylindrical sealed container used to blend material into a small scale by using a verity size of the ball, the milling balls fabricated from stainless steel material, which used to crushing structure into more exceptional form [35] by mechanical corrosion **Figure 1.18**. Since the kinetic energy form grinding would transport to particles to perform reduction [34]. The ball milling technique used to produce nanoparticles [36].
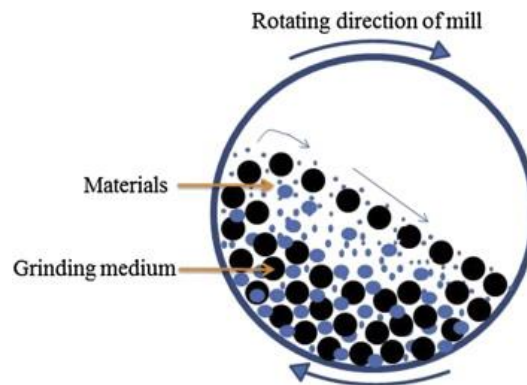
Figure 1.18: Schematic diagram of the ball milling technique [37].

1.5.2 Bottom-Up Method

Nanofabrication approach, which design component starting from atom, molecule, or cluster to be building up one by one, is producing nanoparticles. It would be a physical or chemical method according to its phase [34]. ***A gas-phase route*** which involves plasma arcing and chemical vapor deposition [34]. ***Liquid-phase routes,*** such as sol-gel and self-assembly [34].

Chemical Vapor Deposition is a process used to prepare a thin film with nanoparticle size by changing the phase of the chemical precursor into the vapor

phase by heating in the precursor of inert gas **Figure 1.19**. CVD produces high quality and high-performance thin-film e.g., carbon nanotube, metal, graphene, and diamond [38].
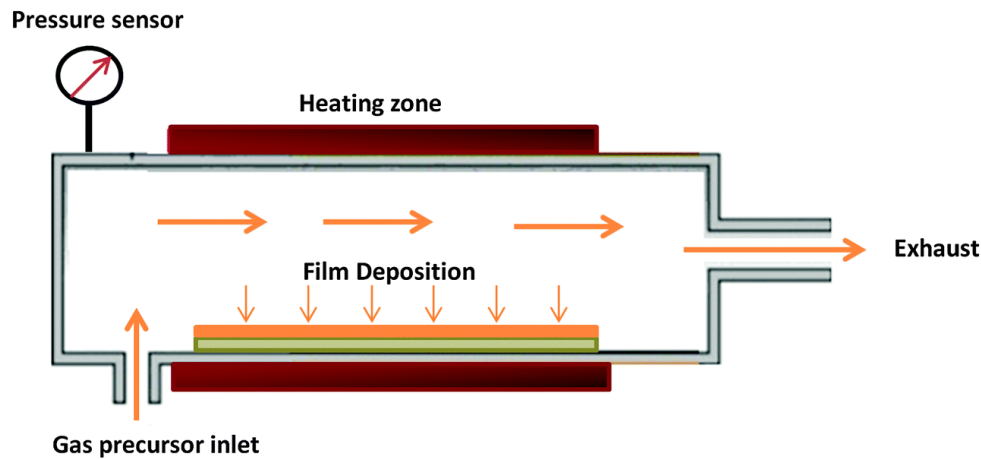
Figure 1.19: Schematic sketch of a chemical vapor deposition (CVD) system [39].

The sol-gel method is a process that uses high purified homogenous liquid precursors or organic polymer to obtain controlled nanoparticle structures in a different size. The colloidal pass through various chemical reactions involves hydrolysis, condensation, nucleation, finally, growth colloidal particles at typical conditions such as temperature, pH, and time **Figure 1.20** [40].
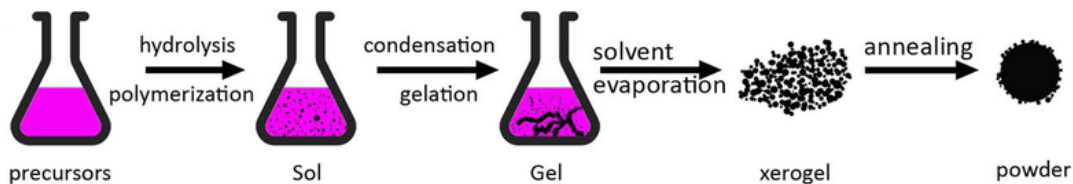
Figure 1.20: Diagram clarifies the mechanism of the Sol-Gel process [41].

