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Green Chemical and Biological Synthesis of Nanoparticles and Their Biomedical Applications

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Abstract

To generate nanoparticles with particular shapes and dimensions, various techniques including physicochemical and biological routes have been developed. The physical and chemical processes are typically expensive and require hazardous chemicals. In this chapter,

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we introduce current advancements in the green synthesis of nanoparticles as eco-friendly, cost-effective, and simple approaches. The microbial synthesis of nanoparticles using bacteria, fungi, and viruses; phototrophic eukaryotes including plants, diatoms, and algae; heterotrophic human cell lines and some other biological agents is especially emphasized in this review. It also declares the applications of these nanomaterials in a broad range of potential areas, such as medical biology, labeling, sensors, drug delivery, dentistry, and environmental cleanup.

Keywords: Green chemistry, Bio-inspired synthesis, Nanoparticle, Green synthesis

1. Introduction

During the last decade, nanotechnology has become a cutting edge and highly interdisciplinary research area including basic sciences, material science and medicine. The word “nano” has been derived from a Greek word “nanos” translated from “dwarf” and refers to the size of one billionth (10^{-9} m). Due to the more surface atoms and larger surface energy of nanomaterials, compared to bulk materials, they present considerable changes in physical, mechanical, chemical, electrical, magnetic, optical, and biological properties [1, 2]. Recently, nano-biotechnology, as one of the most imperative areas, has attracted much attention in the nanoscience. Typically, nanomaterials are considered as the next generation of biosensors and various bioelectronic applications, as a result of enhanced Rayleigh scattering and quantum size effects [3].

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Latest innovations in nanotechnology have resulted in the synthesis of nanomaterials with different shapes, such as wires, tubes, and particles for doable applications in different fi elds. Nanoparticles with dimensions smaller than 100 nm is normally produced by using two following techniques: top-down and bottom-up [4]. Bulk materials are little-by-little collapsed to nanoparticles in top-down methods; conversely, in bottom-up approaches, a nanomaterial is constructed by bonding of atoms or molecules. The latter route is generally comprised of chemical and biological techniques. In view of the fact that the size, shape and crystallinity of nanomaterials may be a vital effectual parameter of their physicochemical properties, the preparation of monodispersed particles with desirable dimensions and shapes for different applications is a main challenge [5]. For this purpose, particular techniques have been employed to produce nanoparticles with specific shapes and sizes. Unfortunately, in common wet methods, different unsafe initial precursors, for example tetrakis(hydroxymethyl)phosphonium chloride, poly- *N* -vinyl pyrrolidone, and sodium borohydride, are normally utilized. On the other hand, in dry methods, UV, lithography, and aerosol are not regarded as environment-friendly techniques. Remained toxic elements on the surface of the synthesized materials lead to restrictions in clinical applications. Hence, an increasing tendency has been created to develop biocompatible materials by environment-friendly routes [5, 6], simultaneously considering economical issues for future commercial purposes.

The growing knowledge in the direction of green chemistry has led to a necessity to expand plain, inexpensive, and environment-friendly procedures [5]. Green nanotechnology aims to design novel materials having profits on financial, medicine, and environment issues, in order to solve the negative aspects of nano from the commencement [7]. To assemble an enhanced

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command for using nanoparticles in medicine, nanoparticles are required to be produced throughout “green” techniques with minor toxic materials. It is necessary to widen capable green synthesis routes, given that the majority of applied methods involve organic solvents, low materials conversion, toxic reducing agents, difficult and wasteful purifications. Employing apt solvents, reducing and stabilizing agents in the preparation of nanoparticles via green technologies are different from other methods. Thus, there is a strange prospect to employ science and engineering to develop new products which take human and environmental health into the consideration. Following this opportunity has resulted in the development of the “Green Nanoscience” idea [8]. Although green processes are regarded as harmless, inexpensive, sustainable, and biocompatible, they comprise some shortcomings in handling microbes and in providing improved features over dimension distribution, form, and crystallinity. Furthermore, the nanoparticles synthesized by biological techniques have no monodispersity and involve a time-consuming process. However, the aforementioned points could be organized by the optimization of parameters, including pH, temperature, time, and the quantity of biological materials [9]. In this chapter, we aim to focus on the production of nanoparticles using different techniques in the scope of green nanotechnology.

2. Categorization of Nanomaterials

A wide range of nanomaterials with different physical and chemical behaviors has been developed. The classification of nanomaterials is continually being changed, due to new inventions in nanotechnology. Nanomaterials can be divided into a number of various groups, including nanoclusters, nanopowders, nanocrystals, nanoparticles, nanorods, nanospheres, nanodiamonds, and quantum dots [10].

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3. Physicochemical Synthesis of Nanoparticles

To synthesize metallic nanoparticles (MNPs), several techniques including laser ablation [11], sol-gel [12], ion sputtering [13], solvothermal [14], and chemical reduction [9] have been employed. Moreover, micropatterning, photolithography, and ink jet printing have been introduced as known examples for top-down approaches [9].

3.1. Laser Ablation

Laser ablation is considered as a “green technique” for attaining noble MNPs. In this method, a bulk plate is immersed into a solution and nanoparticles are formed with a plasma plume produced by the laser ablation. The high energy needed and the slight control over the growth rate of the produced nanoparticles may be considered as the main weaknesses of the laser ablation technique [11].

3.2. Inert Gas Condensation

Inert gas condensation (IGC) has been considerably utilized to produce metallic nanoparticles [15]. Through the IGC technique, the metal is placed in a high vacuum chamber. He and Ar gases are usually employed at the pressure of around a few hundred Pascal. The metal is evaporated through this process and again condensed as a result of losing its kinetic energy through collisions with the gas atoms in the environment. As a result,

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nanocrystals are formed by the Brownian coagulation and coalescence. The synthesis of Au/Pd nanoparticles with a controlled dimension has been reported by this technique [16].

3.3. Sol–Gel Method

As a wet chemical route, the sol–gel method has been recently developed in the nanomaterials science. Inorganic nanoparticles are produced by the sol–gel technique, through a sequential process including the formation of a colloidal suspension (sol) and gelation in a continuous liquid state (gel). The size and stability of nanoparticles can be controlled by adjusting parameters and adding different mixtures. However, the basic crisis of aqueous sol–gel methods is the complexity of the procedure and is the fact that the as-synthesized products normally have an amorphous structure. Another mode of the sol–gel process can be done via a nonaqueous chemistry route, whereas the transformation of the initial materials occurs in an organic solvent. The non-hydrolytic methods are able to surmount some of the foremost constraints of aqueous modes, thereby signifying a powerful and multipurpose choice. The benefits are a direct outcome of the manifold function of organic constituents in the reaction system (e.g., solvent, surfactants). Currently, the family of nanoparticles, ranging from plain binary metal oxides to multi-metal and doped systems, is preferred to be synthesized by nonaqueous techniques [9, 12].

3.4. Hydrothermal and Solvothermal Synthesis

The hydrothermal and solvothermal synthesis processes of inorganic materials are considered as a prominent technique in the preparation of nanomaterials. In hydrothermal techniques, the

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synthetic process happens in an aqueous solution over the boiling temperature of water, while in solvothermal techniques the reaction is performed in organic solvents at about 200–300 °C above their boiling temperatures. Although the hydrothermal and solvothermal methods have a long history, these methods have been recently employed in materials production processes. Generally, hydrothermal and solvothermal reactions are performed in a particularly sealed container or autoclave. In the mentioned states, the solubility of reactants is notably enhanced, facilitating the reaction to happen at lower temperatures. Amongst several instances, TiO₂ photocatalysts have been synthesized throughout a hydrothermal route [17]. Due to the inexpensive cost and energy expenditure, hydrothermal methods may be applicable for industrial manufacturing. Furthermore, solvothermal techniques enable the selection amongst various solvents or blends thereof, thereby rising the adaptability of the synthesis. For instance, nanostructured TiO₂ have been produced using solvents HF and 2-propanol [18].

