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Review

Biogenic Nanoparticles: Synthesis, Characterisation and Applications

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Abstract: Nanotechnology plays a big part in our modern daily lives, ranging from the biomedical sector to the energy sector. There are different physicochemical and biological methods to synthesise nanoparticles towards multiple applications. Biogenic production of nanoparticles through the utilisation of microorganisms provides great advantages over other techniques and is increasingly being explored. This review examines the process of the biogenic synthesis of nanoparticles mediated by microorganisms such as bacteria, fungi and algae, and their applications. Microorganisms offer a disparate environment for nanoparticle synthesis. Optimum production and minimum time to obtain the desired size and shape, to improve the stability of nanoparticles and to optimise specific microorganisms for specific applications are the challenges to address, however. Numerous applications of biogenic nanoparticles in medicine, environment, drug delivery and biochemical sensors are discussed.

Keywords: biogenic synthesis; nanomaterials; nanoparticles; drug delivery; biochemical sensors

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1. Introduction

The advent of nanotechnology in the 1960s commenced a new era of materials science. The field has brought together many academic disciplines such as biology, chemistry, materials engineering, medicine and physics, with the aim of developing materials at the nanoscale. Nanoparticles include many types of materials comprised of dimensions less than 100 nm in size [1]. They are classified by the number of dimensions in which an electron can be confined to, i.e., 0-dimensional (0D), 1-dimensional (1D), etc. Some of the common geometries include spheres (0D), wires and rods (1D) and thin films (2D). The synthesis of nanoparticles is of great importance because of the unique properties they exhibit including electronic, magnetic, physiochemical features including control of size, increased surface area to volume ratio and functionalities [2]. The main reasons for these unique properties of nanoparticles are due to (i) confinement of electrons in such particles, (ii) particle size changes to modify bandgap energies and (iii) large surface to volume ratio [3].

These unique properties of nanoparticles, including biological, chemical, electrical, magnetic, optical and physical properties [4], differ greatly from the same materials in their bulk form. For examples, nanomaterials offer enhanced Raman and Rayleigh scattering properties in metal NPs (such as gold and silver), supermagnetic properties in magnetic materials and a quantum effect in semiconductors [5]. Such NPs form the next generation building blocks for biomedical [6], chemical, electronic and optical applications [7]. In recent years, nanoparticles have also found applications in the environmental [8,9], petroleum [10,11], food [12] and textile industries [13]. Whereas, in the past metal nanoparticles such as gold and silver were studied in great detail, the last decade has seen the rise in research of other metal nanoparticles such as copper [14], palladium [15], platinum [16] and various metal oxides.

There is a great need for the control of NP geometries that result in desired electronic, optoelectronic and physicochemical properties. Yet, it is challenging to synthesise monodispersed nanoparticles with control over crystallinity and geometry. Earlier studies have focused heavily on using chemical and physical methods, which are used extensively. However, the use of toxic chemicals for synthesis is still a major concern, along with high costs [17]. In addition, the toxic elements on the nanoparticle surface hinder their application in biomedical fields and are of concern for polluting the environment. As a result, non-toxic and environmentally safe nanoparticle synthesis methods must be developed. Despite being sustainable and environmentally friendly, biological synthesis methods often necessitate the time-consuming cultivation of microbes. The development rate of biologically synthesised nanoparticles is sluggish, and they are not monodispersed. These are some of the issues associated with biological synthesis; however, careful selection of microorganisms, optimization of control factors such as pH and temperature and concentration of precursors may allow the implementation of such methods in large-scale production. It is also hypothesised that microbes can be genetically engineered to synthesise nanoparticles with greater control over shape and size [18,19].

Although the exact mechanisms behind biogenic synthesis still have not been fully understood, ongoing studies are trying to improve the understanding of the biological processes behind nanoparticle synthesis and have unearthed new abilities of microorganisms with unprecedented potential for new types of applications. The discovery of microbes producing magnetite nanoparticles, for instance, offers the opportunity to synthesise nanoparticles with unique magnetic properties [19]. Metal nanoparticles, particularly gold and silver, have been studied extensively for biomedical and sensing applications. Some of the recent examples of nanoparticle applications include magnetic nanoparticles for imaging [20], silver nanoparticles for photodetectors [21], gold nanoparticles for light-induced magnetism [22], barium titanate nanoparticles for breast cancer treatment [23] and gold nanoparticles for detection of SARS-CoV-2, the COVID-19 virus at the centre of pandemic attention [24]. This article reviews the recent advances in biogenic synthesis of a range of nanoparticles using different microorganisms, their characterisation techniques and some exemplar applications.

2. Biogenic Synthesis of Nanoparticles

Microorganisms are capable of producing many unique nanostructures. This has led scientists to become more interested in utilising these microbes to synthesise nanostructures for various applications. Inorganic molecules can be generated by bacteria and fungi by biologically mediated and induced synthesis [25]. By controlling the biological synthesis, nanostructures of desired geometries and composition can be formed. Despite the accuracy of the nanoparticle physicochemical synthesis, biological synthesis of nanoparticles is still limited in terms of particle geometry controllability and process scalability [26]. Nevertheless, biologically induced synthesis has allowed scientists to synthesise inorganic nanoparticles using common metal precursors [27], while also offers a wide range of composition.