Laser Ablation in this method, a laser beam with high frequency was performed to the target (solid material) in order to generate photoionization from heat energy.

Immediately, particles will volatilize as a fog, forming plasma then deposited into the substrate to compose thin-film **Figure 1.21** [42].
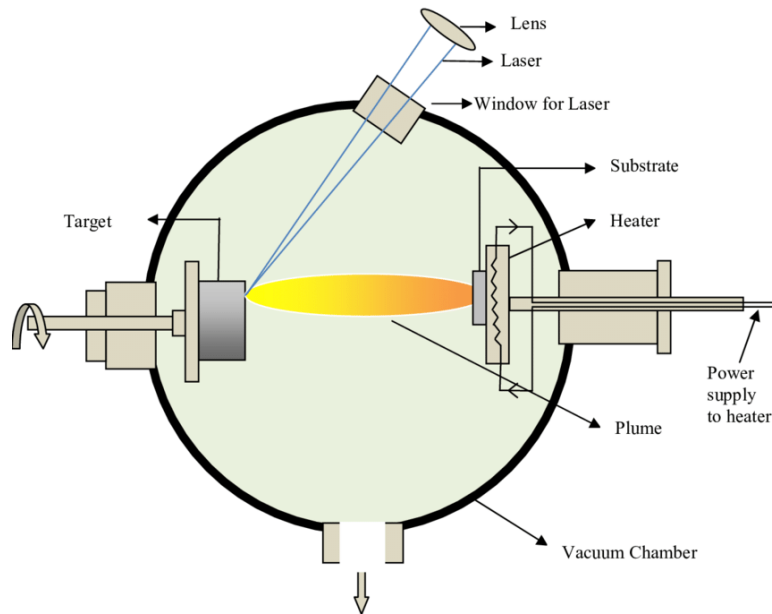
Figure 1.21: Schematic diagram of laser ablation technique [43].

1.5.3 Fabrication of Metal Nanoparticles

The noble metal nanoparticles open new attractive and possible research in various fields, as a result of their individual estimation and properties of utilization. Deposition from the gas phase or laser ablation is a physical approach, while the chemical reaction of liquids is distinguished as a chemical approach. Furthermore, there is another method of nanoparticle creation, which classified as a biological method that uses the microorganisms to produce metal nanoparticle [36].

The typical preparation of nanoparticles in a chemical method is using citrate as capping metal from different salts. Chemical synthesis colloidal particles would be described as spheroids regarding its ratio and size. The centrifugation must be used to separate the nanoparticles from the solvents and unlikable material, which leads to purifying the nanoparticles [36].

1.5.4 Fabrication of Magnetic Nanoparticles

Previously, the synthetic of the super magnetic relaxation was performed in Fe, Co, Ni by electrolysis using mercury cathode. In contrast, modern chemical methods have commonly used specially coating nanoparticles with different surfactants to prohibit agglomeration occurrence. Also, polymers based fabrication methods have been invented to synthesized coated and density uniform clusters of magnetic nanoparticles such as nanoflower [36].

Ferrite nanoparticles have been synthesized by thermal decomposition; its particle size could be diverse by varying the temperature of decomposition, for example, Nickle nanoparticle. While in Iron and Cobalt nanoparticle, the amorphous of the particle could be formed by thermal deposition. Another method could be used to prepare iron nanoparticles by exposing iron nitrides by ammonia at high temperatures. Also, $NaBH_4$ can be adding to the solution for the reduction of metal ions [36].

