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A Review of Bismuth Nanoparticles and Surface Plasmon Resonance; Synthesis and Properties for Medical Physics Applications

Aya M. H. Kinaanah*, Raad M. S. Al-Haddad

Department of Physics, College of Science, University of Baghdad, Iraq

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****Corresponding Author:***
Aya M. H. Kinaanah
Aya.Hasan2304@Sc.uobaghdad.edu.iq

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Abstract

The Study describes the efficient synthesis of bismuth nanoparticles due to their effective properties for medical physics applications, such as cancer therapy. The optical properties of nonmetalsare being exploited for multimodal therapeutic applications, in particular in the field of studying cancer cells and trying to inhibit their activity. Nano bismuth can be prepared in an environmentally friendly way called the green method, using plant extracts and lemon extract, which is one of the good types for use in preparing nano bismuth studying its properties, and using it in various applications. The good absorption of near - infrared radiation by bismuth nanoparticles has encouraged the use of bismuth in the field of therapeutic studies for cancer, where it has become strongly present, but there is a major challenge facing this type of study because cancer as yet one of the main causes of human demise and the side effects of the traditional treatments have remained without unresolved. In addition, it is present in other areas due to the good efficiency shown by its optical properties. Bismuth using in various applications over the past decades is mainly due to their properties which ensure the high quality of their application. Furthermore, interrelationships in scientific research between various disciplines, for example, between physics and biology, as well as between engineering and biological disciplines. This interconnection between scientific disciplines,can be employed in studying the properties of metallic nanomaterials and thus the possibility of using them and benefiting from them in medical fields.

1. Introduction

Materials whose diameter ranges from one nanometre to one hundred nanometres are called nanomaterials [1]. The structure of this type of materi al is determined by preparation methods, quality of solvent, temperature andcatalyst [2]. The physical and chemical properties of different substances are the basis for the development of antibiotics [3-7]. Nanoparticles have three physical dimensions that are on the nanometre scale, and exhibit different size-related characteristics [8]. The biological interaction between nanoparticles and living systems occurs through adsorption and requires high absorption energy between nanoparticles and the surface of cells. This is determined by the total interaction energy between the nearby surfaces [9,10]. Nanotechnology is developing significantly through the production of nanoparticles that have physical and chemical properties that differ from larger materials due to their difference in size [11]. Bismuth nanoparticles have distinctive properties, including alow level of toxicity, stability, large X-ray factor of attenuation, high absorption of near-infrared radiation, and high efficiency in photo thermal transformation processes [12−20]. The surface Plasmon resonance phenomenon of non-metals can be obtained after high energy absorption at specific frequencies [21]. The purpose of this review is mainly focuses on synthesized ismuth nanoparticles by green method with studying the properties of surface Plasmon resonance and benefiting from them in biomedical applications. The shape-controlled chemical syntheses metal nanoparticles have also been hbighlighted in this study. The review ends by identifying the main challenges that need to be overcome and suggesting ways in which the most promising developments are likely to take place in future.

2. Bismuth

Bismuth is an element with semi-metallic properties such as the long mean free path of the charge carrier, it was measured at one micron at room temperature [22], magnetic resistance is large [23], has quantum confinement properties that affect nanostructures extending over tens of Nanometers [24]. These unique properties are created from the electronic band structure for bismuth, which is a rhombohedral, the Brillion zone has many different characteristics, as shown in Figure (1a) [25], which describe the changes in the carrier cavit, which is variety with the direction,close to the T-point of the Brillouin zone, bismuth has a single hole cavity (hole Fermi surface it aligns with the triangular z-axis and the alignment shape is elliptical). Close to three equivalent points, denoted by L- point, there are three similar electronic cavities (elliptical electrons) aligned symmetrically around the Fermi surface hole at an angle of approximately 6.5 out of the plane that is bounded the bisector and biaxial axes. The valence band and conduction band at the L-Point are separated by an energy gap of 36 meV at room temperature as shown in Figure (1b) [26, 27].

The semi-metallic properties of bismuth are due to the presence of a Fermi level in the conduction band at the L-point and the valence band at the T-point, where the electron holes pairs are presence, as shown in Figure 1(b). bismuth has a very small free carrier density due to its semi-metallic properties, which lies in the range (10^{18} to 10^{19} cm^{-3}). bismuth contains a large group of low energy bands, as shown in Figure (1c), Which was measured theoretically early [28, 29].

Bismuth is classified as a P-block Chemical Element/Metalloid and it is also considered an element with a small effective mass [30–33], bismuth is considered to have good efficiency when used in studying and observing the phenomenon of quantum confinement and finite size, as well as magnetic properties related to resistance, electrical and thermal properties [31, 32, 23, 34]. The study of the optical properties of bismuth has not received the same amount of attention as the study of its electrical properties previously. Some works have dealt with the optical properties of bismuth, specifically thin films of bismuth, bulk bismuth, and nanostructures of bismuth, but currently, interest in bismuth has increased due to the properties of its nanostructure represented by optical resonance, which is studied through the near-infrared, ultraviolet, and visible regions. It has been speculated that the resonances are of Plasmon origin, and it was also expected that a Plasmon resonance response will occur from the region of far infrared to terahertz and also the Mie dielectric resonance in the mid-infrared region to the far-infrared region. In addition, experimental and theoretical studies of nano bismuth about its optical resonance properties for various applications, including photo catalysis [35, 36]. Bismuth is an interesting element because of its good electronic structure, which gives it an optical response. However, its optical properties are less present than its electronic properties [23-25].

The optical dielectric function for $\varepsilon = \varepsilon_1 + i\varepsilon_2$ for bulk bismuth has been described by several authors in certain regions of the spectrum and is dispersed due to the quality of the sample, as shown in Figure (2). Currently, works are describing the optical properties of bismuth crystals and their thin films [29, 37, 38].

In particular, characterization was performed using far-infrared spectroscopy and ultraviolet spectroscopy on bismuth films to give dielectric function for bismuth (Kramer's and artefact) [39].

The dielectric function must be measured in wider spectral regions because, although it shows clear changing in the optical properties in the mid-infrared and near-infrared regions [38].