Microorganisms such as bacteria, fungi and algae are increasingly being used to create nanosized particles. There are a wide variety of microbes, which mostly react differently with metal precursors to produce nanoparticles. For example, bacteria and fungi are capable of intracellular and extracellular production, and both processes have different pathways in different microbes. Intracellular synthesis utilizes the cell wall to transport metal ions, where the ions with a positive charge interact with the negative charge wall. Enzymes in the cells reduce these ions to metal NPs. Figure 1 shows gold nanoparticle synthesis using bacteria *Lactobacillus kimchicus* [28]. Nucleation of HAuCl ions takes place at the beginning of the process, which leads to the creation of nanoclusters through an electrostatic interface. Afterwards, nanoclusters are gradually transferred across the microbe cell wall. The mechanism behind the extracellular synthesis of nanoparticles includes the aggregation of metal ions on the cell surface and the involvement of reducing ions via enzymes. Ameen et al. used *Cupriavidas* sp. for extracellular synthesis of silver NPs [29]. The study concluded that silver ions are trapped on the cell surface and nitrate reductase (an enzyme) reduces them to atomic silver NPs. Huge research efforts went into designing such techniques for generating a wide range of NPs (including gold, palladium, silver, titanium oxide, etc.).

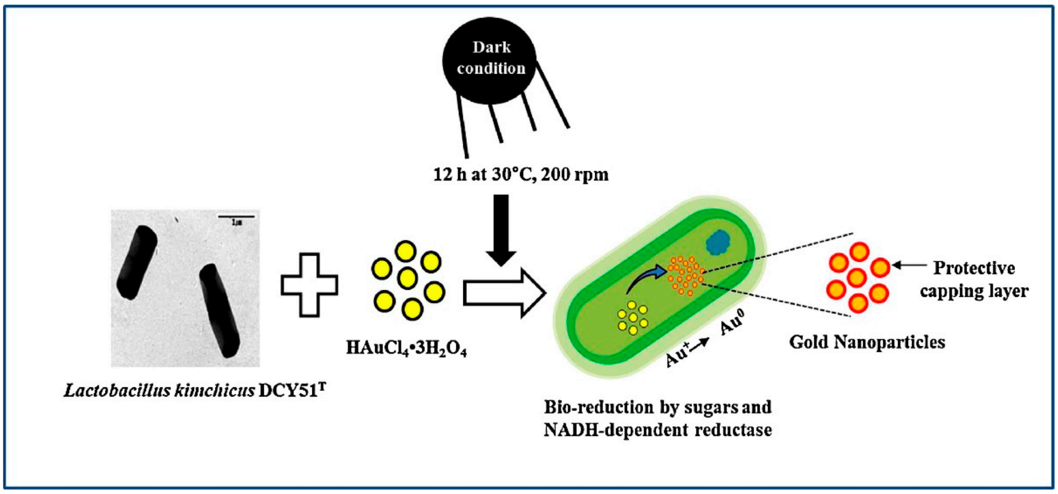

Figure 1. Mechanism of the intracellular-cell bound synthesis of gold nanoparticles (AuNPs) using *L. kimchicus* DCY51^T [28].

2.1. *Types of Nanoparticles*

2.1.1. Silver

Silver nanoparticles (AgNPs) have been researched extensively for applications in different fields and have raised considerable interest in the biomedical field because of its antimicrobial properties and antioxidant potency [30]. Their antibacterial properties depend on size, with smaller particles being more effective against many pathogens. They have been shown to successfully counter Gram-negative and positive bacteria, and also have a variety of uses in wound dressings [31].

2.1.2. Gold

As another metal that has been studied extensively, gold nanoparticles (AuNPs) have found numerous applications relating to cancer therapy, drug delivery and other biomedical applications such as antibacterial [32]. Studies have shown that nanobubbles containing gold nanoparticles can be targeted to a tumorous area and burst due to increased heat from a laser or infrared radiation source [33]. These nanoparticles enter the cancer cell, decreasing its growth rate. AuNPs are also being used for various applications such as Raman spectroscopy and imaging [34].

2.1.3. Metal Oxides

Studies on metal oxides have also been reported including include zinc oxide (ZnO), copper oxide (CuO), magnesium oxide (MgO), titanium dioxide (TiO_2) and aluminium (Al_2O_3), iron oxide (Fe_3O_4) and many others. Iron oxide has been a recent and exciting nanomaterial due to its magnetic properties. Iron oxide (Fe_3O_4) nanoparticles are being used in different applications including biomedical, catalysis and environmental safety. The most common applications of such NPs include targeted drug delivery, biosensor, MRI, diagnosis of cancer and tissue engineering [35]. Tin oxide (SnO_2) and tungsten (tri)oxide (WO_3) have unique electrical properties that depend on the size of these nanoparticles, and these are used as gas sensors [36]. Titanium dioxide finds applications in the optical and solar energy sectors due to its electrical conductivity [37]. Magnesium oxide nanoparticles are used to reduce pollution in the air and also catalysts in organic reactions [38,39]. Copper oxide nanoparticles find applications in the catalysis field including oxidation and photothermal uses [40].

2.2. Bacteria

Bacteria are readily available from the environment, can be cultivated quickly and are able to adapt to different conditions, making them great candidates for nanoparticle synthesis. It is relatively easy to control bacterial culture conditions such as temperature and oxygenation. It is necessary to control such conditions as to be able to synthesise different sized nanoparticles for different applications [41].

Utilizing bacteria has proved a promising approach to produce metal nanoparticles. They are well known for synthesising gold, silver and other nanoparticles (see Table 1 for examples of nanoparticle synthesis using bacteria).

Table 1. Examples of recent studies on nanoparticle synthesis using bacteria.