1.6 Applications of Nanotechnology

1.6.1 In Agriculture and Food

The nanomaterial becomes the most effective of daily life as a significant influence on sustainable agricultural product material. Nanotechnology contributes to enhancing the bioavailability of plants starting from food processing to the end of packaging performance. Including economic benefit, providing safety nutritive stodge, and high quality [44, 45]. The purpose of nanoscience in sustainable agriculture is to minimize diffuse chemical products and reduce nutrient absence in enrichment [46].

A primary concern of using agriculture nanotechnology implementation such as nano fertilizer and nano pesticides is trail product and nutrients standards to maximize advantages of a product without contamination of the soils, waters, and product the plant against insects and other diseases [46].

Nano-sensor is an alternative development that discovers the food component rapidly. Nanosensors associated with modern information and communication technologies provide a verity novel style for different components detection with high precision, divers type nanosensor evolved to obtain different obligations in food examination. For instance, carbon nanotube could be detected cations, anions, and organic components food [44].

1.6.2 In Medicine

Emerging nanotechnologies in the world encourage a medical strategy to be more modified in disease diagnosis and treatment, where the development indicates a novel method for healthcare [47, 48]. The pharmaceutical nanotechnology system could be segmented into two fundamental types, either nanomaterials or nanodevices. Nanomaterials are sub-classified into nanocrystalline and nanostructure; structured nanomaterial comprises nanoparticles, dendrimers, micelles, metallic nanoparticles, etc. [48].

Nanoparticles drug delivery system maintained by lipid polymer capsules to minimize distribution and dissolution, then its concentration is optimized in targeted tumor sites or specified cells [49, 50]. Cancer therapy performing by micelles and liposomes, which is another option for drug delivery agents, which are insoluble drugs due to their hydrophilic and hydrophobic nature, it could be used in magnetic resonance imaging to produce excellent tumor sites image [48].

As a matter of fact, the nanoparticle in medicine could be used in several cases. For instance, multifunctional nanoparticle (intravenous delivery), virus-based nanoparticles (affect as nanocarriers), lipid and polymer nanoparticle (strong effect response), magnetic and metallic nanoparticle (optimizing targeted drug delivery and detecting earlier stage of disease), aerosol dried powder (useful for inhalation pulmonary medication) eventually, smart nanomaterials (regulate via exterior stimulus). Nanotechnology would be used in surgery as flesh welder to weld artery with high accuracy [48, 51].

1.6.3 In Energy

Solar energy is one of the most remarkable types of renewable energy; it has been developed in nanotechnology for generating electricity and enhancing power efficiency [52, 53]. Appling specific nanoparticle layers to semiconductors (silicon plate), could improve the performance of the solar cell efficiency by converting sunlight absorption to electric power [52, 54].

1.6.4 In Water Remediation

Nanotechnology provides an innovative solution for water polluted problems in the environment and makes it suitable for human utilizing and consumption. Water desalination and purification using superior adsorption nanomaterial [55]. For example, graphene, carbon nanotubes, metal nanoparticle (e.g., silver, iron, and zinc), and magnetic-core (e.g., cobalt, nickel, and iron) [56]. These nanomaterials have the ability to treat water via densification wastewater from pathogens and remove heavy metals such as chromium, mercury, and cadmium [55, 57].

1.6.4.1 Filtration

It is a procedure to separate solid material from solution via allowing the solution to pass across pores medium [55]. Membrane filtration could be categorized into two types; either dead-end filter or cross-flow filter, the water in the dead-end filter has perpendicular flux so that all accumulation solid stuck to the membrane surface. On the other hand, the cross-flow filter flows the water in a parallel direction, which causes shear force. Most noteworthy is the flux in a cross-flow way is higher than the dead-end method [58].

1.6.4.2 Photocatalysis

A principle of heterogenous photocatalysis is a catalyst to attract UV or near UV from sunlight radiation [55]. Light absorbing leads to the transfer of an electron from the valance band to the conduction band [59]. The excitation would originate due to light radiation if the light energy were larger than the bandgap energy of materials [55].

As a consequence of photon absorbed adequate energy, the electron transfer from the valance band left a hole behind; this hole will drifting undersurface of the valence band. Major of charge carriers from photo generation involve redox reaction and submit to distract its blend compound in adsorbed molecules at photocatalysis surface follow that degrade detoxification organic and inorganic molecules [55]. The photo induces chemical reactions when semiconductor powder radiate at solid-liquid interference, this chemical reaction has the ability to degrade organic and inorganic molecules [58].