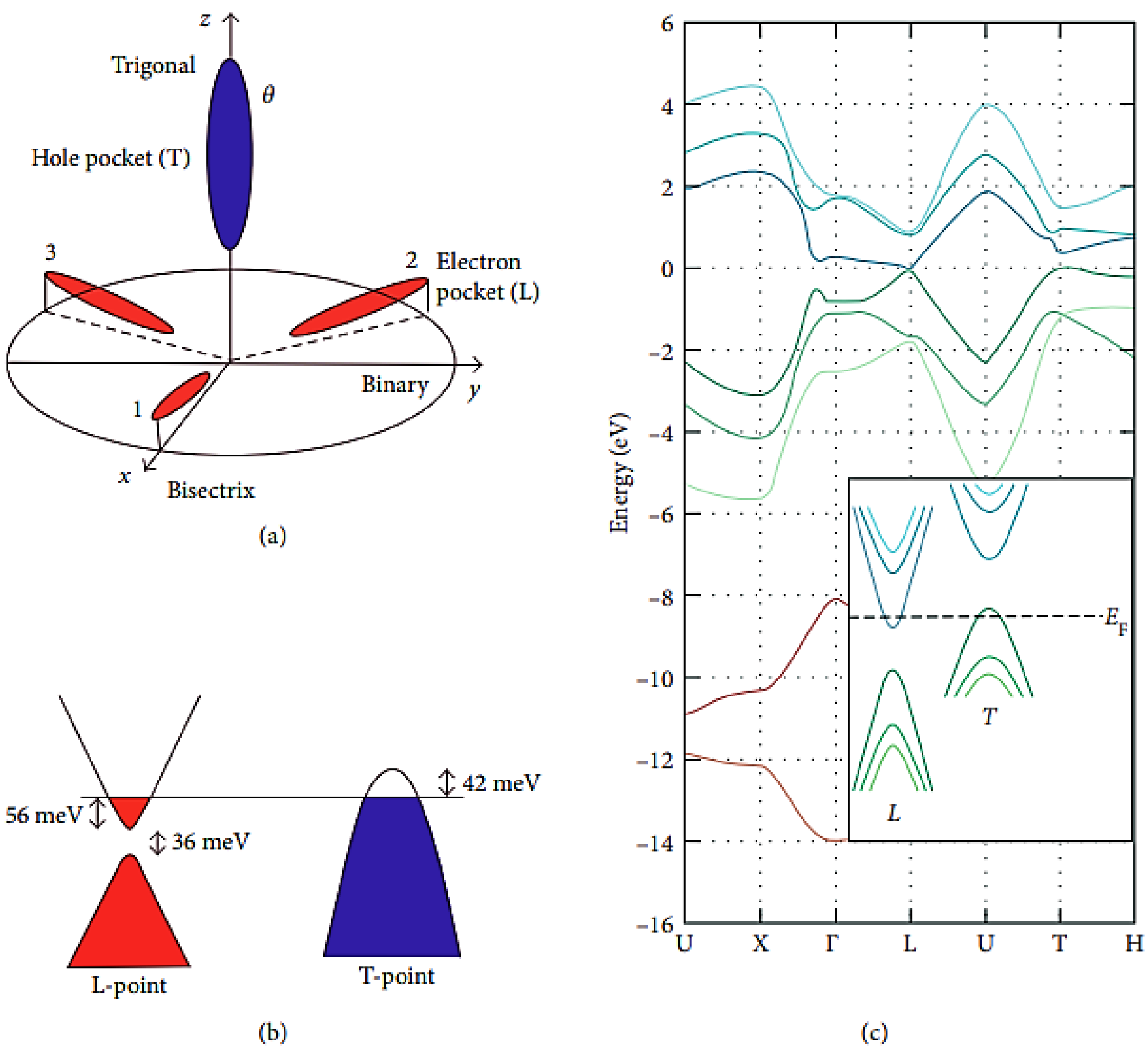

Figure (1): (a) The Brillouin zone of bismuth element, **(b)** The energy band gap and fermi level at room temperature for bismuth [34, 36], and **(c)** Energy band diagram for bismuth [27].

Through the value of the isolation function, as shown in the figure, its value is $\varepsilon 1 < 0$ in the visible, ultraviolet, near-infrared spectrum,which leads to the plasmonic response occurring at the boundaries of this regions [35], the negative value of $\varepsilon 1$ its origin is due to the large changes between the bands, which reach their maximum value at energy 0.8 eV while the value of the dielectric function $\varepsilon 1$ is negative in the far infrared and terahertz region arising from free charge carriers, the plasmonic effects induced due to nanostructure of bismuth is appear as spectra in two ranges:

(i) in the far-infrared and terahertz radiation because of the total excitation of free charge carriers.

(ii) in the uv-visible and near-infrared regions where, the resonances in nano bismuth are called (plasmonic inter bands) resonances because they occurr by inter band transitions, unlike to the well-known Plasmon resonance of metal nanoparticles [39].

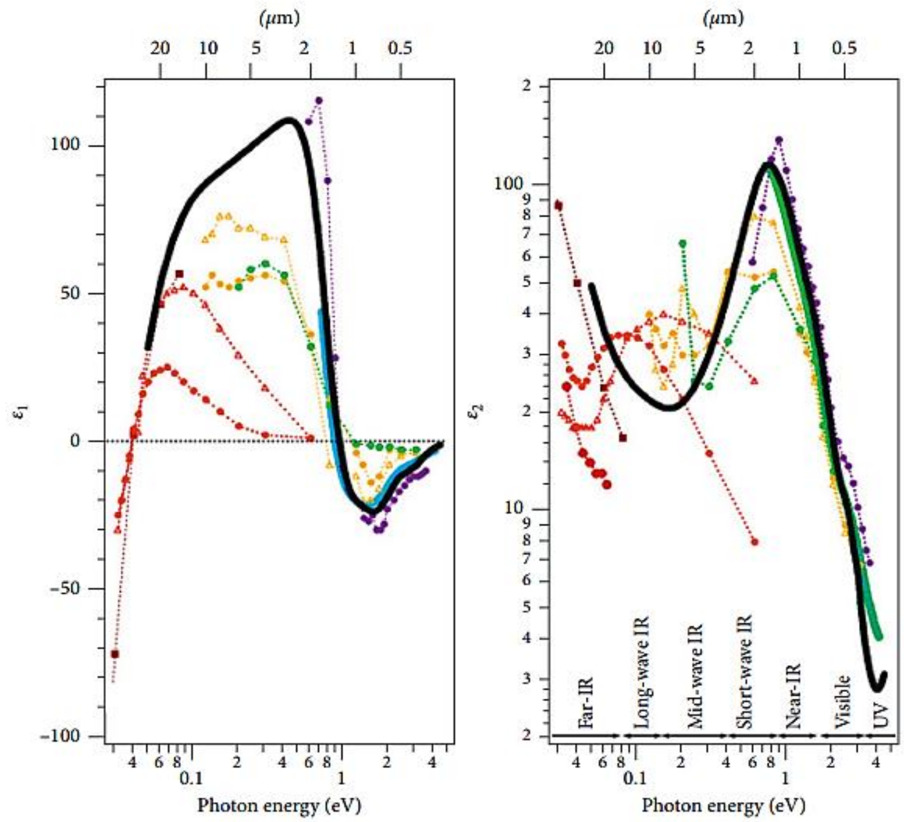

Figure (2): The dielectric function behavior of bismuth [37, 38].