3.5. Colloidal Methods

Crystallographic features on the nucleation and growth of metallic nanoparticles has broadly been accomplished by means of colloidal systems. Overall, metallic nanoparticles are synthesized by reducing precursor salts with compositions similar to hydrazine, borohydride, citrate, etc., followed by surface modification with appropriate capping ligands to avoid aggregation and to present superior surface characteristics. The particular applications of organic solvents in this synthetic way regularly increase environmental matters. Multi-shaped nanoparticles are produced using the mentioned technique which needs differential

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centrifugation and thus possesses a low yield. Consequently, the expansion of trustworthy experimental protocols for synthesizing of the nanomaterials, over a range of chemical composition, size, and enough monodispersity, demands concerns in the modern nanotechnology [19, 20]. In this situation, current researches focus on the development of green and biosynthetic technologies for making nanocrystals with a needed size and a desired shape.

4. Green Chemistry Synthesis of Nanoparticles

4.1. Tollens Process

The tollens synthesis is a one-step method that, for example, can yield Ag nanoparticles with a controlled size [21, 22]. Through a study conducted on the saccharide reduction of Ag⁺ ions by the tollens process [22], it was found that small particles of 57 nm in size are formed with glucose at low ammonia concentrations (0.005 M). Different particle sizes can be achieved by varying the concentration of ammonia, whereas the higher concentration of ammonia would lead to a larger particle size [23]. Le et al. [24] also pointed out a modified tollens technique, in which oleic acid is added as a stabilizer and a UV radiation is simultaneously used with treatment by glucose during the reduction process, to attain silver nanoparticles with a controlled size. Yin et al. [21] examined the potential of the tollens method in preparing silver nanoparticles. In another method described by Yin and colleagues [24], there is a delay period greater than 5 min, which allows the complete mixing of reactants. Most

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have concluded that, the synthesis by the tollens method is environmentally green, due to the use of nontoxic chemicals.

4.2. Microwave Irradiation

Microwave (MW) heating of particles was discovered in 1940s and has become successful in the food industry with applications in chemistry [25]. Microwave irradiation is an electromagnetic radiation between frequencies of 0.3–300 GHz. Microwave chemistry is based on the principle of dielectric heating [26]. There are two main mechanisms for microwave irradiation, namely dipolar polarization and ionic conduction mechanisms. The irradiation of matter in turn causes the alignment of dipoles or ions in the electric field [27]. Because electromagnetic radiations (EMR) produce an oscillating field, these dipoles or ions attempt to realign themselves within this field and produce heat through molecular friction [27]. Using microwaves to heat the samples is a green method for the synthesis of nanoparticles, while it also yields desirable features, including shorter reaction periods and better product yields [28].

Microwave irradiation has several advantages within the realm of chemical synthesis. For instance, in the preparation of inorganic nanoparticles, conductive heating is carried out by using an external heat source; however, this method is slow and relatively inefficient. In contrast, microwave irradiation produces efficient internal heating, while uniformly raising the temperature of the entire reaction mixture. Furthermore, microwave heating increases the reaction rate; for instance, Au nanowires have been synthesized under the microwave irradiation method within 2–3 min [29]. Moreover, the heat source does not come into direct contact with reactants, allowing the precise control of reaction parameters and the reduction

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of chemical wastes. There are also limitations to the use of irradiation techniques, including the short penetration depth [30]. MW-assisted heating has been used for the preparation of nanostructures, including Ag, Au, Pt, and Au–Pd. In addition to spherical nanoparticles, crystalline polygonal plates, sheets, rods, and wires have also been prepared within only a few minutes under MW irradiation conditions [31]. Besides requiring less energy, microwave irradiation should be more environment- friendly than conventional heating methods [32].

4.3. Use of Polyoxometalates

Polyoxometalates (POMs) are anionic structures composed of early transition metal elements in their highest oxidation state [33]. Since POMs are soluble in water and have the capability of undergoing stepwise, multielectron redox reactions without disturbing their structure have the potential for synthesizing Ag nanoparticles [33, 34]. Ag nanoparticles with different shapes and sizes can be obtained by using different POMs, in which POMs serve as a reductant as well as a stabilizer [23]. Zhang et al. [35] described a synthesis method of metal nanoparticles. They found that for the efficient synthesis of Pd and Pt nanoparticles, reduced POMs were constructive, as both reducing and capping agents at room temperature in water. Georgakilas et al. [36] focused on the process of decorating carbon nanotubes (CNTs) with nanoparticles in order to produce novel nanohybrid materials for a wider range of applications. The attachment of Au nanoparticles to CNTs' sidewalls has shown to be promising for highly efficient electrochemical cells and photoelectronic sensor devices. POMs serve as reducing, encapsulating and bridging molecules and avoid the introduction of other organic toxic molecules. The nanohybrids produced using the POMs enhance photocatalytic activities under visible light irradiations.

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5. Bio-inspired Green Synthesis of Nanomaterials

Green chemistry is gradually incorporated into up-to-date developments in maintenance with a worldwide attempt to decrease the production of dangerous wastes and to develop energy-efficient synthesis methods. To do so, any synthetic means or chemical procedures have to deal with the basic standards of green chemistry, by using environmentally kind solvents and nontoxic chemicals [37]. The green synthesis of nanoparticles ought to encompass main steps, which are consistent with green chemistry outlooks with regard to the choice of: biocompatible and nontoxic solvents, environmentally reducing materials, and nontoxic agents for stabilizing the produced nanoparticles. Applying the aforementioned decisions into nano- science will aid the processing of intrinsically safer nanomaterials and nanostructured devices. Consequently, green nanotechnology aims to apply green chemistry theories in developing nanoscale materials, and to design production techniques with decreased dangerous waste generation and safer applications [38].

Moreover, biochemical processes can occur at low temperatures, as a result of the high specificity of biocatalysts. Thus, a synthetic method containing one or more biological steps would cause the energy saving and lesser environmental impacts, compared to conventional techniques. In order to optimize safer nanoparticle fabrication, it is popular to use bio-based techniques minimizing the dangerous forms of material production. Using examples from nature, the fact that living organisms create inorganic materials during bio-guided routes should be adopted as an advanced approach to nanomaterials assembly [39]. Typically,

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biomineralization methods develop biomolecular models, which relate to nano-scaled inorganic materials, leading to very competent and controlled syntheses. The structures of these materials are well controlled at both nano- and macro-scale levels, allowing the design of multifunctional behaviors. Simpler organisms including bacteria, algae, and fungi, have developed plans for biominerals production throughout 100 millions of years of advancement. The objective of templating biomolecules in the mineralization process is to present an artificial microenvironment in which the inorganic phase morphology is firmly controlled by a range of low-range interactions.

Nature has devised a variety of progressions for the creation of nano- and micro- scaled inorganic materials, contributing to the improvement of fairly innovative (Fig. 1) and mostly unexplored research areas in regard to the biosynthesis of nanomaterials [9, 40]. Biosynthesis of nanoparticles is a category of bottom-up methods in which the foremost chemical reaction is reduction and oxidation. Antioxidant and reducing agents in microbial enzymes or plant phytochemicals are typically considered for reducing metal constituents into nanoparticles [41].