Nanomaterial photocatalysis has a large surface area to volume ratio, which permits to adsorb molecules [55]. A major development, photocatalysis with metal

oxide nanoparticles such as Titanium dioxide (TiO_2) and Zinc oxide (ZnO), is used to purified waste and effluent water; it also used to reduce air pollution [55].

1.7 Literature Survey

Y. J. Lee et al., (2019) used chitosan and green tea as stabilizing and reducing agent to synthesized gold nanoparticles capped with chitosan in 3 variant shapes (nanospheres, nanostars, and nanorods) using green tea extract as a reducing agent of gold salts UV visible spectra showed the Surface Plasmon Resonance (SPR) band of all three types. Lattice structures for all shapes of nano were confirmed in the high-resolution transmission electron microscope device. The three colloidal solutions of AuNPs were applied to cancer cell lines. The results following orders nanospheres, nanorods, and then nanostars, respectively. The green strategy with a designed shape of gold nanoparticles has an assistant in therapy application [60].

Parang and Moghadamnia (2019) synthesized silver-cobalt nanoparticles by chemical reaction; its effectiveness was proven in medicine application due to its anti-fungal properties [61].

Bhattacherjee et al., (2018) used a weed named *Alternanthera Philoxeroides* in eco-friendly to prepare gold nanoparticles. They used many techniques (UV, DLS, zeta potential, FTIR, EDAX, SEM, AFM) to characterize their sample. Synthesized green Au nanoparticles demonstrated significant results in spite of antimicrobial activity [62].

Choi et al., (2018) used the *Platycodon Grandiflorum* plant as a reducing agent in green preparation of gold and silver nanoparticles. Their result illustrated that AuNPs and AgNPs were prepared at 15nm and 18 nm, respectively. Both samples were face-centered cubic structure. The studies suggested a successful synthesis of green nanoparticle's versatile applications [63].

Alsammarraie et al., (2018) used *Turmeric powder* as a reducing and capping agent to prepare silver nanoparticles. AgNPs were characterized using UV, FTIR, TEM, and energy-dispersive x-ray spectroscopy (EDS). The highest absorption of UV monitored at 432 nm. TEM showed the spherical shape of particle size at 18± 0.5 nm. EDS used to detect the presence of the silver element. The process of preparing nanoparticles was environmentally compatible, and the synthesized AgNPs promising candidate for many agricultural applications [64].

Chandirika and Annadurai (2018) prepared AgNPs by treating silver ions with *Abutilon Indicum* extract. The as-formed silver nanoparticle was characterized by UV-Vis spectrophotometer, Fourier transforms infrared spectroscopy, scanning electron microscope, and used their prepared samples in antimicrobial studies. Through which known the radius of nanoparticles was defined with a range of 50-100 nm. The results of AgNPs were found as effectual and encouraging nanomaterial [65].

Kaur et al., (2018) used pomegranate peel to fabricate iron nanoparticle, iron-silver (FeO/AgNPs), and iron-gold (FeO/AuNPs) core-shell nanoparticles. The characteristic of surface Plasmon resonance peak was identified to be 465 nm for (FeO/AgNPs) and 530 nm for AuNPs. The electron microscope technique detected that the shell of silver encircled 13 nm, whether the gold shell was less than 100 nm. The activity of antibacterial and antifungal core-shell nanoparticles (CSNPs) ascertained by the inhabitation method and showed good results towards antibacterial activities. Hence, the as-prepared approach is a reasonable and cost-effective application for water purgation technology [66].

Muhy and Duman (2018) describe the synthetic of magnetic nanoparticles ($CoFe_2O_4NPs$) using the coat of *Aesculus hippocastanum* plant

extract as a non-toxic and eco-friendly technique. Fabricated NPs were characterized by UV-Vis, DLS, XRD, FT-IR, SEM, and TGA. The results indicated that magnetic nanoparticles could be utilized in water removal and purification [67].