2.1. Nano Bismuth Synthesis

Nano bismuth has been successfully prepared, which includes zero-dimensional nano bismuth such as nano spheres, nano cubes and nanoparticles. One-dimensional, such as nanotubes, nanowires and nano rods and two-dimensional bismuth nanostructures such as thin films, ultrathin films, nano sheets and nano plates, while the preparation of nanostructures continues to be improved continuously [40–62]. This structure extends from a few atoms to a few microns, which allows it to be used in many applications, including thermal and electrical applications, large magnetic resistance, superconductivity applications, quantum transport, and topological insulation applications [23, 63–66]. The size effect is involved in Plasmon fields and nano photonics, the wavelength depends on the dimensions of the nanostructures mainly and the wide range of nanostructures would provide different wavelengths from the ultraviolet-visible region , far infrared and terahertz region, which suitable for optical systems [37, 38, 67–69]. Methods for preparing nano bismuth have been explored, mainly affecting on its characteristics ,some of them are based on the template that uses a specific matrix to prepare bismuth nanoparticles [64, 70–74], and some of them do not have a template. Another effect that is involved in the preparation of bismuth nanoparticles is the effect of stress, especially in the preparation of bismuth nanowires [22, 75]. One of the most important methods for preparing nano bismuth that has proven its efficiency is the physical vapour deposition method, especially in the preparation of bismuth nano columns, bismuth nanowires, and nano rods as well [43, 44, 46]. One of the methods used to prepare bismuth nanoparticles is the solution phase, which enables great control of its shape and at various nanoscale dimensions, including zero-dimensional nanostructures, one-dimensional and also two-dimensional [23, 49–52, 50, 62, 76, 77]. Laser is considered one of the induced methods for preparing bismuth nanoparticles including thin films, nanoparticles and nano rods [37, 38, 47, 55, 67]. Other preparation methods for obtaining nano bismuth are: the plasma force synthesis, the epitaxies of molecular beam, irradiation by electrons [57, 61, 66, 78]. In the next section, focus was placed on one of the most important methods for nano bismuth synthesis, which is the green method.

2.2. Green Synthesis

Nanoparticle synthesis by greener method is considered an amazing development compared to other methods because it is economical, environmentally friendly, simple, and the nanoparticles prepared in this way are often more stable. Microorganisms can be using to prepare nanoparticles by the green method, but the synthesis rate is slow because this method is used at a certain range of sizes and shapes when compared to plant materials. Preparing nanoparticles by green method does not require high temperature, energy and high pressure. Most researchers have turned to the green method rather than industrial methods, as it produces nanoparticles that are less polluting and more stable, and depend on plant parts to prepare nanoparticles. Because of the advantages possessed by the green method, it has gained great importance in many fields, as many studies and research are being conducted into more production, in addition to the unique features such as low cost and consideration of the environment in the production of nanoparticles, one of the common extracts used in the green synthesis method is tea leaf extract to prepare nanoparticles [79, 80], some fruits have been used in the green synthesis to prepare nanoparticles, such as the Termalia fruit [81], black tea extract [82, 83], banana fruit extract and colocasia plant[84], extract of bran plant [85], eucalyptus trees [86], and extract of Tridax procumbens plant [87].

Chemical reduction and electrochemical methods are considered the most common methods for synthesizing nanoparticles, although there are other technical including thermal, photochemical, and radiation and methods based on microwaves. Nanoparticles have a specific size shape, and although nanoparticles can be obtained by other methods the green method remains the best because traditional methods include side effects, including the emission of toxic substances that affect human health, in addition to being expensive, unlike the green method, which is cheaper and environmentally friendly. For this reason, it has received great attention [88]. During the preparation process, moderate conditions of pressure, temperature, and non-toxic solvents are provided [89, 90, 91]. In the green method, a type of fungi and bacterial organisms are available, instead of chemical reducing agents, in addition to vitamins, proteins, and sugars, all of which help in the process of creating nanoparticles [92, 93]. The elements that have been frequently used in the preparation of nanoparticles by green method are silver, gold, platinum, magnetite, zircon, silica, and quantum dot [94, 95-100]. Therefore, this biological method used to prepare nanoparticles is more environmentally friendly than chemical and physical methods, as they do not require toxic and harmful chemical elements and do not require high cost [101-105]. Plants are considered important sources of biological compounds that aid in processes such as coating and reduction.

Lemon fruit contains elements that ain reduce oxidation, such as phenols and limuloids, and various vitamins and acids, such as ascorbic and citric, which work to reduce large oxidation ions. It is an environmentally friendly way to generate bismuth nanoparticles from lemon juice for reducing and coating [106]. Nanotechnology plays an important role in the engineering, scientific, and environmental fields because of its efficiency in fighting pollutants, as it is used to sterilize water and polluted places. There is a global trend in using environmental methods in preparing nanoparticles, and metal oxides are essential elements in this, based on their characteristics such as small size, surface, magnetic, and biological properties. In addition, the production of nanoparticles must be inexpensive, accepted by society, and not harm the environment [107].

Many studies and research have been occurred on biological systems in the recent past, which including the use of bacteria, fungi, and plant parts, and it was found that they cause the transformation of metal ions into metal nanoparticles, therefore, the green method gained great popularity two decades ago and extended to our contemporary time due to the urgent need for it in global problems related to pollution, as making the product harmless to the environment and sustainable is of importance in the process of synthesizing nanoparticles [108, 82, 109].

The decomposition of organic compounds in the green method, i.e. using plant extracts, occurs due to the presence of polyphenols in the substance that is used for treatment. Many studies have been conducted on many plant extracts in the preparation of metallic nanoparticles, and it was found that metal oxide particles are effective as a sterilizing material, which helped predict their exploitation in the clinical fields and pollution treatment and in other industrial process due to its antibacterial, antifungal, optical properties in the UV spectrum region, and its photocatalytic and chemical activity [110]. Another reason for the importance of green synthesis is preserving the cells structure and reducing the pollution resulting from the reaction [111].

3. Surface Plasmon Resonance (SPR) in Metal Nanoparticles

The absorption and light scattering inside a medium containing small nanoparticles are relied upon when studying the optical properties of these particles. This including collective oscillation resulting from the electrons in the conduction band [112].

One of the efficient and advanced properties in nano metals is the surface Plasmon resonance (SPR) resulting from difference in shape and size[113].surface Plasmon resonance is worth noting that non-metals show effective Plasmon properties due to the interaction of light radiation with electrons on the surface of the non-metal, forming what is known as localized surface Plasmon [114]. The electromagnetic (EM) excitation that spreads vertically at the interface between the conductive material and the insulating material leads to the generation of surface Plasmon Polari tons(SPPs). These surface electromagnetic (EM) waves arise through their association with the oscillations accompanying of the electron plasma. In general, surface Plasmon Polaritons (SPPs) are classified into two main types: localized and propagated Plasmon Polaritons [115]. The strong absorption of light by nanoparticles occurs due to the interaction of conduction electrons with the electromagnetic wave This collective oscillation of conduction electrons when they interact with electromagnetic waves is known as a Plasmon. To describe the creation of Plasmons and dipoles, one can consider the metal plasma as having a cloud of positive ions and an equal cloud of negative conduction electrons. In the neutral state, interference occurs between the positive cloud and the cloud of negative conduction electrons resulting from the external effects such as the interaction of conduction electrons with electromagnetic waves. The cloud of conduction electrons moves away from their equilibrium positions. If the electron density increases in one area, they repel and return to their equilibrium positions with kinetic energy. Consequently, the electrons move back and forth around their equilibrium positions. The charge difference resulting from this process occurs at the boundaries of the surfaces of the nanoparticles. The electrons that contribute most to the oscillation process are the surface electrons, and the oscillations of the collective surface electrons are called the surface Plasmon. Resonance between surface oscillations and the incident electromagnetic wave leads to a strong peak in the visible spectrum zone called surface Plasmon resonance [116, 117].