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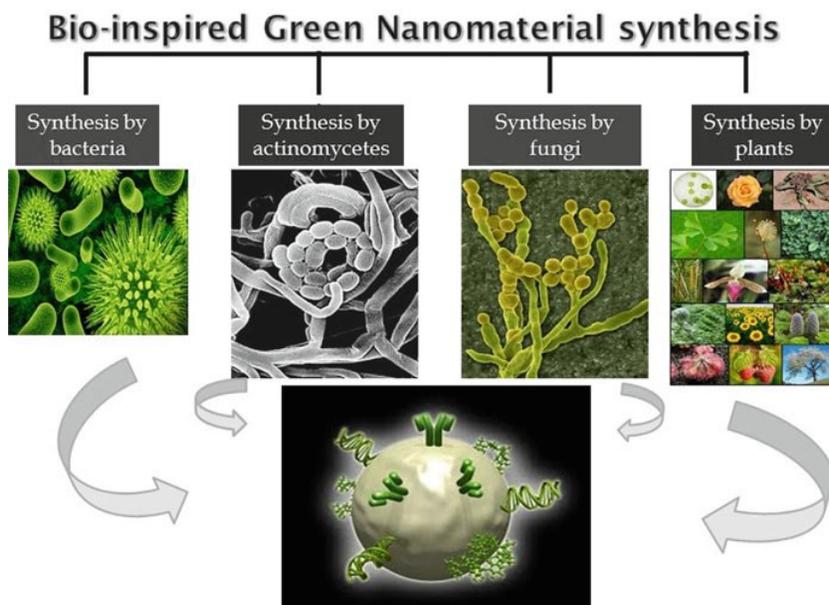


Fig. 1. A schematic representation of bio-inspired green synthesis of nanomaterials.

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5.1 Microbial Synthesis of Nanoparticles

The microbial synthesis of nanoparticles is considered as a green chemistry method that correlates between nanoscience and microbial biotechnology. Biosynthesis of Au, Ag, Au–Ag alloy, Se, Pt, Pd, SiO₂, TiO₂, ZrO₂, quantum dots, magnetite, and uraninite nanoparticles using bacteria, fungi, yeasts, viruses, and actinomycetes have been reported. However, biological nanoparticles, in spite of stability, are not monodispersed and their synthesis rate is time-consuming. To conquer these crises, numerous factors including microbial cultivation techniques and extraction methods are useful, where combinatorial approaches, for example photobiological methods, may be utilized. Cellular, biochemical, and molecular mechanisms

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that contribute to the preparation of biological nanoparticles need to be assessed in depth to enhance the production rate and to improve nanoparticle properties.

Due to the rich biodiversity of microbes, they as biological materials for nanoparticle production are still up for investigation investigated. Investigating natural secrets for the production of nanoparticles by microbes is considered as strong eco- friendly green nanofactories. The synthesis of nanoparticles using microbial techniques has appeared as a talented research area in the nanobiotechnology field, which interconnects biotechnology and nanotechnology [6].

The chemical detoxification and ion efflux from cells by membrane proteins may be the main reason for the resistance of the majority of toxic heavy metals to microbes. The solubility alteration may be another reason for the microbial resistance. Hence, microbial systems are able to detoxify metal ions by reduction and deposition processes. Additionally, the inorganic toxic ions convert to metal nontoxic nanoclusters [6]. Microbial detoxification may be prepared by extracellular biomineralization, complexation, biosorption, precipitation, or intracellular bioaccumulation.

Extracellular synthesis of metal nanoparticles possesses further commercial uses in different fields. Since polydispersity is the main issue, it is essential to consider the optimization parameters for monodispersity in a biological process [42]. Regarding the intracellular approach, the accumulated particles have specific sizes with a lesser amount of polydispersity. However, further steps including ultrasound processes or reactions with appropriate detergents are needed for intracellularly synthesized nanoparticles. This may be employed in the recovery of expensive metals from wastes and leachates. Moreover, bio-matrix metal nanoparticles as catalysts in chemical reactions will aid to maintain

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nanoparticles for permanent applications in bioreactors [43]. Microbial production of metal nanoparticles is related to the localization of cell reductive constituents. Once reductive enzymes in cell walls or secreted enzymes are engaged in the reduction of metal ions, it is clear to get metal nanoparticles extracellularly. Compared to intracellular approaches, extracellular synthesis has been found to have wide applications in electronics and bio imaging.

5.2 Biosynthesis of Nanoparticles by Bacteria

Bacteria play a vital role in biogeochemical cycling and metal mineral creations in surface [44]. Employing microbial cells for the synthesis of nanosized materials is accounted as a new advancement for the production of metal nanoparticles. While attempts for the biosynthesis of nanomaterials are being currently made, relations between microorganisms and metals have been well reported and the capacity of microorganisms to extract metals is applied in commercial biotechnological approaches including bioleaching and bioremediation [45].

Bacteria usually synthesize inorganic materials, using intracellular or extracellular mechanisms. Microorganisms are regarded as a possible biofactory for the manufacturing of nanoparticles like Au, Ag and CdS. As known bacteria, prokaryotic *Escherichia coli*, *Pseudomonas stutzeri*, *Pseudomonas aeruginosa*, *Plectonema boryanum*, *Salmonella typhi*, *Staphylococcus currens*, *Vibrio cholerae* have attracted much attention for the synthesis of metallic nanoparticles through extracellular and intracellular processes [46]. Moreover, some bacteria for the production of inorganic nanoparticles have been recognized, such as

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magnetotactic bacteria which are employed for magnetic nanoparticles and S-layer bacteria for producing gypsum and calcium carbonate layers [47].

A number of microorganisms are able to live and grow at the high concentrations of metal ions, owing to their resistance to the metal. The mechanisms involve: efflux systems, solubility alteration and toxicity, bioaccumulation, biosorption, an extracellular complex at the precipitation of metals and the lack of particular metal transport systems [48].

Recently, bacterial activity has been used in the precipitation of mineral ores. For Fe- and Mn-oxide precipitation processes, *Pedomicrobium*-like budding bacteria in an Alaskan placer has previously been utilized; also, it has recently been employed to synthesize Au [1, 16]. *Bacillus subtilis* 168 reduces water-soluble Au⁺³ ions to Au⁰, synthesizing octahedral structures in the cell walls with the size of around 5–25 nm [49]. Also, the bioreduction of chloroauric acid to Au⁰ nanoparticles by means of *Escherichia coli* DH5 α has been recently reported [50]. The produced nanoparticles on the surface of cells were mainly sphere-shaped with a few other features of triangles and hexagonals. These cell-bound nanoparticles have been recognized as a suitable choice in describing the electrochemistry of hemoglobin and proteins [50].

As a typical instance, Fig. 2 indicates a dark-field TEM photomicrograph of S-algae cells accompanied by Pt nanoparticles deposited in a periplasmic space. At the ambient temperature and neutral pH, S-algae were placed anaerobically in a H₂PtCl₆ solution. In the existence of lactate as the electron donor, PtCl₆⁻² ions were converted to 5 nm Pt nanoparticles within 1 h [51].

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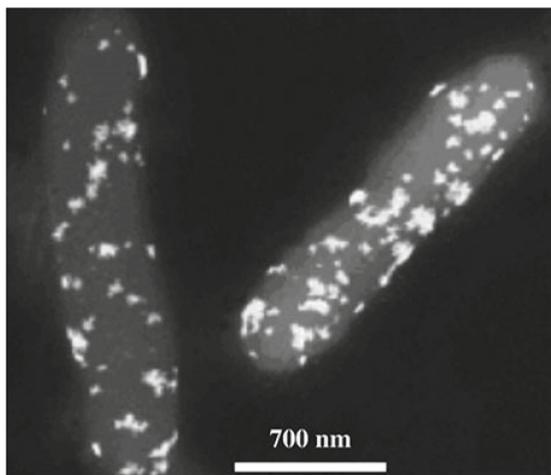


Fig. 2. Dark-field TEM image of S-algae cells with platinum nanoparticles deposited in the periplasmic space. Reprinted from ref. [51] with permission by Elsevier

5.3 Biosynthesis of Nanoparticles by Fungi

The production of fungal-mediated metal nanoparticles is a quite modern research area. Fungi have been considerably employed for the biosynthesis of nanoparticles, where the mechanistic characteristics governing the nanoparticle synthesis have been considered for a small number of them. Nanoparticles with monodispersity and appropriate dimensions may be achieved using fungi. Fungi could be utilized as a source for the synthesis of a huge quantity of nanoparticles against bacteria, since fungi produce the higher amounts of proteins leading to higher nanoparticle production [40]. As an Ascomycetes class of fungi, yeast has presented an excellent ability for nanoparticle production. Fungi are more favorable in comparison to other microorganisms, plants, and bacteria in regard to easier handling, simpler fabrication ability, withstanding flow pressure and agitation in bioreactors.