Nanoparticle	Bacterium	Application	Intra/Extra	Reference
Gold	*Lactobacillus kimchicus*	Drug delivery, cancer diagnostic	Intra	[28]
Gold	*Staphylococcus epidermidis*	Catalysts	Extra	[42]
Gold	*Paracoccus haeundaensis*	Antioxidants	Extra	[43]
Silver	*Cupriavidus* sp.	Antibacterial	Extra	[29]
Silver	*Bacillus subtilis*	Antibacterial	Extra	[44]
Zinc oxide	*Bacillus subtillis*	Synthetic dyes	Extra	[45]
Zinc oxide	*Staphylococcus aureus*	Antibacterial	Intra	[46]
Nanoselenium	*Bacillus* sp.	Biomedical	Extra	[47]
Platinum and palladium	*Desulfovibrio vulgaris*	Catalysts	Extra	[48]

AuNPs (15–35 nm) were developed extracellularly using marine bacterium *Paracoccus haeundaensis* [49], they demonstrated non-toxicity to normal human cells and prevented the growth of cancerous cells A549 and AGS at differing concentrations.

In a study by Mathivanan et al. to produce silver nanoparticles (AgNPs) using *Bacillus subtilis* [44], they investigated the effects of crude and calcined (200 °C for 30 min) AgNPs on pathogenic bacteria such as *Pseudomonas fluorescens* MTCC 1749, *Proteus mirabilis* MTCC 425, *Escherichia coli* MTCC 1610, *Bacillus cereus* and *Staphylococcus aureus* MTCC 2940. The bacterium was isolated from samples of sediment and cultivated. AgNPs were produced by reduction of silver ion (Ag+) by enzymatic processes involving NADH dependent reductase. Silver ions presence is determined inside by detecting colour transition from yellow to brown. The extracellular development of AgNPs was determined from their change of colour. The antibacterial activities were studied using the well diffusion method. It was found that crude AgNPs improved the inhibition of bacteria compared to calcined AgNPs.

Biochemical mechanisms governing the microbial synthesis of for nanoparticle have partially been identified and they are presently still being studied for further understanding. The mechanisms employed by microbes for nanoparticle synthesis involve modifications in solubility and toxicity, bioadsorption, bioaccumulation, precipitation of metals and efflux systems [50]. These processes form the mechanisms of microbial resistance for cellular detoxification of inorganic particles by enzymes. The main type of enzymes involved is oxidoreductase, such as nitrate reductase and sulphite reductase, and cellular transporters.

Certain bacteria have showed the potential to synthesise nanoparticles of organic materials. Aerobic acetic bacteria such as *Gluconacetobacter* have been used to synthesise cellulose nanocomposites [51]. Bacterial cellulose is a 3-D network of cellulose nanofibrils with improved properties compared to nanocrystalline cellulose and nanofibrillated cellulose. The main applications for bacterial produced nanocellulose are biomedically related, such as antimicrobial agent and drug delivery systems, and biosensors.

Microbes are also capable of synthesising nanomineral crystals, magnetic and oxide metals. Especially magnetotactic bacteria are adept at building magnetosomes, which are suitable for producing magnetic radicals [52]. It is possible to control the geometry and composition of nanoparticles. Magnetosomes are organic-coated nanocrystals of iron oxide and iron sulphide, biosynthesised by both magnetotactic and non-magnetotactic bacteria. The magnetic properties are determined by species of bacteria, and the organic layer is the result of the bacterial phospholipid bilayer membrane [53]. Applications of magnetosomes include cancer therapy, molecular imaging [54] and toxicity assessment biosensor [55].

Bacteria are capable of synthesizing nanoparticles extracellularly or intracellularly. However, there are limitations of bacterial synthesis of nanoparticles. The main issues are purification of nanoparticles and difficulty in controlling the geometry due to a lack of full understanding of mechanisms [56]. It is challenging to control the particle shape and size, produce monodispersed particles and large-scale capability. Therefore, these methods require further study to improve the understanding of the mechanisms before they can be considered for industrial uses.

2.3. Fungi

Nanoparticle synthesis using fungi offers certain advantages in comparison to bacteria; thus, research in this area has seen an increasing interest over the last decade. Some of the advantages of mycelium include easy to scale up and downstream the process, economically feasible and ecologically friendly so they can cover a large surface [57]. Fungi contain enzymes in the cytoplasm and cell wall, which transform metal ions into nanoparticles [58]. The metal ions have a positive charge, which is attracted by the fungi and triggers the biosynthesis. Certain proteins are also induced by metal ions, and these hydrolyse the ions. Fungi are able to secrete high amounts of protein, thus increase nanoparticle synthesis. See Table 2 for some of the recent studies conducted on nanoparticles synthesis using fungi.

Table 2. Examples of recent studies on nanoparticle synthesis using fungi.