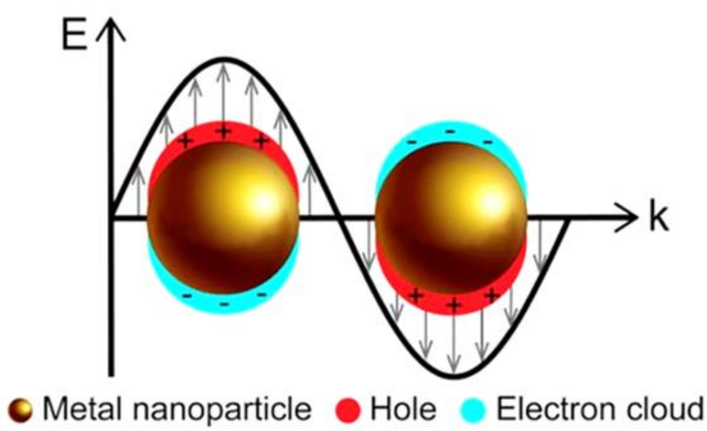

Figure (3): A scheme shows the rotation of electron clouds opposite the direction of the electric field near nanoparticles, where the wavelength of the incident light rays is larger than the size [118].

Plasmon nanoparticles enhance the electromagnetic field because light may observed or scatter. In the case of localized surface Plasmon, a reaction occurs between particles much smaller than the incident wavelength, and the collective oscillation is confined to a specific area. This happens in the case of metal nanoparticles, and is called localized surface Plasmon resonance. It creates a strong electric field that extends a few nanometres and improving the cross sections of the molecules absorbed on the surface. Local surface Plasmon resonance depends on the refractive index of the medium surrounding the metal, which can have measured using electrodynamic examination [119, 120]. The efficiency and refractive indexes of plasmonic sensors depend on nanoparticles with geometric symmetry and parameters have shapes and widths less than 20nm [121].

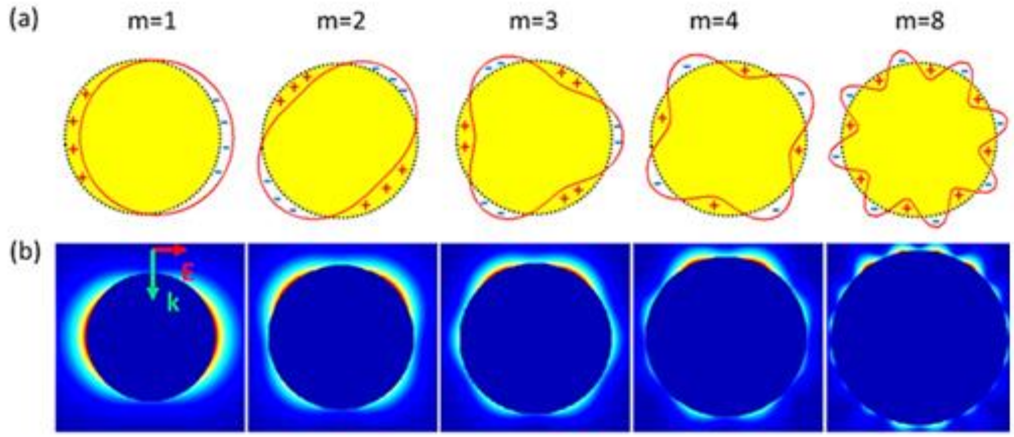

Figure (4): (a) A scheme shows the distributions of charges for several orders of surface Plasmon resonant cases, and (b) shows the electric field patterns of a nano sphere [115].

Some nano metals show high sensitivity to the refractive index, such as gold, copper and silver. However, silver has a higher value than other nano metals [122]. The parameters that include radiation damping, surface scattering, transitions between inter band, and dynamic depolarization are among the influential factors on which of the Plasmon sensitivity of nano cubes depends [123]. The dielectric properties, surface polarization, and dielectric constant of medium in contact with it, affect the frequency, and the intensity of the Plasmon resonance, any change in the shape and size of nanoparticles leads to a change in the spectral case of the Plasmon. It must be taken into consideration that the most important process is studying the effect of changing the shape and size of particles on localized surface Plasmon resonance, and through Maxwell's equation, the interaction of nanoparticles with electromagnetic waves can be studied [124]. Maxwell's equations are relied upon in their analytical formulas known as Mie's theory, in special cases such as a solid sphere, an infinite cylinder, and the concentric spherical shell [124]. The dielectric dipole approximation and some numerical methods and approximations are used to describe the interaction of electromagnetic waves with nanoparticles of arbitrary geometric shapes [125, 126].

The effect of shape on localized surface Plasmon resonance is studied using the dipole-dielectric interaction and it is integrated with measured dipole approximation and with experimental studies to understand the spectral state of the localized surface Plasmon resonance obtained from the nanoparticle sample [127]. The manufacture of nanoparticles Plasmon is subject to these calculations, which provide useful guidelines for their fabrication and design [127]. Different shapes and spectra of localized surface Plasmon resonance of silver metal nanoparticles as shown in Figure (5).Within the range of forty nanometres, the spectra of silver nanoparticles were obtained, represented by extinction and absorption spectra And scattering as in a silver sphere inside water , as shown in Figure (5A) and other forms using Mie's theory, which is based on the dielectric dipole approximation method [126]. The spectrum of cubic silver with an edge length of 40 nm appears from dielectric dipole approximation measurement in Figure (5B), the absorption of particle shows two peaks in the resonance spectrum: a dipole at 410 nm and a quadrupole at 370 nm. The quadruple resonance is weaker because it results from a loss of energy due to the light falling on the sphere in an irregular way. This leads to a weaker quadruple resonance and is characterized by the presence of parallel dipoles with different charges [128, 129]. The frequency and intensity of the Plasmon are determined for nano metals through surface polarization because it is responsible for providing the important restoring force in the oscillation of electrons, and any difference in the size and shape of the nanoparticles and the medium leads to a change in the surface polarization [130]. It appears in Figure (5B) that nano cubes exhibit many symmetries of dipole resonance compared to just a one symmetry for a sphere in Figure (3A). Therefore, nano cubes show more different peaks than spherical particles [131]. The same orientations were also observed for tetrahedral and octahedral, despite the decrease in the scattering cross section due to these dissimilar symmetries and their small structures in Figure (5C and D) , localized surface Plasmon resonance peaks appear that proportional with tetrahedral symmetry, and are red-shifted due to the presence of sharper angles than cubes. Tetrahedral resonance appears on three sides due to sharper angles. Likewise, for shells or hollow spheres, they show resonance peaks in the direction of red shift as shown in 3E and Figure (5E and F), which indicates that the electric field causes surface polarization, that is, the charges are distributed inside and outside the shell, and the same process is the same for the hollow sphere. To compensate for the incident field, the particles must have a dipole moment, similar in charges in kind to the same pole, as they have a charge on the inner surface. A sign similar to that of the charge on the outer surface. To increase the charge separation process, the oscillation frequency is reduced. For thin shell a strong coupling process occurs between the inside and outside of the shell, which leads to charge separation, and we obtain spectral peaks towards the red shift, as in Figure (5F). These metal nano shell represents a special case of radiation and field properties that can be greatly and effectively controlled [132].