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Nowadays, fungi such as *Colletotrichum* sp. [52], *Fusarium oxysporum* [53], *Trichothecium* sp., *Trichoderma asperellum*, *T. viride* [54], *Phanerochaete chrysosporium* [55], *F. solani* USM 3799 [56], *A. fumigatus* [57], *F. semitectum* [56], *Aspergillus niger* [58], *Coriolus versicolor* [59], *Phoma glomerata* [60], *Penicillium brevicompactum* [61], and *Penicillium fellutanum* [62] are used for producing nanoparticles. For example, Au nanoparticles have been intracellularly produced by the *Verticillium luteoalbum* fungus [40]. The production rate and the size of nanoparticles can be controlled by adjusting pH, temperature, concentration of Au, and incubation time. A biological process with this ability to rigorously control the particle shape would be a significant benefit.

The extracellular secretions of reductive proteins can be simply handled in downstream processing. In addition, given that the nanoparticles form at the outer layer of the cells and unneeded cellular constituents are avoided, it can be directly employed in different applications. The nanoparticles formed by the extracellularly reduced approaches is larger than those formed within microorganisms. Thus, the size limit could have been corresponded to the nucleation of particles inside the organisms [6].

Mukherjee et al. [63] focused on the use of eukaryotic microorganisms in the biological production of Au nanoparticles using *Verticillium* sp. (AAT-TS-4). According to this research, the Au nanoparticles of about 20 nm in size, well-defined dimensions and good dispersity were reported on the surface of the cytoplasmic membrane of fungal mycelium. TEM analyses indicated ultrathin sections of fungal mycelia, with nanoparticles of triangles and hexagonal morphologies on the cell walls and of quasi-hexagonal morphologies on the cytoplasmic membrane. *Trichothecium* sp. was also used to synthesize Au nanoparticles intracellularly [64].

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The synthesis of nanoparticles in cell outer layers (extracellularly) has many usages, since it evades adjoining cellular constituents from the cell. Typically, fungi are considered as organisms that synthesize nanoparticles extracellularly, due to their vast range of secretory components, which involve in decreasing particle size and capping of nanoparticles. Shankar et al. [52] found an endophytic fungus, *Colletotrichum* sp. isolated from the leaves of geranium plants (*Pelargonium graveolens*), which quickly reduced Au ions to zero-valent Au nanoparticles with a polydispersed spherical morphology. These Au nanoparticles had a combination of disk and rod-like structures. Glutathiones as the capping agents of Au nanoparticles bind with free amine groups or cysteine residues [65].

As one of the classifications of prokaryotes, Actinomycetes have main characteristics of fungi. Additionally, a new extremophilic actinomycete, *Thermomonospora* sp. was found to produce extracellular monodispersed Au nanoparticles. These synthesized Au nanoparticles had a spherical morphology with a size of around 8 nm [66].

5.4 Virus-Mediated Biosynthesis of Nanoparticles

A few biomolecules similar to amino acids, fatty acids, and polyphates are utilized for the synthesis of semiconductor nanostructures. Especially, through a change in the ratio of fatty acids, various shapes of CdSe, CdTe, and CdS nanocrystals can be obtained [67]. Moreover, there exists other biological materials for the environment-friendly production of inorganic materials such as DNA [68], protein cages [69], viroid capsules [70], biolipid cylinders [71], bacterial rapidosomes [72], multicellular superstructures [73] and S-layers [74]. By using glutamate and aspartate on the outer layer of virus, tobacco mosaic virus (TMV) has been

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utilized to produce iron oxides by hydrolysis, co-crystallization of CdS and PbS, and the sol-gel synthesis of silica [75]. For the synthesis of quantum dot nanowires, the self-assembled viral capsid of genetically engineered viruses was exploited as biological templates.

A7 and J140 peptides with the capability of ZnS and CdS nanocrystal nucleation were expressed as pVIII proteins into the crystalline capsid of viruses. ZnS nanocrystals were assembled on the viral capsid with a size of about 5 nm and hexagonal wurtzite morphology, and CdS nanowires were assembled with a size of 3–5 nm. Hybrid nanowires including ZnS and CdS were obtained with a dual peptide virus engineered to express A7 and J140 within the same viral capsid [76, 77] (Fig. 3).

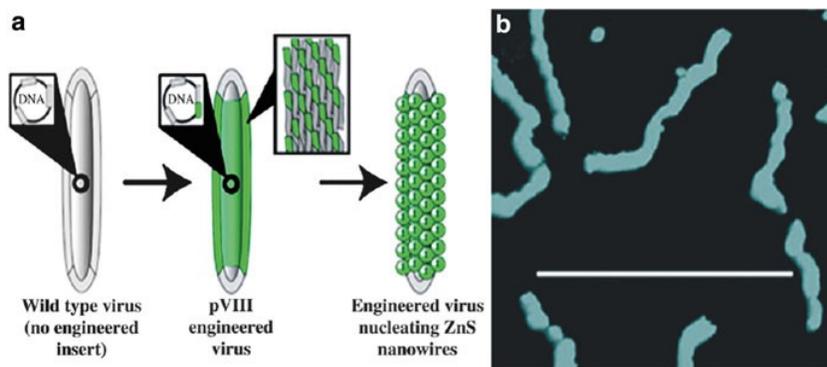


Fig. 3 A7-pVIII-engineered viruses related to the synthesis of ZnS nanocrystals. (a) The diagram showing A7 peptide expression on pVIII protein upon phage amplification and assembly, then the consequent nucleation of ZnS nanocrystals. (b) ADF STEM images that show the morphology of ZnS-virus nanowires. Reprinted from ref. [77] with permission by

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5.5 Biosynthesis of Metal Nanoparticles by Terrestrial Phototrophic Eukaryotes

(Plants)

Since phototrophs are sustainable supplies, they may be utilized mostly in the green synthesis of nanoparticles. In this regard, the green chemistry method is an alternate method for producing biocompatible nanoparticles with chemical synthesis, which is the most recent doable route of linking material science and biotechnology in the field of nanobiotechnology [5]. Nanobiotechnology has more benefits compared to usual techniques, because of the availability of more constituents by biological bodies for the formation of nanostructures. The rich biodiversity of such biological bodies needs to be studied for the production of bionanomaterials. Molecular cloning and engineering of genes encoding particular enzymes, that facilitate the bioreduction of metals, are investigated to help the simplistic manufacturing of nanomaterials [5].

Until today, different phototrophic eukaryotes including plants, microbes (diatoms), algae, and heterotrophic human cell lines and some biocompatible agents, which are considered as effective environment-friendly green nanofactories, have been notably employed for the synthesis of different inorganic nanoparticles. Phototrophic eukaryotes including plants, algae, diatoms and heterotrophic human cell lines and other biocompatible agents have been expressed to produce green nanoparticles such as Co, Cu, Ag, Au, SiO₂, Pd, Pt, Ir, bimetallic alloys, magnetite, and quantum dots. Due to their variety and sustainability, applying phototrophic, heterotrophic eukaryotes and biocompatible agents for the development of nanomaterials is still to be entirely investigated [5].