Nanoparticle	Fungus	Application	Intra/Extra	Reference
Iron oxide	*Aspergillus niger* BSC-1	Wastewater treatment	Extra	[59]
Silver	*Aspergillus terreus*	Antibacterial, anticancer	Extra	[60]
Silver	*Cladosporium cladosporioides*	Antioxidant, antimicrobial	Extra	[61]
Copper	*Aspergillus niger*	Antidiabetic and Antibacterial	Extra	[62]
Selenium	*Mariannaea* sp. HJ	Medicinal and electronics	Both	[63]
Cobalt oxide	*Aspergillus nidulans*	Energy storage	Extra	[64]
Gold	*Cladosporium cladosporioides*	Antioxidant, antimicrobial	Extra	[65]
Gold	*Cladosporium oxysporum*	Catalysis	Extra	[66]
Platinum	*Fusarium oxysporum*	Nano medicine	Extra	[58]

There are an increased number of studies on silver nanoparticle synthesis using fungi, where their applications include antimicrobials, antioxidants, electronics and other biomedical applications. Despite the increased research into the microbial synthesis of gold nanoparticles, there are fewer studies on using fungi. Many of the studies have focused on silver and metal oxides. Joshi et al. synthesised gold nanoparticles using the fungus *Cladosporium cladosporioides* obtained from seaweed *Sargassum wightii* [65]. The study examined the mechanism of nanoparticle synthesis and concluded that the NADPH-dependent reductase enzymes and the phenolic compounds were responsible for the synthesis of nanoparticles.

There are several experiments on using *Fusarium oxysporum* fungus to synthesise nanoparticles in several experiments, including many studies on AgNPs. Srivastava et al. synthesised AgNPs (10–15 nm in size) using fungus *Fusarium oxysporum* [67], and demonstrated promising antibacterial effects on *Escherichia coli* and *Pseudomonas aeruginosa*. Other examples of nanoparticles produced using *F. oxysporum* include copper [68], gold [69] and magnesium oxide [70].

Like other microbes, fungi produce nanoparticles intra/extracellularly. Many of the nanoparticles produced within the organism are smaller than the ones that are created externally. The size limit is related to the nucleation of the particles within the species. Intracellular formation also offers many beneficial advantages. Depleted metals including platinum and copper must be eliminated from the environment to repair effects of environmental pollution. Fungi that produce intracellularly would be ideal to use because of the ease to extract the contamination from the sample [71].

Extracellular synthesis of NPs often has many applicable uses as the material is devoid of unwanted cellular constituents. Fungi are commonly known to be extracellular species since they secrete several secreted molecules to assist in the sequestration of nanoparticles. Extracellular synthesis provides greater simplicity and is relatively low cost. Manjunath and Joshi found that *Cladosporium cladosporioides* could be used in producing AgNPs in sizes ranging from 30 to 60 nm [61]. AgNPs showed uniform size and spherical form in FESEM images.

As well as metal nanoparticles, fungi are capable of synthesising metal oxide nanoparticles. Magnetite is a widespread iron oxide that exhibits magnetic properties. Fungi such as *Aspergillus* are capable of producing such nanoparticles [59]. Nanomaterials are being used to remove heavy metals and radioactive materials, due to their high (and fast) surface area to volume ratio [72]. Magnetite NPs are more efficient compared to other metal nanoparticles for this particular application because their superparamagnetic behaviour allows them easily to be separated from wastewater due to electrostatic and surface complexation.

Bionanocomposites of fungus-Fe_3O_4 for nuclear waste management have been reported [73]. Nano Fe_3O_4 particles were obtained from *Penicillium* Shijie, a fungus that grows on wood. SEM results revealed that the particles were uniformly decorated with a thin coating of Fe_3O_4 on the fungus' surface. FTIR results revealed that the iron oxide particles being chemically bonded to the surface of the fungus. They found that in the case where ions were present, fungus-Fe_3O_4 sorption was not affected by ion strengths, implying that its surface complexion that was assumed to influence sorption.

Magnetite NPs have found wide uses in applications such as MRI [51], and for oscillation damping and position sensing [52], and recording machines. Like bacteria, using fungi also has a major drawback with regards to biosafety. Fungus like *F. oxysporum* is dangerous since they are mostly pathogenic and thus are a concern to health. However, there are several non-pathogenic fungi examined that are suitable to synthesise nanoparticles. Variations of the *Trichoderma* fungus are such examples that have been utilised in applications related to food [74], medicinal and paper industries.

2.4. Algae

Algae are part of the Protista kingdom and include autotrophic and aquatic photosynthetic organisms, being single or multicellular. They are eukaryotic organisms without the multicellular structures of the plant. Algae can vary greatly in size, from microscopic microalgae to giant macroalgae. They are known for producing oxygen and form the food source for most aquatic forms of life. Seaweed is a typical example of macroalgae, which has been the source of food containing vitamins, minerals and protein. Microalgae have been known to transform metals ions into malleable forms, and are considered green gateways to synthesise nanoparticles [75]. The ability of algae to synthesise nanoparticles is attributed to the inclusion of active compounds in cell walls. Examples of such compounds include alginate and laminarin, which contain reactive groups [76]. Stabilization and capping of nanoparticles are accomplished by polypeptides by their amino acids or cysteine amides.

A typical process of algae-assisted nanoparticle synthesis involves (1) preparation of algae extracts in solution at elevated temperature, (2) preparation of reagents and (3) gestation of algae and reagent solutions and then stirring for a specified period of time (Sharma et al., 2016). To initiate the reaction, the algal extract is mixed with the metal precursor. A change of colour shows the beginning of a reaction which illustrates nucleations, followed by the growth of NPs where the adjacent nucleonic particles join and form thermodynamically stable NPs of various geometries [77]. The extract biocompounds facilitate the synthesis of NPs, and pH, temperature, concentration and time are the driving factors involved.