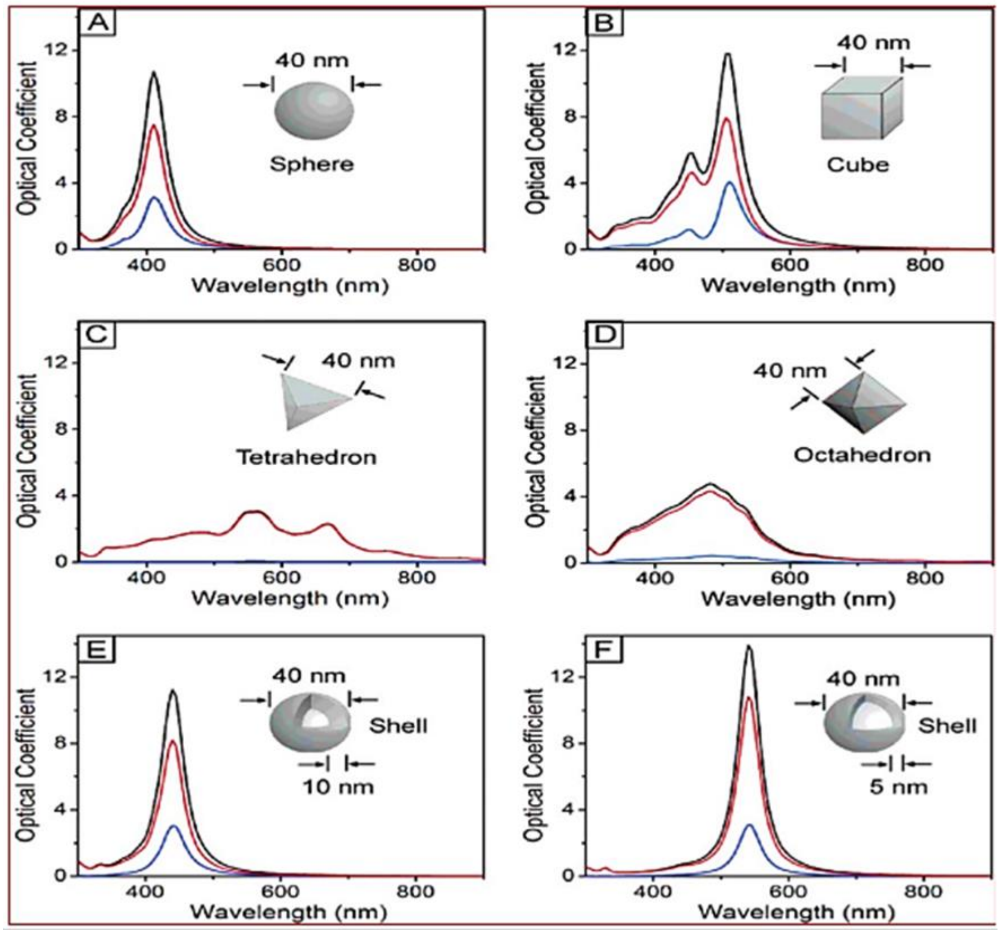

Figure (5): Ultraviolet-visible spectrum of metallic silver nanoparticles: **(A)** single dipole resonance spectrum, **(B)** cube, **(C)** tetrahedral case, **(D)** an octahedron spectrum, **(E)** representing the hollow sphere case, and **(F)** peak representing thin shell case [131].

3.1. Nanoparticle Plasmon Structure and Shape Controlled

The direction has been to prepare nanoparticles of different shapes and sizes in the last two decades, and the focus has been on mechanisms to control the shapes of the nanoparticles that have been prepared [133-135, 116, 117, 123, 131, 136-140]. Wolff's theory describes that single crystals of noble nano metals in an inert gas are truncated octagonal in equilibrium [141, 142]. As for the methods of preparing the solid phase of nanoparticles, they differ from those adopted by the Wolff-Wolf theory with polyhedral shapes due to the difference in properties that are affected by different interactions for many surfaces with capping factor and dissolvent. The prepared twin structures have lower energies than cuboctahedron, the reason is that the methods for preparing the solid phase for Plasmon are more powerful and reliable than the vapor phase, in which the shape of the noble metal nanoparticles is controlled [143–148]. Metal nanoparticles are considered a model system for the Plasmon formation of metal nanoparticles with different shapes and localized surface Plasmon resonance properties and it is considered an ideal system to experimentally study the effects of the quantum confinement phenomenon on magnetic properties and to study its effect on electrons as well and other properties. Controlling the shape of nanoparticles is facilitated when prepared with povidone(PVP) which was used as a covering agent. It has been proven that the use of povidone in the preparation of metal nanostructures leads to the formation of double defects in the initial stage of preparation, after which they grow into different shapes. A single crystal seed can develop into an octagonal crystal, cubes and cuboctahedron by controlling growth rates along both {111} and {100} directions [148, 149]. The cubic seeds structures and single cuboctahedron crystals be controlled to grow nanostructures with properties of one dimensional into octagonal and others rectangular cross sections [149].

A bipyramid can be produced by a single, twinned seed and can develop into a multi-twined icosahedron or icosahedron, depending on the stability of the {100} side face of the multiple seeds[150–152]. Seed-like plates can also grow, and this leads to the formation of hexagonal or triangular plates with an upper and lower face {111} and there are also side faces {100} and {111} [153, 154]. The nucleus is formed when the starting material is reduced, and after it grows and reaches a certain size, it turns into a seed with a single crystalline structure, or a single twin, or it may have a multiple twin structure, or it may grow into nanostructures by vibrations and it when preparing Nanoparticle Plasmon it is difficult to control of the seed structure from the inside because due to the temperature levels, there may be an unstable seed inside the crystal structure [155].

Sometimes nanostructures are formed in a single crystal structure and addition to twin metal nanostructures due to instability. Therefore, the double seeds must be removed to prepare a single seed. kinetic control, and oxidative etching are used to control seed structure synthesis [156, 157] and also by capping factors [150].

3.2. Optical and Plasmon Properties of Nano Bismuth

Plasmon resonance occurs between beams in nanostructures, as mentioned previously in section 2. In the region of the ultraviolet and infrared spectrum where the real part of The dielectric function of bismuth is negative ($\varepsilon 1<0$) by comparing the value of the dielectric function for bismuth and nano bismuth, it was found that the Plasmon behavior of the nanostructures in the ultraviolet and visible spectrum region, as well as the infrared spectrum region, is very small relative to a spherical structure of wavelength. for incident light and with e2 it has a small energy dependency a quasi-stationary dipole Plasmon resonance process occurs at a photon energy value $\varepsilon_1(E)= -2\varepsilon_m$, with ε_m of real value to the surrounding medium , when the value of the dielectric function increases, a condition is met Fro¨hlich in the region of the ultraviolet-visible spectrum and in the presence of media such as SiO_2 or Al_2O_3 [67].