In the past, only prokaryotes had been used for the biosorption and bioreduction of insoluble toxic metal ions to soluble nontoxic metal salts or valency changes. However, it

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was understood that highly developed organisms such as plants, algae, diatoms, human cells and other components of eukaryotes have the ability to reduce metal ions to metal nanoparticles. Eukaryotes give further information in their genetic material to encode a variety of reducing/stabilizing agents that facilitate the production of metal nanoparticles. Phototrophic eukaryotes obtain energy from sunlight, using photosynthesis, and thereby fix inorganic carbon into organic materials, while heterotrophic eukaryotes similar to human cells employ organic carbon synthesized by other organisms for growth. Terrestrial environments comprise predominant phototrophs like plants, algae, and diatoms in aquatic environments [5].

The benefit of plants for the synthesis of nanoparticles is that they are accessible, harmless to handle and have a wide variability of metabolites that help in reduction. Some of the plants have been recently explored for their function in the production of nanoparticles (Fig. 4) [9]. Au nanoparticles with a size variety between 2 and 20 nm have been produced by live Alfalfa plants [78]. Moreover, Ag, Co, Ni, Zn, and Cu nanoparticles have been produced in the live plants of Alfalfa, *Brassica juncea* (Indian mustard), and *Helianthus annuus*. Some of the plants, for example *B. juncea*, have been known as hyperaccumulators, synthesizing more concentrations of metal ions, as compared to others [79].

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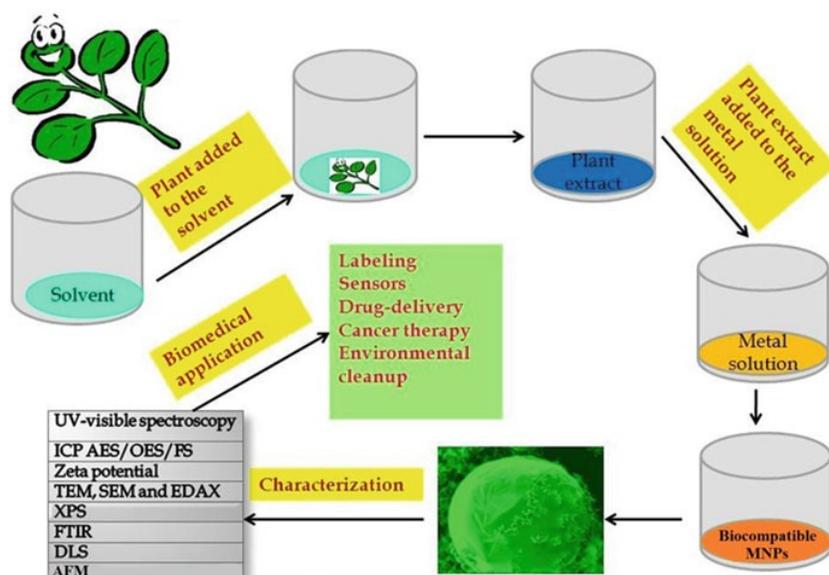


Fig. 4. A schematic representation of plants as a source of green nanosynthesis, its characterization and biomedical applications. Reprinted from ref. [9] with permission by

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Today, much research has been conducted on the reduction of metal nanoparticles with plants and the particular function of phytochemicals. The main water-soluble phytochemicals such as organic acids, flavones, and quinines which can conduct reduction processes. The phytochemicals existing in *Cyprus* sp. (Mesophytes), *Bryophyllum* sp. (Xerophytes), and *Hydrilla* sp. (Hydrophytes) were investigated for their role in the production of Ag nanoparticles. The Xerophytes consist of emodin as an anthraquinone, which could undergo redial tautomerization, resulting in the precipitation of Ag nanoparticles. Currently, Au nanoparticles have been produced using the extracts of *Magnolia kobus* and *Diospyros kaki* leaf extracts. The influence of temperature on the synthesis process of nanoparticles was examined, and it was reported that at lower temperatures, polydispersed particles with a size

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of between 5 and 300 nm was acquired, whilst the formation of smaller spherical particles happens at higher temperatures [80].

Although the synthesis of metal ions by using microbes, including fungi and bacteria, requires a relatively longer reduction duration, water soluble phytochemicals perform it in a much lesser period. Accordingly, in comparison to the microbes, the plants are superior selections for the production of nanoparticles. Fahmy et al. [81] pointed out green nanotechnology as an entrance technique for the beneficiation of natural cellulose fibers. Plant tissue culture routes and downstream processing mediate in manufacturing metallic and oxide nanoparticles on a trade scale, once matters such as the metabolic status of the plant etc. are correctly addressed.

Plants are considered principal photosynthetic autotrophs as the high level and food chain manufacturers, with a high biomass production in terrestrial environments. Plants receive about 75 % of light energy from sun and convert it into the chemical energy of glucose. In comparison to prokaryotic microbes which require costly techniques for maintaining microbial cultures and downstream processing, the plants and their products are regarded as sustainable and renewable resources for the production of nanoparticles. Phytomining has been known as an inexpensive and eco-friendly approach compared to conventional chemical routes. Phytomining employs the plants in order to recover noble metals from ore mines and runoffs. Compared to other chemical routes which are less effectual for producing the low levels of metals, it is able to synthesize even a very low level of metal accumulated in tissues.

Nontoxic chelators, such as thiourea, iodide, bromide, thiocyanate, cyanide, and thiosulfate, can solubilize metals from ores and mediate a proper uptake by plants. Accumulation of metal ions in plants is mostly utilized in phytoremediation which has been

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considered as a cost-effective, environment-friendly, and proficient method for the cleanup of polluted sites [82]. In phytomining, plants that bioconcentrate metal ions into their biomass from a large volume of soil are hunted for, which can be harvested and recovered from contaminated sites. In *Berkheya coddii* and *Brassica juncea*, hyperaccumulation of Au was found with thiocyanate solution as the solubilizer, whereas *B. juncea* and chicory hyperaccumulated Au with bromide, iodide, cyanide, thiosulfate, or thiocyanate solutions. The solubilizer, cyanide induced a higher accumulation of Au in leaves and stems of *B. juncea* and *B. coddii*, while the accumulation was found to be higher in roots with the addition of thiocyanate. As a result of the effect of plant's internal pH on complexes, the mentioned distinctions in the translocation abilities between cyanide and thiocyanate are observed [83]. Many investigations have been performed in order to eliminate high concentrations of Au (III) ions from solutions and soils with different solubilizers.

Several metal nanoparticles possess catalytic activities, and in homogeneous solutions they are hard to recover after the downstream procedures of chemical reactions. Sharma et al. [43] used the roots and shoots of *Sesbania drummondii* for the intracellular synthesis of Au nanoparticles, when grown in sterile aqueous agar containing Au ions. The reduction process was believed to be facilitated by the existence of secondary metabolites in the cells. TEM results of the root cells indicated the existence of monodispersed nanoparticles with a size of 6–20 nm in organelles and multiple spherical nanoparticles surrounding the cell organelles in the cytoplasm. In this regard, for the reduction of industrially toxic pollutants like 4-nitrophenol, the biomatrixed nanomaterial containing Au nanoparticles was employed as the stable catalyst (Fig. 5).