Kangama et al., (2018) applied chitosan with poly aluminum chloride and (Al (OH)$_3$+HCl) in the water flocculation process to remediate tap water and decrease its price. They found 96.38 % of muddiness, and more than 80.1 % of the aluminum was eliminated. More than anything else, it was as cost-effective treatment [68].

Diaz-Hernandez et al., (2018) prepared magnetic iron oxide nanoparticles using chitosan as warping material. They used transmission electron microscopy, Fourier transform spectroscopy, and X-Ray diffraction tools to characterize their products [69].

Kumar et al., (2017) used *Andean blackberry* extract as stabilizing agents and as reducing silver ions to prepare AgNPs. From the result, the plasmonic band and the crystallinity nature were discussed by UV and X-Ray. The author used prepared samples as a great potential drug against diseases [70].

Jayaprakash et al., (2017) used *Tamarind fruit* extract as reducing and capping under microwave irritation as eco-friendly synthetic to prepare AgNPs. The formation shape, stabilization, and particle size were performed using various analytical instruments. The prepared silver nanoparticle was studied against antibacterial activity [71].

Raja et al., (2017) Synthesized silver nanoparticles using *Calliandra haematocephala*, as a reducing after that characterized prepared sample by UV, X-ray diffraction analysis, and Zeta potential. The prepared samples were applied in therapeutic applications against antibacterial activities [72]

Alymov et al., (2017) prepared different sizes of iron nanoparticles by reducing the iron hydroxide layer in flowing hydrogen then passivated in argon. A systematic characterization of FeNPs was performed using X-Ray diffraction analysis [73].

Ansari et al., (2017) used the hydrothermal method to synthesized cobalt nanoparticles; oleic acid was used as a capping agent. They used X-Ray diffraction, Raman spectroscopy, and Infrared spectroscopic studies to characterize CoNPs. They investigate that CoNPs contains the ferromagnetic parameter. Further, the temperature depends on magnetic parameters, saturation, permanent coercivity, and reduced permanent magnetization were specified with CoNPs. Above all, prepared samples suggested high effective against cancer cells and the human bloodstream [74].

Devath et al., (2016) used iron nanoparticles in domestic wastewater treating. The authors used UV-Vis spectroscopy to determine the peak of surface Plasmon for FeNPs. It also characterized by a microscope technique to detect the presence of iron nanoparticles [75].

K. Lee et al., (2015) synthesized spherical, triangular, and hexagonal shapes with 23nm diameter gold nanoparticle using *Inonotus Obliquus* extract at room temperature. Synthesized samples exhibited good results against antibacterial, antioxidation, and cytotoxicity against human breast and stomach cancer cell lines [76].

Patra and Baek (2015) prepared AuNPs using a *melon peel*. They used different techniques like UV, SEM, XRD, FTIR, and thermogravimetric analysis to characterize their prepared samples. Surface Plasmon Resonance was at 560nm. Their result showed that the samples were prepared as spherical nanoparticles with

different sizes (20-140 nm). Besides, they used a melon and rind as stabilizer and surfactant agents. The sample was used as a potential antibacterial activity [77].

Ibrahim (2015) prepared AgNPs with environmentally, friendly, and cost-effective approaches using *banana peel extract* (BPE). BPE used as reducing and capping agents for silver salt. Thereafter, silver nanoparticles were characterized by different techniques such as UV, X-Ray, SEM, TEM, and FTIR. The as-prepared silver nanoparticles assist in inhibiting the growth of bacteria [78].

Abdollahi et al., (2015) synthesized chitosan-coated with Fe_3O_4 nanoparticles and used to purify water by minimizing arsenic concentration. The prepared sample was characterized by transmission electron microscopy, Fourier transforms infrared and vibrating sample magnetometer. They cofired that, prepared samples could implement to turbidity water in order to adsorb arsenic, follow that, applying a magnetic field to separate materials [79].

Salman et al., (2014) prepared magnetic cobalt nanoparticles with spherical shape and 400 nm of the diameter by liquid-phase reduction method using hydrazine. They investigated that; dendritic nanoparticles were created at 298 K when the concentration of hydrazine decrease — moreover, large dendritic nanoparticles formed at a 353 K [80].