Many quasi-static resonance states occur for bismuth with a spherical structure at different photon energies due to the polarization of the incident light and the shape of the nanostructures. In the case of spherical structures, the condition of Fro¨hlich become $\varepsilon_1(E) = (1 - 1/Lu)\varepsilon_m$ and value Lu, it is a factor that depends on the shape of the nanostructure and affects the polarization value towards the axis (u). Therefore, spherical nano bismuth has two resonance values the first is called longitudinal resonance, which is the resonance of polarized light that extends along the phase of the rotational axis, and the second is transverse resonance, which is perpendicular to it. Transverse resonance turns to smaller photon energies, and longitudinal resonance turns to higher photon energies in the spherical structure, when the ratio of height to diameter increases or decreases or the ratio of width to height increases or decreases. This makes it possible for resonance to occur deeper in the spectrum region of ultraviolet passes through the visible towards the near infrared region. The value of the dielectric function of bismuth turns negative in the ultraviolet, visible, and near-infrared spectrum region when transitions between bands are excited [38].

Many works have described various methods, including numerical and analytical, to describe the optical response of bismuth nanostructures and thus improve the Plasmon properties and their response quantitatively. This depends on some influences such as: the small size compared to the wavelength of incident light and the finite element method also [35], and Mie method [38, 58].

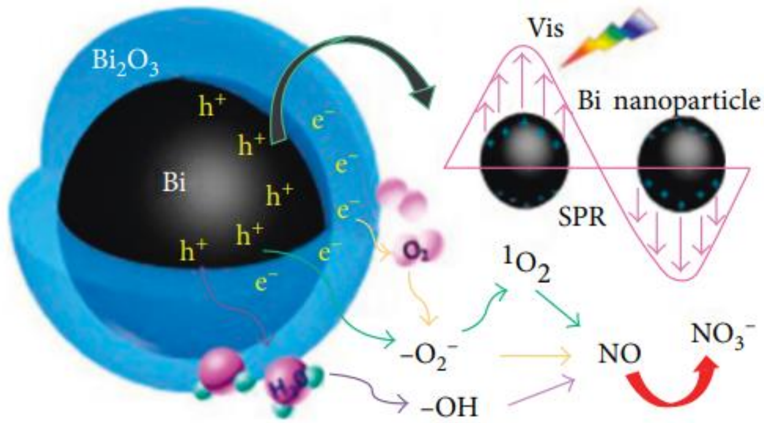

Figure (6): Surface Plasmon resonance of spherical bismuth nanostructures [158].

In order to stimulate the optical cross section of bismuth nano spheres were used measurements of finite difference time domain [130] and strengthening it within a range of up to a few hundred nanometres and to enhance the optical cross-section of a flattened bismuth spherical nanoparticle is used with a modified wavelength approximation over a range of a few hundred nanometres [67]. To predict the longitudinal and transverse cross sections of nanostructures, measurements are used finite difference time domain within a range of up to a few hundred nanometres [68]. To calculate the optical extinction cross section of spherical bismuth nanoparticles and nano prisms and enhance them in the near field [131].

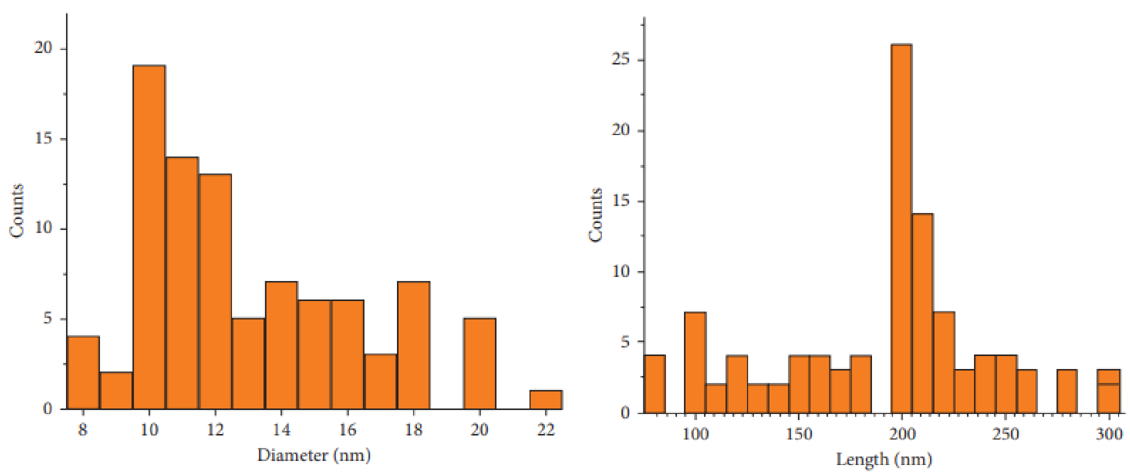

Figure (7): The distribution of the bismuth nano rods: (a) Diameter, and (b) length [47].

4. Bismuth Nanoparticle and Plasmon Property Applications

The human body contains small units called cells that the body depends on to perform many functions, and it is difficult to understand. Any deviation in the principle of cell work or activity would expose the body to a functional imbalance and thus expose it to diseases and be at risk if the cause of the defect has not been diagnosed [159]. The strong presence of antibiotics and the attempt of microorganisms to resist them requires the development of other methods to protect against diseases [160]. Studies have shown that the presence of nanoparticles with antibiotics has an effective effect against bacterial activity [161]. Therefore, metal nanoparticles give excellent efficiency in combating bacterial activity that causes diseases by using them in special techniques used in medical devices, as well as protecting foods, and in techniques used in water sterilization. Metal nanoparticles are also used in the field of treating skin inflammation and wounds [162-164]. Nucleation and growth processes are considered essential in determining the structural properties of materials in their final form and are involved in all methods for preparing these materials that are used in industry [165]. Nanoparticles are used in many applications, including medical and biological applications, as well as in optical devices and display screens [166]. In the future, organic materials may be used more than inorganic materials due to the efficiency of their properties [167]. Bismuth nanoparticles have been prepared recently, although still in their infancy, However, it has attracted the attention of researchers, especially in the medical and biological fields, because it possesses excellent properties, including high surface area, stability, and good electrical and magnetic properties, especially in the presence of a magnetic field. In addition to it also possess efficient catalytic activity and a low percentage of toxicity, they also possess flexibility in controlling the size and shape of their particles. When prepared, this paves new horizons in exploiting bismuth nanoparticles for therapeutic applications in the future [12]. Bismuth is a diamagnetic element, therefore it has strong magnetic properties and is a non-toxic and economical element, which makes it a strong presence in the preparation of nanoparticles that are used in therapeutic and diagnostic applications such as photo thermal imaging and radiography, in cancer therapy and tissue engineering, and the applications of biological sensors because of the amazing properties of bismuth,which including, physical, chemical characteristics and structure, for example, absorption of near-infrared radiation, conversion of light energy into heat, as well as a high value X-ray attenuation coefficient. Bismuth compounds are also can be used in therapeutic applications, such as bismuth chalcogenides, bismuth chlorides, bismuth oxides, bismuth selenides, bismuth oxy halides, and bismuth telluride.