Seaweeds such as *Sargassum wightii* and *Fucus vesiculosus* have been utilised to synthesise nanoparticles [78,79]. Numerous studies involving the synthesis of gold and silver using algae have been reported (see Table 3 for examples). *Tetraselmis kochinensis* has been shown to produce intracellular gold nanoparticles [79]. Besides seaweed, AuNPs and Au-silica bionanocomposites can be synthesised in microalgae like diatoms (*N. atomus* and *D. gallica*) [80]. Algae is just as essential in nanoparticle synthesis in comparison to other micro-organisms, such as bacteria and the fungus, and thus an ecofriendly approach has recently been studied for nanoparticles' algae-mediated biosynthesis. Although algae offer green synthesis of nanoparticles, they still have limitations, which must be overcome before this method can be considered sustainable in the long run. The process of extract preparation is time-consuming and nanoparticles yield is less compared to physical and chemical methods [81]. Various control factors involved in the synthesis require detailed examination to improve future prospect of algal synthesis.

Table 3. List of algae for nanoparticle production.

Nanoparticle	Algae	Application	Reference
Silver	*Portieria hornemannii*	Antibacterial	[82]
Silver	*Botryococcus braunii*	Catalysis	[83]
Gold	*Caulerpa racemosa*	Biomedical	[84]
Iron oxide	*Colpomenia sinuosa* and *Pterocladia capillacea*	Antibacterial	[85]
Gold	*Egregia* sp.	Biomedical	[86]
Gold	*Cystoseira baccata*	Cancer	[87]

2.5. Characterisation of Nanoparticles

Nanoparticles have unique properties and features, which make them useful for numerous applications. It is crucial to assess them through extensive characterisation, particularly for biomedical applications, to be able to ensure them fit for purpose. This is achieved by using various techniques and equipment that can provide the required information. The most commonly used techniques include dynamic light scattering (DLS), atomic force microscopy (AFM), energy-dispersive X-ray spectroscopy (EDS), Fourier transform infrared (FT-IR) spectroscopy, Raman spectroscopy (RS) and scanning and transmission electron microscopy (SEM/TEM). These techniques are used in studying nanoparticle size, shape, structure, surface properties and interactions with materials such as human tissues. Table 4 shows a summary of some of the methods used to characterise the physicochemical properties of nanoparticles. For a detailed review of nanoparticle characterisation techniques, it is suggested to read the following review paper by Mourdikoudis et al., "Characterisation techniques for nanoparticles: comparison and complementarity upon studying nanoparticle properties" [88].

Table 4. List of techniques for characterisation of nanoparticles.

Techniques	**Characteristic**
Atomic force microscopy (AFM)	Geometry, structure, distribution
Differential scanning calorimetry (DSC)	Thermal performance
Dynamic light scattering (DLS)	Hydrodynamic size distribution
Fluorescence spectroscopy	Optical properties
UV-VIS/Infrared spectroscopy	Structure, Functional group analysis
Mass spectrometry (MS)	Molecular weight, composition, surface
Nuclear magnetic resonance (NMR)	Structure, composition, purity
Scanning electron microscopy (SEM)	Aggregation, size and shape
Transmission electron microscopy (TEM)	Aggregation, size and shape
X-ray photoelectron spectroscopy (XPS)	Elemental and chemical composition

2.5.1. Geometry

Size and shape determine the unique properties of nanoparticles to be effective for respective applications. At scales less than 100 nm, advanced equipment with excellent magnification and resolution are utilised to examine the size and shape of nanostructures. Two of the most widely used nanoscale imaging techniques are high-resolution transmission electron microscopy (HRTEM), and field-emission scanning electron microscopy (FeSEM), which can image and identify nanoparticle atomic composition. TEM uses a beam of electrons to illuminate the nanoparticles and can reveal scale, shape, aggregation state and morphology detail. An example Transmission electron microscopy (TEM) image is shown in Figure 2, showing gold nanoparticles in an average size of 20.93 nm.

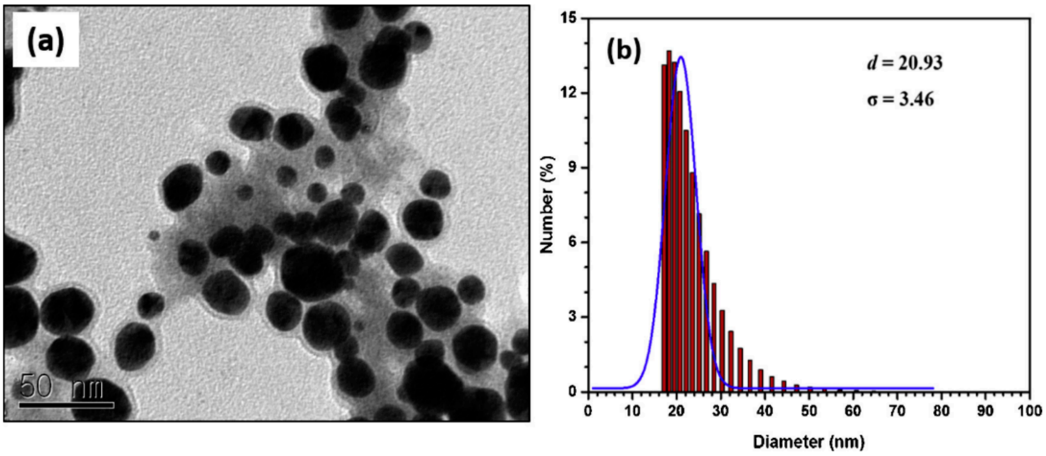

Figure 2. (**a**) Transmission electron microscopy (TEM) image showing bacterial synthesised AuNPs and (**b**) histogram showing particle size distribution with the average size being 20.93 ± 3.46 nm [43].