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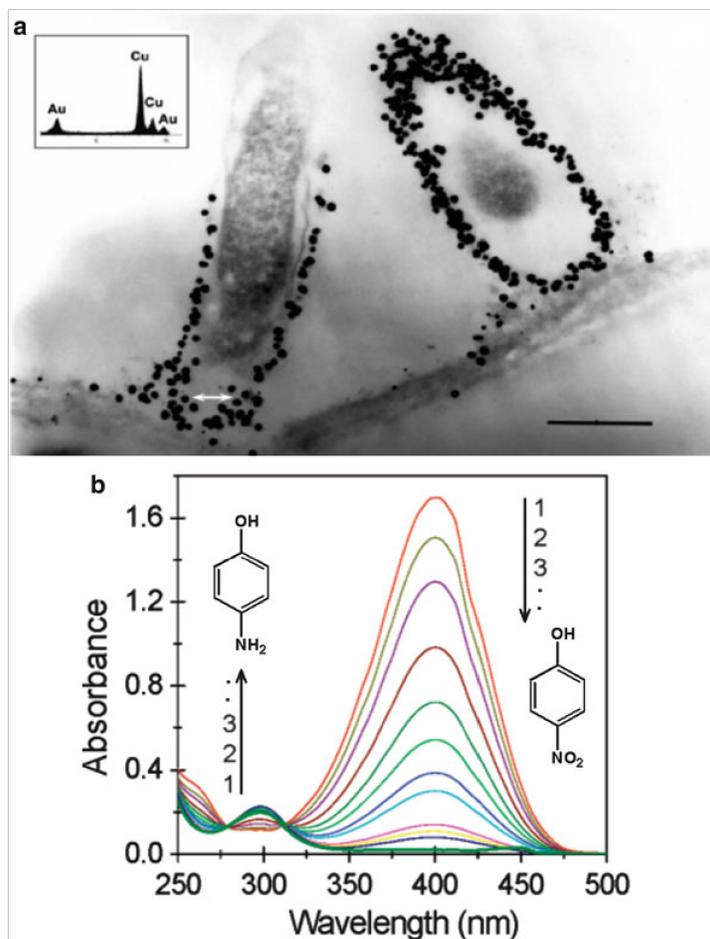


Fig. 5. (a) TEM micrograph of *Sesbania drummondii* root, which shows gold nanoparticles that surround organelles (scale marker = 500 nm). (b) UV-visible absorption spectra during the successive reduction of 4-nitrophenolate ions by gold nanoparticle-rich biomatrix.

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As previously mentioned, plant biomass is a renewable energy supply attained from living or dead plants. These are usually utilized to produce electricity, biofuel, biogas, etc. Thus, the use of biomass wastes in the production of nanoparticles is of high importance. Commonly, the generation of biomass by phototrophs is cost-effective, as it only requires sunlight, water,

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carbon dioxide, and inorganic salts. In the situation of the alarming rise of global warming, the fabrication of plant biomass is a natural bioprocess of carbon sequestration from the air. Alfalfa biomass produces Au nanoparticles of ~100 nm and irregular shapes by the reduction of Au (III) ions in a pH-dependent mode [84]. Also, Herrera et al. [85] reported the binding of Ag (I) ions by alfalfa biomass from an aqueous solution in a pH-dependent mode.

The existence of different reducing agents including secondary metabolites, proteins, and enzymes is normally involved in the production of metal nanoparticles by plant components. In bioaccumulation, the nanoparticle localization is according to the attendance of specific enzymes or proteins. The recovery of these nanoparticles from plant components is time-consuming and costly, and requires enzymes to surround and then degrade cellulosic materials [86]. Accordingly, the production of different metal nanoparticles by plant extracts is simple in downstream and scaling up processing of nanoparticles. Most recently, plant extracts are extensively utilized as a practical and simplistic approach for the production of metal nanoparticles, compared to physical and chemical routes. Geranium plant extracts from stem, leaf, and root have been reported for the extracellular synthesis of Au nanoparticles. Shankar et al. [52] reported the biological reduction of Au ions to Au nanoparticles, by using geranium leaf broth, with the size of 20–40 nm and multiply twinned particles. In the reduction process of Au ions, the ethanol groups of terpenoids are oxidized to carbonyl, and an amide (II) band of proteins was involved in stabilizing molecules in the formation of nanoparticles. Nanoparticles with a size of around 14 nm and a spherical morphology were formed by geranium stem extracts [52]. Shankar et al. [47] showed the synthesis of Ag nanoparticles with adding Ag(NO₃) to the leaf extract of neem after 4 h. Since the redox has lesser ability for the reduction of Ag ions to metallic Ag compared to Au, this process takes a

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long duration. Ag nanoparticles with a size range of 5–35 nm and spherical morphology have been produced using terpenoids in the leaf extract, which facilitate the reduction of Ag ions by the oxidation of aldehyde groups in molecules to carboxylic acid.

Dried powder of alfalfa was also employed in the production of new nanomaterials, according to bimetallic particles such as Eu–Au nanoparticles, which has a broad application in nuclear medicine and nanophotonics. Europium (Eu) is a material with low oxidation resistance and most reactive among rare elements. Eu–Au bimetallic nanoparticle with the size range of 2–20 nm was synthesized by the reduction of Eu^{+3} and Au^{+3} into MTP clusters of Eu^0/Au^0 at $\text{pH} = 8.0$ [87]. There are some plants which produce several kinds of nanoparticles. For example, the leaf extract of *Azadirachta indica* is employed for the production of Au, Ag, and Au core–Ag shell nanoparticles. The synthesized Au–Ag core–shell structure had a mixture of Ag and Au ions in the ratio of 1:1, with spherical shape and a size of 50–100 nm [47].

Platinum group metals (PGMs) are valuable D-block transition metals, which have a tendency to come together in mineral deposits having remarkable chemical catalytic properties for the transformation of toxic elements and in electronic devices. The aqueous extract of the fruit of *Gardenia* was utilized in the bioreduction of PdCl_2 to Pd nanoparticles as the catalytic hydrogenation of p-nitrotoluene with the size of 3–5 nm and uniform distribution. Antioxidants such as geniposide, chlorogenic acid, crocetin, and crocins reduced and stabilized nanoparticles [88].

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5.6 Biosynthesis of Nanoparticles by Aquatic Phototrophic Eukaryotes (Algae)

Algae are eukaryotic aquatic oxygenic photoautotrophs, which generate their food using sunlight photosynthesis with the production of O₂. Their photosynthesis mechanism has been developed from cyanobacteria via endosymbiosis, which is of the main producers in many aquatic environments. Amongst a variety of algae, *Chlorella* sp. was found to synthesize different heavy metals such as Cd [89], U, Cu, and Ni [90]. *Chlorella vulgaris* is a single-celled green alga belonging to phylum Chlorophyta, and its extracts indicated antitumor performances [91]. Dried algal cells were understood to present a strong binding ability to tetrachloroaurate (III) ions in order to produce algal-bound Au, which was afterward reduced to form Au (0). Almost 88 % of algal-bound Au reached the metallic state and Au crystals were synthesized in the inner and outer layer of the cell surfaces with tetrahedral, icosahedral, and decahedral structures.

In this approach, the optimization of parameters such as pH, temperature and metal ions (solute) concentration for accelerating the biological accumulation of nanoparticles with thin sizes and appropriate shapes is compulsory. Up to now, only very few researches have been focused on optimization in biological processes. For synthesizing Au nanoparticles with a controlled size and shape, and a hexagonal morphology, a 28-kDa “gold shape-directing protein (GSP)” in the extract of green alga, *C. vulgaris* has been employed, where with the increase of concentration in GSP, Au plates with lateral sizes up to micrometers were accumulated [92].

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5.7 Biosynthesis of Nanoparticles by Aquatic Phototrophic Eukaryotes (Diatoms)

As the nonmotile and unicellular eukaryotic photosynthetic algae, diatoms are encased inside a silica unique cell wall. Diatoms are also a manufacturer of around 25 % of the world net primary production from solar energy. Diatoms are different nanostructures producing organisms, by finding the correlation between morphogenesis and the diatom genome. Controlling the 3D shape and pattern of diatoms leads to the appearance of a new research area called “diatom nanobiotechnology.” Marine diatom cells of *Cyclotella meneghiniana*, *Glyphodiscus stellatus*, *Isthmia nervosa*, and *Roperia tessellata* that create amorphous clear silica glass valves with special shapes and sizes in microscale or nanoscale structures have found broad applications such as biomedical, electronic, optical, semiconductor nanolithography, sensing, and drug delivery (Fig. 6) [93].