The properties of the prepared bismuth nanoparticles can be modified to enhance their efficiency by using proteins and polymers whose biological properties are compatible with bismuth nanoparticles and lead to increase in the stability of the colloidal solution and using this property to reduce toxicity and expand blood circulation [12]. The phenomenon of Plasmon in nanoparticles plays an important role in biomedical applications such as treatment and imaging, as these techniques depend on the interaction process between antibodies while the metal nanoparticles can be used to convert thermal energy and absorb light [168–171].

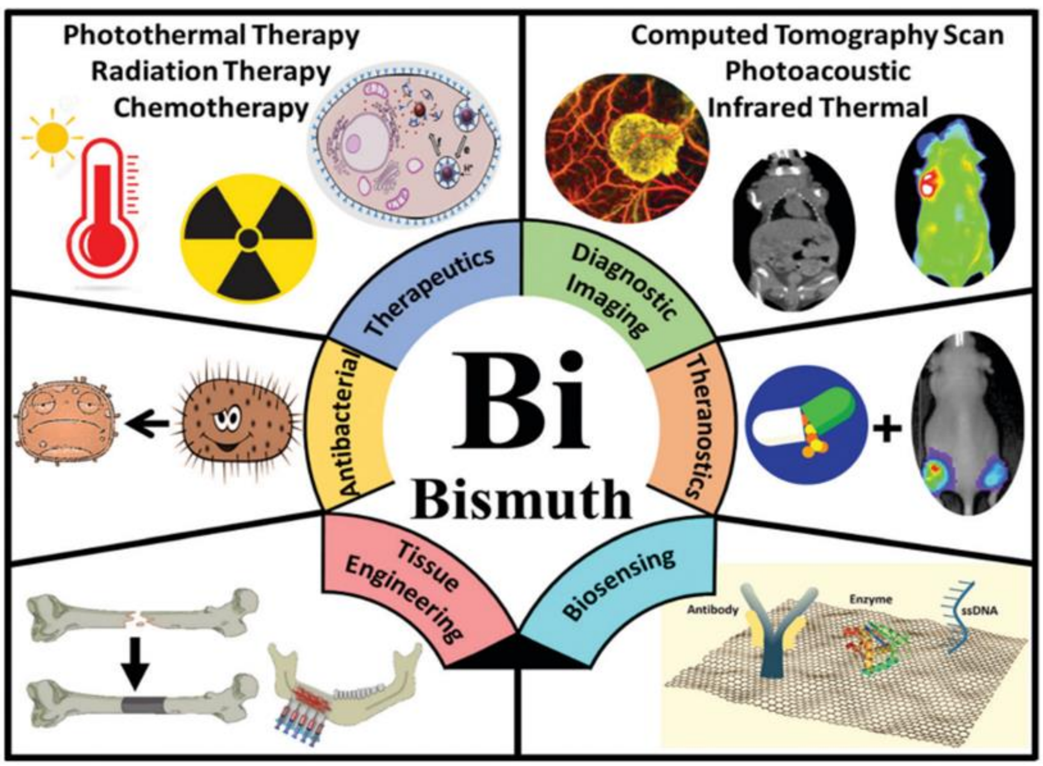

Figure (8): The main biomedical applications application of BiNPs [12].

An important applications of Plasmon are in thermal imaging and fields therapeutic [168–174], also it has been linked to nanostructures in order to benefit from it in biological and medical applications such as tissues and cancer cells [171]. The light absorbance process occur by nanostructure and converting it into heat. Thus, the sample can be imaged at the moment, cancer cells can be targeted, or a specific sample can be removed [173, 169]. The wavelength of the applied laser must equivalent with the absorbance of the nanostructures for the purpose of their use in photo thermal imaging. The small size of the nanoparticles is more effective in medical applications, especially in detection and imaging. by taking advantage of the properties of localized surface Plasmon resonance, they can also be used in cancer treatment and optical diagnosis [174].

4.1. Nanoparticles Toxicity Influence

The harmful side effects of nanomaterials on biological organisms are being studied in nanotoxicology, as the increasing engineering applications of nanoparticles in biomedicine have raised concerns about their safety for humans [175, 176]. However, size of nanoparticles [177], their morphology with surface functional groups [178],and dose dependent characteristics [179] one of the main reasons why nanomaterials are toxic and harmful to human tissues and cells . Many studies and research have proven that nanomaterials manufactured using chemical methods are more toxic and dangerous to human cells than nanomaterials manufactured using biological methods, because they contain synthetic chemical elements and functional factors [180]. Conversely,biologically preparated nanoparticles exhibit toxicity when they interact with living cells and decompose into simpler forms or accumulate [181, 182].

The surface area of nanoparticles increases with decreasing particle size, which in turn leads to an increase in chemical and biological reactions. Therefore, the characteristics that most affect toxicity are the surface area and volume, as well as shape, height, solubility, agglomeration, and crystallization [183]. For example,the number of particles present on the surface increased when the size of the nanoparticles decreased from 30 to 3 nanometers, and this was expressed from 10 to 50% [184]. When nanomaterials interact with cellular components, toxicity occurs even if the nanoparticles have the same chemical composition because the effect of particle size and surface area is the main factor. In other words, nanoparticle have greater toxicity than larger-sized particle [185]. Severe toxicity causing cell death and histopathological changes in mice has been reported due to silver nanoparticles with diameters of 10, 60, and 100 nanometers and thus infection in cellular necrosis and liver congestion as for the spleen, its congestion was observed after the administration of 10 nanometers of silver nanoparticles, not 60 or 100 nanometers. Therefore, smaller nanoparticles have greater acute toxicity in mice[186]. Different nano sizes (90, 60, and 30 nm) and 600 nm of amorphous silica have been verified for toxicity. After intrabronchial instillation of mice the effect of this on the heart and blood vessels was observed. Silica concentrations in the serum and heart were evaluated using coupled optical emission spectroscopy. High levels of proteins associated with inflammation, cytokines, and necrosis factor were observed in mice given nanoparticles by inhalation. The process of evaluating the respiratory system depends on the amounts of nanoparticles deposited in it [187].

Table (1): A previous literature review.