Zola et al., (2014) utilized different methods to prepare cobalt nanoparticles; the first one is reducing cobalt salt by polyalcohol; the second method is demonstrated by decomposition, an organometallic, and eventually reduce metallic salt by borohydride. They confirmed that the nanoparticles' shape and size distribution would be changed with varying preparation methods [81].

Li et al., (2014) used magnetic chitosan and graphene oxide- ionic liquid to enhance the treatment and remove heavy metal ion as chromium Cr (VI) from

wastewater. Most important, they demonstrated their work by Fourier transform infrared, scanning electron microscopy, and X-Ray diffraction [82].

Sujitha and Kannan (2013) synthesized gold nanoparticles by reducing HAuCl4 using *Citrus Limon, Citrus reticulata, and Citrus sinensis* juice extract as a surfactant and stabilizer. The synthetic samples characterized using different spectroscopic techniques like UV, TEM, and XRD. TEM studies offered different shapes with small sizes for particles while Dynamic Light Scattering (DLS) graph sized display larger particle comparing with TEM. In this research, the effectiveness of gold nanoparticles and its biological application [83].

Jayaseelan et al., (2013) synthesized AuNPs using *Abelmoschus esculentus* seeds. And configured these samples using UV, XRD, FTIR, AFM, FESEM, and EDX were analyzed. As a result of characterization, all particles have a spherical shape, and it is the size in the range 45-75nm. The fungus area has been identified and applied to Gold nanoparticles, an effective anti-fungal of the prepared samples was studied [84].

Logeswari et al., (2013) *Solanum Tricobatum, Syzygium Cumini, Centella Asiatica, and Citrus sinensis* used to synthesize green silver nanoparticles. They used many techniques, such as UV, XRD, AFM, and FTIR devise. The result of mediated was 53, 41, and 52 nm, corresponding to *Solanum Tricobatum, Syzygium Cumini, Centella Asiatica, and Citrus sinensis*, respectively [85].

Prathna et al., (2011) used a rapid and straightforward method to synthesized silver nanoparticles using the extract of *Citrus Limon*. The samples were identification by UV, X-Ray Diffractometer (XRD), and Fourier transform infrared (FTIR) spectroscopy. The results obtained the *Citrus Limon* were used as a capping and reducing agent. FTIR revealed the involvement of bioactive compounds from

Citrus Limon in capping and stabilization of AgNPs. TEM showed the formation of a spherical shape under 50 nm [86].

Bankar et al., (2010) used *banana peel extract* (BPE) as a green strategy for preparation gold nanoparticles. It was boiled, mashed, rinsed with acetone, and then dried. Peel powder was used to reduce chloroauric acid. Different nanoparticles were formed when the conditions of the interaction changed with respect to consideration of PH and chloroauric acid, components of PBE, and temperature duration. Their preparing sample was characterized using several techniques, including UV, SEM, X-Ray, and FTIR. Samples had efficacy against antimicrobial activity to most fungi and bacteria [87].

1.8 Aims of the Thesis

1- Preparation of some magnetic, noble metal with different nanoparticles sizes and shapes such as (Ag, Au, Fe, and Co) using different chemical methods.

2- Ultraviolet-visible spectroscopy (UV-VIS) will be employed to investigate surface plasmon band and their position dependence on the particle sizes of the synthesized samples.

3- Study the size distribution and morphology of the prepared samples using high resolution transmission electron microscope (HR-TEM), and the particle size will be estimated from TEM images.

4- The crystallinity of prepared samples will be studying using x-ray diffraction pattern (XRD) as well as the average crystalline size of nanoparticles will be calculated.

5- Fourier transform infrared spectroscopy (FTIR) will be used to study the chemical interaction between nanoparticles and functional groups of surfactant materials.

6- Due to the high reactivity and strong sorption of nanoparticles, the prepared samples will be used to decrease nickel concentrations in water and the effect of the particle's sizes, shapes on changing nickel concentrations will be explaining.