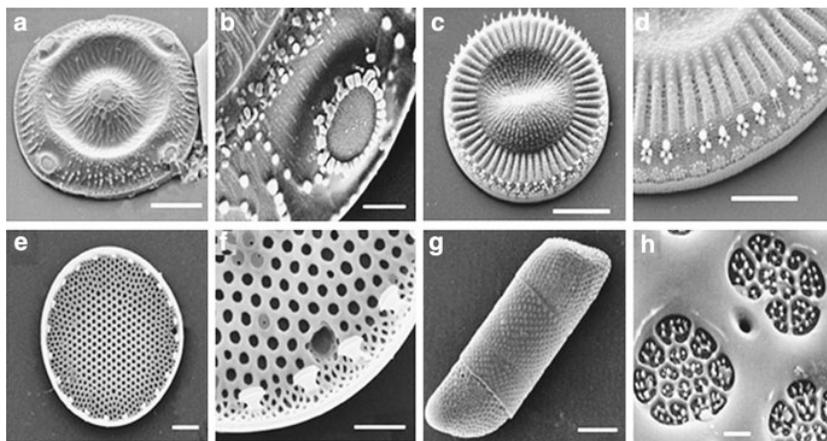


Fig. 6. Transmission electron microscopic images of marine centric diatoms and close-ups of surface features, courtesy of Mary Ann Tiffany. (a and b) *Glyphodiscus stellatus*, (c and d) *Cyclotella meneghiniana*, (e and f) *Roperia tessellata*, and (g and h) *Isthmia nervosa*.

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The heavy metal pollution of water bodies from industries like metal smelting, casting, electroplating, and mining waste materials is currently a vital issue. The application of microalgae for removing the heavy metals contamination, even at low amounts, is more than that of plants, algae, bacteria, and fungi. It is the cost effective and environmentally friendly process, and the use of the microalgae that synthesize metal nanoparticles from insoluble heavy metal pollutants which has dual benefits in the recovery and production of valuable nanoparticles. Similar to a microbial biomass, microalgae adsorb confiscate heavy metal ions by the production of phytochelatin [94]. However, the microalgal biomass synthesis is more costly compared to terrestrial plants.

Diatoms usually make silica for their cell wall during the biomineralization processes, together with particular organic macromolecules including silaffins to form a complex microscopic configuration. These silaffins that diatoms exploit to direct silica precipitation could be utilized in the semiconductor industry. In the same way, in diatom, *Coscinodiscus granii* and cationic polypeptides quickly induce the deposition of silica from silicic acid in vitro. Furthermore, adding polyamines produces silica by the precipitation of silicic acid. The formed nanostructured materials are monodispersed particles of 100–200 nm in size with a spherical morphology. Therefore, the research on the components involved in the biosilica of diatoms aids to biomimic the natural process and results in the precipitation of complex nanostructures at ambient conditions and neutral pH [95].

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5.8 Biosynthesis of Nanoparticles by Heterotrophic Eukaryotic Cell Lines (Human)

Human cells are heterotrophic in nutrition and require to be supplied with energy for their survival. Human cancerous and noncancerous cells, mimicking the natural environment of cells are able to synthesize some metal nanoparticles in vitro intracellularly.

By using a tetrachloroaurate solution (1 mM), cancer cells such as SiHa (malignant cervical epithelial cells), HeLa (malignant cervical epithelial cells), and SKNSH (human neuroblastoma) and non-cancer cells like HEK-293 (nonmalignant human embryonic kidney cells) have produced Au nanoparticles with sizes between 20 and 100 nm. These nanoparticles were produced in the cytoplasm and in the nucleus of the cells. The size of these nanoparticles in nucleus was smaller than that of the cytoplasmic particles [96].

6 Applications of Metal Nanoparticles in Medical Biology

In the research field of nanomaterials, metal nanoparticles have attracted very much interest because of their broad uses in catalysis, electronics, photonics, sensing, environmental cleanup, imaging, and drug delivery [9, 97]. The reason why nanoparticles are attractive for biomedical applications is due to their distinctive properties including high surface-to-mass ratio compared to other particles, their quantum properties and their ability to adsorb and bring other compounds such as drugs, probes and protein to determined locations. The biological application of metal nanoparticles has indicated a fast advancement in the area of labeling, delivery, heating, and sensing. Typically, the optical properties of colloidal Au

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nanoparticles have been employed for new biomedical applications with an importance on cancer diagnostics and therapeutics [9].

6.1 Labeling

Metal nanoparticles are used to produce contrast due to their electron absorbing properties. Au nanoparticles are suitable as a contrasting agent in transmission electron microscopy, since they highly absorb electrons. In addition, due to the same size of nanoparticles with proteins, they are utilized for bio tagging or labeling [98]. Au nanoparticles provide a very high spatial resolution and so have been applied in some of labeling applications, as a result of their small size and functionalizing properties, i.e., with antibodies (immunostaining) [99]. Furthermore, optical detection methods are extensive in the biological field, due to the change in the optical or fluorescence properties of nanomaterials. Correspondingly, the optical properties of particles including strong absorption, scattering and particularly plasmon resonance, make them valuable for light-based methods such as photothermal or photoacoustic imaging. Moreover, radioactive Au nanoparticles make it applicable for sensitive detection and as an X-ray contrast agent [9].

6.2 Sensors

Metal nanoparticles can be utilized as sensors. The electronic and optical sensing properties of biomaterial surfaces is a usual practice in analytical biochemistry. Thus, the immobilization of biomolecule–nanoparticle conjugates on the surface provides a broad approach for the development of optical or electronic biosensors. Metal nanoparticles like Au

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or Ag indicate plasmon absorbance bands in the visible spectral region, which are controlled by the particles size. Their optical behavior can be altered by binding to special molecules, allowing the ion detection and quantification of analytes. The absorption properties of Au nanoparticles change considerably when agglomeration occurs. Many researches have been documented on bioassay labeling and tissue staining, using metal particles as an approach to observing biological processes. Espectral shifts which come from agglomerated metal nanoparticles, like Au, are considered in the development of biosensors, based on a hybrid system being composed of biomolecule and nanoparticles. For example, nanoparticles that were functionalized with two types of nucleic acid, which were matching to two parts of an analyzed DNA, were hybridized with analyzed DNA, resulting in agglomeration of the nanoparticles and in the detection of a red shifted interparticle plasmon absorbance of the agglomerated nanoparticle [100].

6.3 Drug Delivery

Nanoparticles have an appropriate prospect in the form of drug therapies [101]. An effective dose of drugs could be reached to a definite targeted tissue but engineered to deliver in a planned time period in order to ensure the highest efficiency as well as the patient's safety. Due to the nontoxicity and nonimmunogenicity and functionalization properties, Au nanoparticles are superlative for the preparation of scaffolds and vehicles for drug delivery. Aubin-Tam et al. [102] designed a drug delivery system with Au nanoparticles and infrared light which released multiple drugs in a controlled fashion, since the different shapes of nanoparticles respond to various infrared wavelengths. For example, nanobones and

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nanocapsules are melted at light wavelengths corresponding to 1,100 and 800 nm, respectively. Thus, excitation at a specific wavelength can melt specific kinds of Au nanorods and release a specific kind of DNA strand. Brown et al. [103] also conducted research on Au nanoparticles for an improved anticancer property of the active component of oxaliplatin. To do so, naked Au nanoparticles were functionalized with a thiolated poly(ethyleneglycol) (PEG) monolayer capped with a carboxylate group, and then [Pt(1*R*,2*R* diaminocyclohexane)(H₂O)₂]₂ NO₃ was added to the PEG surface to make a supramolecular complex with drug molecules. The cytocompatibility, drug uptake, and localization in lung epithelial cancer cell line (A549) and colon cancer cell lines (HCT116, HCT15, HT29, and RKO) were studied for platinum-tethered nanoparticles. The platinum-tethered nanoparticles presented a significant improvement in biocompatibility, compared to oxaliplatin in all of the mentioned cell lines, and an extraordinary ability to infiltrate the nucleus in the lung cancer cells. The light absorbing behavior of Au nanoparticles formulate it appropriate as heat mediating objects, where the absorbed light energy is scattered into the particles environment, producing a high temperature in their surrounding area. This result may be utilized to open polymer microcapsules for drug delivery applications and even destroy cancerous cells. Moreover, nanoparticles are functionalized with antibodies corresponding to cancerous cells. These nanoparticles specifically attach to targeting cells, which are then killed by hyperthermal therapy.