Authors	Method	Nanoparticle	Optical properties	Materials	Structural & morphology	Application	Ref.
M.d. Mahiuddin & B.Ochiai	Green Method	Bismuth	Many absorption bands has been showed by FTIR spectrum.	$Bi(NO_3)_3 \cdot 5H_2O$	Size and morphology has been showed by scanning electron microscopy (SEM) analysis , which confirmed that bismuth nanoparticles has spherical shape with the size at (50 -100) nm. Transmission electron microscopy(TEM) showed the nanoparticles are		106

					spherical with diameter at (8-30)nm. The crystallite size of bismuth nanoparticles was calculated to be 20 nm.		
Sally, et al	Pulsed laser ablation	Bismuth	Plasmon absorption bands by bismuth has been confirmed by (UV-Vis) spectrum.	Bi target	Temperature effect on bismuth nanoparticles size , at the range between (28- 55)nm has been confirmed by Field emission scanning electron analysis.	Antibacterial treatments	165
G.Carotenut , et al	Thermal de-compositi on	Bismuth		$Bi(SC_{12}H_{25})_3$	The surface morphology analyses of bismuth nanoparticles was confirmed the spherical shape & rhombohedral crystal structure.		20
Rusul & Raad	Near Infrared Lasers & Alternatin g Magnetic Field	Fe_3O_4@Au @SiO_2	The stability about (-49.1 mV), Core-shell have been optimized for biological field through synthesis with optical and magnetic properties.	Fe_3O_4,Au	Field emission scanning electron microscopy confirmed the small size of core- shell nanoparticles about (22.5)nm. X-ray diffraction (XRD) showed the average crystallite size about (22.8)nm.	Cell lines	188
Sally, et al.	Pulsed laser ablation	Bismuth	Bismuth coating process by silica has been completed success and confirmed by (UV-Vis) spectrum.	Pure bismuth granules	Bismuth nano metal coated by silica has been confirmed by EDXS and XRD analysis and TEM analysis has been confirmed the synergism between bismuth nanoparticles		21

					and silica coating effectively.		
M.Yarema, et al	Reproduci-ble synthesis	Bismuth		$Bi[N(SiMe_3)_2]_3$,$Li[N(SiMe_3)_2]$	Bismuth nanoparticles with spherical shape and crystalline size about (11-22)nm.		19
A.L.Brown & A.M. Goforth	Chemical Reduction	Bismuth	The peaks potions that obtained from (FTIR) spectrum indicated to absence of carboxy-late at greatest value about (1593,1408) cm^{-1} and also there are peaks of the amine at (1527 ,1502) cm^{-1}.	$Bi(NO_3)_3·5H_2O$	It has been confirmed that most of the bismuth nanoparticles obtained are spherical in shape, and some are hexagonal, triangular and also has cubic shape. A rhombohedral structure of bismuth nanoparticles has been confirmed by Powder X-ray diffraction (PXRD) analysis.		18
J.S.Son, et al	Colloidal chemical methods	Bismuth		Bismuth dodecane-thiolate	Good thermal and electrical properties has been obtained for bismuth nanoparticles size with (6,8,11,14,20 &27)nm.		17
B.Wei, et al	Facile Synthesis	Bismuth	highly mono dispersed.	$Bi(NO_3)_3•5H_2O$	Bismuth nanoparticles has been obtained with highly uniform size and antioxidant property.	Computed tomography medical imaging(CT)	16
Rusul & Raad	Green Method	Fe_3O_4	Surface Plasmon resonance absorption peaks were obtained at (290-519) nm.	ferricchloride hexahydrate, ferrouschloride tetrahydrate.	spherical nanoparticles and less than 50 nanoscale.	Surface Plasmon Resonance	114

			The peak towards the blue shift.				
Maha, et al	Green Method	Nickel Oxide NiO		$NiCl_2$	Nickel oxide nanoparticles with a face-centered cubic crystal structure were obtained with average diameter equal (45.11) nm.	Antibacterial and Anticancer Agents	5
M.A. Shahbazi, et al		Bismuth		$Bi(NO_3)_3 \cdot 5H_2O$	Various forms of bismuth nanoparticles have been obtained, including: triangular nanoparticles, nano belts, single crystalline bismuth nanoparticles, nano cubes and nano spheres.	Biomedical application	12
P.Lei, et al	Chemical reduction	Bismuth		$Bi(NO_3)_3 \cdot 5H_2O$and PVP	Bismuth nano dots + povidone were formed in spherical shape and very small size particle (2.7 ± 1.1 nm) with diameter about 2.7 nm	Cancer therapy & photo thermal imaging	15
C.Yang, et al	An artificial cell film was used to modify bismuth using ultra-sound method .	Bismuth		oleic acid and trioctyl-phosphine	Bismuth nanoparticles with spherical shape and average diameter of (47 ± 3) nm.	Medical imaging & Photo thermal Therapy	14
M.A. Dheyab, et al	Sono-chemistry method	Gold shell on Fe_3O_4 core		Au, Fe_3O_4		Chemical activity	190
A.H. Habib, et al	chemical method	Iron-cobalt/ ferrite core-shell		Fe–Co		Cancer therapy	189
S.Cicek, et al	Green Method	Silver	peaks were obtained from Uv-Vis spectrum at (390-440) nm.	$AgNO_3$	Spherical shape with particle size (7-20)nm and another at(5-35)nm.	Antibacterial Activity	104

			& (440-458) nm.				
Rusul, et al	Turkevich method	Au		$HAuCl_4$	Absorption peaks were obtained for gold nanoparticles before core shell synthesis at (515)nm and shifted to (518)nm after core shell synthesis.	Surface Plasmon Resonance	113
Mayada, et al	Laser ablation	Ag/Au	peaks were obtained at (400-410) nm.	Ag, Au	Spherical shape with average size (20 -30) nm.	Biological and medical applications	1
Hayder, et al	sol-gel method	Al_2O_3/ MgO		$Al(NO_3)_3.9H_2O$ $Mg(NO_3)_2.6H_2O$,NH_4OH, ,$C_{12}H_{22}O_{11}$,C_2H_5OH	Nanoparticles with particles size (54.9, 59.8) nm with irregulars shape.	Antibacterial test	7
Emmanuel, et al	Anti-microbial potency	Nano material		nanomaterial		Antibacterial test	4
Falah , et al	Pulsed Laser Ablation	Au	Optical properties including an increase in Abs. were obtained when the energy was increased.	Gold target	The average diameter was determined using an atomic force microscope.		6
H.Nadarogl u, et al	Bio-reduction method	Ceria	Optical properties has been showed that the Abs. reduced with increasing temp.	$[Ce_2(SO_4)_3]$	Spherical shape with particles size (8.6–10.5) nm.	Antioxidant activity	102
M. Shah , et al	Green Method	Nano metals via Biological Entities		microorganismsa nd plants		Electronics, photonics, medicine, and agriculture	101

5. Conclusion

Bismuth nanoparticles have made significant strides in terms of their performance in recent years for multimodal therapeutic applications due to its effective characteristics.Inferred from the reviewed data, the green method has the excellent potential to prepare bismuth nanoparticles for the studing of surface plasmon resonance because the plant extract acts as a catalyst of the reaction. The good absorption of near infrared radiation by bismuth nanoparticles has encouraged the use of bismuth for medical fields, in particular in the studying of cancer cells and trying to inhibit their activity. Furthermore, efficient structural properties exhibited by Bismuth nanoparticles, such as their small size, large surface area, suitable morphology and in addation its consideration as a semimetal.

Finally, there is a still a major challenge facing this type of studies because cancer remains one of the main causes of human death, and the side effects of the traditional treatments have remained without unresolved,but researchers are making unceasing attempts to address the obstacles and provide possible solutions to enhance and develop these studies.

Conflict of Interest: The authors declare that there are no conflicts of interest associated with this research project. We have no financial or personal relationships that could potentially bias our work or influence the interpretation of the results.

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