2.5.2. Surface Morphology

Common techniques used to characterise surface morphology are AFM, SEM and TEM. TEM is better capable of providing composition and morphology, allowing resolution of atomic scale. SEM uses a beam of electrons to image the surface of the sample, which means the sample must be conductive prior to analysis. SEM can examine the aggregation and morphology and in used frequently than TEM despite having a poorer resolution. AFM is another important technique that can analyse the topography, particle size and distribution of nanoparticles and can be operated under various conditions such as air, liquid and vacuum.

2.5.3. Magnetic Properties

Iron-based nanoparticles have gained popularity over recent years; therefore, the study of their magnetic properties is necessary. Some of the techniques include electron paramagnetic resonance (EPR), vibrating-sample magnetometer (VSM) and superconducting quantum interference device (SQUID). EPR is used to detect and identify free radicals and paramagnetic centres in chemicals. It allows for the investigation of the physical properties of magnetic nanoparticles and the influence of the external magnetic field by means of interaction with electrons in a sample. For highly sensitive magnetic measurements, VSM and SQUID are employed, having sensitivities of 10^{-6} emu and 10^{-10} emu, respectively. SQUID is employed to characterise media such as powder, thin films and other solid and liquid samples.

3. Applications

3.1. Medical Applications

Advanced development in nanoparticles research has led to their increasing applications, in particular, recently in the biomedical sciences, including diagnostic, drug delivery systems, biosensing and bioimaging [6]. For example, different branches of medicine have taken an interest in nanoparticles as they can deliver the optimal dosage of drugs, result in improved efficiency and reduced side effects [89]. Based on their optical properties, NPs are selected in order to provide efficient contrast for biological and cell imaging applications, where the absorption and scattering properties and optical resonance wavelength of NPs such as Au and Ag can be calculated.

Recently, magnetic nanoparticles such as magnetite (Fe_3O_4) have also been employed for biomedical applications [90]. Super magnetic iron oxide nanoparticles with the right chemistry are used in research to improve MRI, drug delivery, cell separation and immunoassays. For these applications, NPs must be small with high magnetization, have dimensions of no more than 100 nm and have a uniform size distribution (Laurent et al., 2010). Labelling antibodies to carry out identification of tissues is achieved by using a variety of dyes, enzymes, radioactive compounds or AuNPs (Khlebtsov and Dykman, 2010b) [91].

Semiconductor and metal nanoparticles show enormous promise of cancer detection and therapy due to the light scattering and absorption properties. Gold nanoparticles can transform the absorbed electromagnetic energy from an electromagnetic field into heat and can be used to target specific cancerous tissues. In a study on Au-silica NPs for prostate cancer treatment [92], gold–silica nanoshells (GSNs) were combined with MRI-ultrasound imaging to selectively ablate prostate tumorous cells. These NPs absorbed NIR light, which caused an increase in temperature, in turn leading to hyperthermia and tumorous cell death.

Silver NPs have been extensively used in wound dressings, catheters and numerous domestic products because of its antimicrobial effect, particularly compared to traditional silver ion solutions. Antimicrobial agents are essential in water disinfection, medicinal applications, textile and food packaging. The NPs are functionalized with different groups with the purpose of overcoming the varied bacteria populations. Materials such as ZnO, TiO_2, Cu- and Ni-based NPs, are being used for specific functions because of their ideal antibacterial activities.

3.2. Materials and Mechanical Applications

The properties of nanomaterials differ greatly from the respective material in bulk form, which make them useful functional materials. Thus, the advantages of nanoparticles depend upon the ability to be able to customise the geometries of materials at increasingly smaller dimensions to obtain the necessary properties, therefore adding to the growing scientific portfolio. It is possible to produce materials with defined characteristics that yield electrical, physical, optical and imaging properties that are suitable for particular applications [93].

Nanoparticles find applications in the textile industry, where they can be added to or used to treat fabric surfaces, which result in enhanced ballistic protection properties, and reduced wrinkling and bacterial growth. Nanomaterials are emerging to allow washable, resilient "smart fabrics" that are incorporated with nanoscale sensors and electronic components allowing functions such as health tracking, solar energy capture and energy harvesting by movement [94,95].

Nanoparticle based consumer products include new electronics and computers, health trackers and other miscellaneous home products. It is predicted that nanotechnology will eventually be the next breakthrough across several sectors, including food manufacturing and packaging. Resonant energy transfer (RET) systems incorporating noble metal nanoparticles are growing in fields of optics and material science. So that NPs can be used in future commercial products.

Nanoparticles possess excellent mechanical properties such as Young's modulus, stress and strain; mechanically stronger nanodevices can be developed [3]. For mechanical industries, their applications could be useful for coatings and lubricants. They can be embedded in the metal and polymer matrices to enhance the tribological properties. That is because the rolling contact area between the lubricated nanoparticles and the substrate will be greatly reduced, resulting in very low surface friction and wear. Furthermore, NPs provide strong sliding and delamination properties, which could also enhance wear resistance and decrease friction [94].

Coatings can increase hardness and wear resistance by increasing a material's resistance. Alumina, titania and carbon-based NPs have shown to be effective coating agents in enhancing mechanical properties [7].

3.3. Environmental Applications

The growing number of nanoparticle applications for industrial and domestic products can lead to their leakage into the environment [96]. Such applications lead to the direct release of harmful materials in the groundwater and soil, which are common environmental hazards to test ground pollution. Environmental risk of NPs is assessed by identifying their exposure pathways, persistence, reactivity, ecotoxicity and mobility. Nanotechnology advancements have opened new possibilities for improved environmental remediation.