It is worth noting that, for such in vivo purposes, the cell compatibility of the nanoparticles might be considered as an issue and should be studied with care. Due to biocompatibility of Au nanoparticles and their hyperthermal activity, this material has found an extensive application for treating malignant cancerous cells [104]. Recently, Melancon et

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al. [105] showed the photothermal influence of hollow Au nanoshells with the diameter of around 30 nm bound to monoclonal antibody on the destruction of cancerous cells. Au nanoshells directed to the epidermal growth factor receptor (EGFR) and the resulting anti-EGFR-Au indicated a good colloidal stability and proficient photothermal influence in the near-infrared region. The irradiation of A431 tumor cells treated with anti-EGFR-Au with near-infrared laser led to cell death. Au nanoparticles have also been employed to increase the biorecognition of anticancer drugs. Dacarbazine [5-(3,3-dimethyl-1-triazeno)imidazole4-carboxamide; DTIC] is usually utilized as an anticancer drug. Au nanoparticles are negatively charged by PPh₃ and the oxidized DTIC is positive charged. Therefore, DTIC could be simply assembled onto the surface of Au nanoparticles, and the particular interactions between anticancer drug DTIC and DNA or DNA bases are facilitated by Au nanoparticles.

6.4 Nanoparticles in Medicine and Dentistry

In bone implants, if the surface is left smooth, the body will try to reject it. This is due to the fact that the smooth surface will likely cause the production of a fibrous tissue, covering the surface of the implant. This fibrous layer in turn reduces the contact area between the implant and bone, which may lead to loosening of the implant and inflammation in that area. It was shown that having nano-sized features on the surface of the prosthesis could reduce the chances of rejection, in addition to stimulating the production of osteoblasts [99].

Furthermore, in the realm of dentistry, titanium is extensively used, because of its high fracture resistance, and ductility. However, it lacks bioactivity, so that it does not support cell adhesion and growth. Apatite coatings have been used in the past due to their bioactivity and

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ability to bond to the bone. However, the thickness and nonuniformity of apatite coatings on titanium are considered as limitations. Moreover, porous structures are needed to support nutrient transport. Ceramic nanoparticles are used to prepare an artificial hybrid material which could be placed on the tooth surface to improve scratch resistance [99, 106].

Nanoparticles have been also shown to have antimicrobial properties, due to their large surface area. Metallic nanoparticles can be used to effectively inhibit growth in a number of microorganisms and thereby have numerous applications in medicine and dentistry. Specifically, in dental materials, nanoparticles can be used as active antibacterial agents. Secondary caries are found to be the main reason for restoration failure and are primarily caused by the invasion of plaque bacteria such as *Streptococcus mutans* and *Lactobacillus* in the presence of fermentable carbohydrates. In order to ensure a long-lasting restoration and the possible control of oral infections, the use of nanoparticles to make antimicrobial materials should be explored [107].

6.5. Environmental Cleanup as Defense Against-*Environmental* Challenges to Medical Biology

Although metal nanoparticles are widely being used in various areas, their application in environmental biotechnology is still restricted. One of the important environmental issues is the pollution of water bodies by various chemicals, because of different anthropogenic and industrial wastes. One of the most fascinating use of metal nanoparticles is refinement of drinking water polluted with heavy metals. Recent restrictions in the elimination of heavy

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metals have been aimed to be conquered by the adsorption process on metal nanoparticles via the formation of alloys. Au and Hg are found in numerous phases including AuHg, Au₃Hg, and AuHg₃. The relation of Ag nanoparticles with Hg²⁺ ions was examined due to the increased ability of Ag to form alloys in different phases. It was found that the surface plasmon of Ag nanoparticles blue shifted with a reduction in intensity, directly after adding Hg²⁺ ions [108]. The partial oxidation of Ag nanoparticles to Ag ions is responsible for the reduction in intensity, so that the shift is due to the integration of Hg into Ag nanoparticles. The potential of Ag nanoparticles to decrease heavy metals can also be viewed as a technique for alloy nanoparticles preparation, for example Ag–Hg bimetallic nanoparticles. Currently, the colorimetric detection of heavy metals like As, Hg, Pb, etc., has also been investigated by using metal nanoparticles.

One of the key properties indicated by functionalized metal nanoparticles surfaces is the recognition of heavy metals. In this technique, heavy metal biomolecule functionalized Au nanoparticles can be used. An instance of this method is the interaction of metal ions with nucleotides, whereas Hg²⁺ facilitates the thymine–thymine base pairs formation [109]. In related ways, ligands such as (gallic acid (Pb²⁺), cysteine (Hg²⁺, Cu²⁺), and mercaptoundecanoic acid (Pb²⁺, Cd²⁺, Hg²⁺) functionalized metal nanoparticles have been utilized for identifying particular metal ions, leading to the formation of ligand–metal ion complex and the changes in optical properties at low level concentrations (ppm) [110]. The removal of pesticides by metal nanoparticles is an innovative idea to this research area. Amongst other pollutants, the existence of pesticide residue in drinkable water higher than permissible limit is of big alarms to public health. This occurs as a result of the discriminate use of pesticide, in particular belonging to organophosphorus groups, in agricultural

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applications. It is necessary to decrease the amount of pesticide in drinkable water, which is difficult to reach by conventional chemical routes, owing to the broad variation of their chemical structures. To address the mentioned environmental issues, recent research focused on planning techniques based on nanotechnology. Das et al. [111] showed the adsorption of various organophosphorous pesticides on the surface of Au nanoparticles. Au nanoparticles produced on the surface of the *R. oryzae* mycelia in a single set were then employed for the adsorption of different *organo phosphorous* pesticides. Following the adsorption of these pesticides, the surface morphology obviously changes compared to the unadsorbed nanomaterial, as confirmed with atomic force microscopic photomicrographs.

7. Conclusions

Nanomaterials, with typical dimensions in the range of 1–100 nm, are at the leading edge of nanoscience and nanotechnology. Recently, nanomaterials, particularly metal nanoparticles, have attracted special interest in the diverse field of applied science ranging from material science to biotechnology. Moreover, exponentially growing attention has been observed in the biological synthesis of nanomaterials. The knowledge increase towards green chemistry and biological approaches has resulted in the use of eco-friendly techniques for the manufacturing of nontoxic and biocompatible nanomaterials. The development of environment-friendly routes in the production of material is of significant importance to enlarge their biological purposes. Recently, a range of green nanoparticles with definite chemical compositions, sizes, and structures have been produced by various techniques, and

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their uses in many cutting-edge technological areas have been examined. Different biological bodies have been developed in the biosynthetic methods of metal nanoparticles and the use of organisms or constituents that facilitate the synthesis of monodispersed metallic nanoparticles. Consequently, the simplistic biosynthesis of nanoparticles with controlled dimensions and shapes by using molecular cloning and genetic engineering approaches and other photobiological techniques will be a marvelous expansion in the nanobiotechnology area. Expediting research on such organisms, biocomponents, or parameters will eject such conservative dangerous processes. Terrestrial and aquatic phototrophic eukaryotes, heterotrophic eukaryotes, and biocompatible agents have enormous capability to create metal nanoparticles. Phototrophic eukaryotes such as plants, algae and diatoms are considered as potentially sustainable and renewable biofactories for the production of nanoparticles. Nanomaterials by renewable bioresources and biocompatible agents with exceptional physicochemical, optoelectronics, and electronic properties are of immense significance for wider purposes in the areas of chemistry, medicine, electronics, and agriculture.

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