Nanoparticles can help satisfy the demand for accessible, potable water by allowing for the fast and low-cost assessment and management of impurities in water. For example, Cu NPs in paper filters for water purification resulted in high bacteria reduction of *E. coli* and low levels of copper released in drinking water (1 ppm) [97].

Nanoparticles have also been developed to clean up oil spills. Fine carbon particles with engineered surface chemistry have been shown to stabilise oil-in-water emulsions [98]. Functionalised carbon black (CB) NPs showed non-toxic effects in brine shrimp, and also were shown to adsorb benzene. One research found that magnetic NPs coated with green hydrophobic biocomponents isolated from *Anthemis pseudocotula* improved their performance of heavy crude oil collection [99].

Heavy metals such as mercury, lead, thallium, cadmium and arsenic are dangerous to the environment and humans as they are environmentally undesirable and have harmful effects; it is vital to remove such metals to avoid harms. Carbon nanotubes, nano-zeolites and metal oxides have been used to environmental remediation. The most promising agent is nanoscale zerovalent iron (nZVI), as it is non-toxic, economical and easily produced [100]. Another alternative is the use of bimetallic nanoparticles, consisting of elemental iron or other metals in conjunction with metal catalysts such as silver, gold, nickel and palladium, to improve the rate of reduction.

3.4. Applications in Energy Technology

Fossil fuels cannot be relied upon for long-term energy generation, as they are scarce and non-renewable. Thus, it is critical to research and grow green technologies that are not only renewable but also affordable. Nanoparticles can be critical for energy technologies as they offer desired properties such as large surface area, and unique optical and catalytic properties. They can be especially useful in photocatalytic applications. Photoelectrochemical and electrochemical water splitting (or energy) splitting have been employed extensively to promote NP development [101].

There are several ways to split water using chemical precursors, such as electrolysis and thermal and thermolysis, or using the fuel byproduct, these technologies often include solar cells and piezoelectrics [102]. NPs are improving the efficiency of fuel production from raw petroleum materials through better catalysis, enabling reduced fuel consumption in vehicles and power plants through higher-efficiency combustion and decreased friction. Nanoparticles are used in energy storage applications [103]. Figure 3 shows some energy generating devices using NPs.

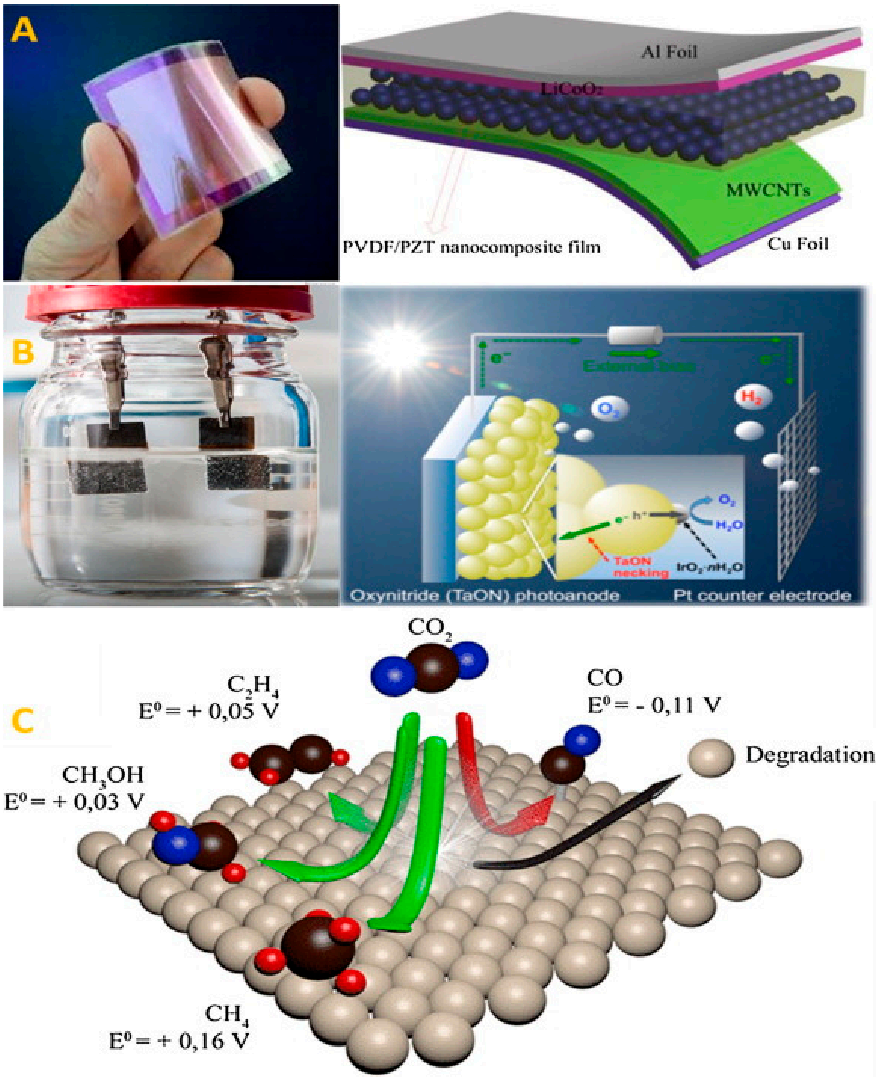

Figure 3. Energy generation approaches from (**A**) piezoelectrics actuators, (**B**) water splitting and (**C**) CO_2 reduction [7].

NPs can be used to make solar panels more energy-efficient, which promises to offer cheaper energy production in the future. NP based solar cells may be less expensive to produce and install since they can be manufactured in flexible rolls and use manufacturing techniques that are similar to those used to that are used in printers.

3.5. Applications in the Petroleum Industry

Nanoparticles are finding increasing applications in the oil and gas industry, some of the examples include drilling fluids [104], enhanced oil recovery [105] and well stimulations [106]. Nanoparticles have certain distinct characteristics, such as their small size and large volume to surface area ratio when compared to those of larger particles, which results in a higher degree of reactivity. The smaller the particles, the more readily they are able to pass into the small pore spaces of the formation. Due to the aforementioned properties, the use of nanoparticles in the petroleum industry is desirable.

A drilling fluid is a viscous mixture used to aid the drilling of boreholes. They have various functions such as removing cuttings, forcing, maintaining bore stability regulating forming pressure, etc. [107]. Different chemicals are usually employed to improve drilling fluids, such as the rheology and filtration. There are numerous features that must be considered when applying traditional additives, such as the temperature and the particulate size [107]. Thus, nanoparticles have found considerable attention for their potential benefits to surmount these issues. In a study by Al-Saba et al. aluminium, copper and magnesium oxide nanoparticles greatly enhanced the rheological properties of drilling fluid [108]. Such nanoparticles offer good potential for bore hole cleaning. Iron oxide nanoparticles were employed to improve the performance of a xanthan gum drilling fluid [109]. The addition of nanoparticles resulted in reduced friction and improved filtration properties. Various other nanoparticles have been studied to improve the lubrication, filtration, wellbore stability and other characteristics of drilling fluids. Some of these include silicon dioxide [110], titanium oxide [111] and zinc titanate [112].

Enhanced oil recovery applications of nanoparticles have also been studied extensively in recent years. Nanoparticles are generally employed to improve the tertial oil recovery techniques such as chemical, gas and thermal injection. Various nanoparticles have been used to for these applications including aluminium oxide for reduced oil viscosity [113], silicon dioxide for improved foam stability and mobility [114] and graphene oxide for improved oil recovery [115].

4. Discussion

Recently, the area of microbial synthesis of nanoparticles has seen considerable advancement. The above-mentioned synthesis methods of nanoparticles have many benefits, including being both cost-effective and environmentally friendly [116]. In comparison to physical and chemical methods, there are no harmful chemicals present in biogenically produced nanoparticles. Another advantage of the biogenic scheme of manufacturing is that such methods need not the addition of a stabilizing compounds on the nanoparticle surface in order to achieve long-term pharmacological activity [117]. Additionally, biogenic synthesis time is much shorter than using physicochemical processes as described in the following examples. Abdel-Raouf et al. demonstrated the synthesis of silver nanoparticles using red alga *Laurencia catarinensis* within 2 min [118]. Their results showed various shaped nanoparticles between 39 and 77 nm in size. Gold nanoparticles have been synthesised using the fungus *Aspergillus flavus* within 2 min [119]. Cadmium sulphide nanoparticles have been synthesised using bacteria in 10–20 min [120]. Various other studies have also shown rapid biogenic synthesis of nanoparticles [121–125].

Despite these advantages, biogenic synthesis faces challenges in controlling the nanoparticles size as polydispersity is an issue. Additionally, substantial effort is required to enhance the ability to regulate particle size and morphology, and to fine tune particle size distribution. For this reason, many biogenic studies have focused on developing methods that can result in monodisperse synthesis of nanoparticles [121]. The morphology of nanoparticles can be affected either by altering the process parameters to understand the optimal synthesis parameters. Parameters such as pH, temperature, reaction time and reagent concentrations equally affect the nucleation process and hence the nanoparticles formation [123]. Another challenge is the difficulty in identifying the best microbial candidates based on their inherent properties such as the growth rate, replicability and biochemical activities. There needs to be attention given to the yield and to the overall biosynthesis rate when attempting to convert the biogenic synthesis large-scale production. The synthesis of biosynthesised nanoparticles faces challenges at the large-scale, due to yields being much lower than chemical synthesis [25]. Additionally, the scale-up or commercial processes for nanoparticle synthesis differ greatly. Nevertheless, due to the vast amount, accessibility and strong growth of microbes, the total cost would be reduced. In addition, there are no organic solvents, thermal stabilisers or expensive techniques used in these methods, further reducing the cost.

5. Conclusions

Over the last decade, great progress has been made in the field of nanoparticle development by microorganisms and their applications. There is, however, a great deal of work required to improve synthesis performance, particle size control and morphology. Two major concerns in the assessment of nanoparticle synthesis are particle size and monodispersity [26]. Studies have shown that nanoparticles synthesised by microorganisms are less stable compared to those prepared through chemical methods [124]. Better understanding of the safety and stability of biodegradable nanoparticles, therefore, is needed. Based on the abundant biodiversity of the microbes, their ability for nanoparticle synthesis remains to be examined. Bacteria produce a much smaller volume of nanoparticles compared to fungi, and this is proportional to their lower protein production, which directly translates to their lower nanoparticle productivity. With the recent developments and continuing attempts to increase the nanoparticle synthesis performance and its industrial use in the field of medicine and health care, this technique and these methods are likely to be widely used in the future.

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