Green Synthesis of Metal nanoparticles by microorganisms; a current prospective

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Abstract

Synthesis and applications of nanomaterials has been an interesting area of nanotechnology since last decade. Several physico-chemical methods have been used to synthesize the nanoparticles of noble metals. Numerous other methodologies are also in practice including the laser ablation, aerosol technologies, lithography, and ultraviolet irradiation. However, traditional methods are less preferred because they remain costly and involve the use of hazardous chemicals. Biological routes of synthesizing metal nanoparticles via microbes is gaining much attention due to their low toxicity, biocompatibility and eco-friendly nature. The development of reliable, eco-friendly, sustainable processes for the synthesis of nanoparticles with precise shapes, sizes and dispersity is a progressive area of nano-biotechnology. Despite the higher stability of biogenic nanoparticles there is still need to optimize the synthesis rate and other factors affecting the synthesis process. Microbial synthesis of silver, gold, platinum, titania, zirconia, magnetite nanoparticles and quantum dots has been described successfully. However molecular mechanisms that mediates the synthesis of nanoparticles should be elucidated further to improve the properties of nanoscale materials and production rate. Due to the rich biodiversity of microbes, their potential as a useful source for the production of nanoparticle is yet to be fully explored. The present review emphases the current status of potential microbial sources for the synthesis of metal nanoparticles.

Keywords: Eco-friendly; Biodiversity; Nano-biotechnology; Reliable; Biological routes

1. Introduction

The" Nano" word has been derived from Greek language related to objects of one billionth (10^{-9}) in size. The history of nanotechnology goes back to 9th century, when artisans of Mesopotamia used metallic nanoparticles for imparting the glittering effects to the pots. Nanoparticles (NPs) behave differently as compared to the matter in bulk and display the unique physical, chemical, biological, thermal and magnetic characteristics. Interestingly, distinct properties of nanoscale materials are significantly influenced by decreasing dimensions of nanoparticles (NPs). NPs have various applications in biomedical [1], cosmetics [2], optics, electronics, space technology, energy [3], catalysis [4] and food [5]. Generally, two strategies are used for synthesis of NPs including the top-down and bottom-up. In former, larger

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materials are broken down to smaller ones. While bottom-up approach usually involves the assembly of atoms in to molecular structures in nanometer range.

Biological and chemical synthesis are Bottom-up approach. Numerous chemical and physical methods have been employed for the manufacturing of NPs [6]. Physical methods are laborious, whereas chemical methods usually include the use of different reducing agents, radiolysis process, and electrochemical techniques. These conventional methods are less preferred due to yielding the hazardous wastes and not being cost effective. The use of toxic chemicals also limits the biomedical applications of NPs specilay in clinical fields. To increase the biocompatibility of NPs, it is necessary to develop eco-friendly, reliable and sustainable procedures for the synthesis of nanomaterials. In this regard enzymatic approaches are useful, as they eliminate the use of toxic materials.

Microorganisms are the potential source of intracellular and extracellular enzymes needed for the synthesis of NPs. Biogenic NPs are much stable with enhanced specificity and catalytic properties. Microbial synthesis of nanomaterials is also supported by the fact that majority of microbes inhabit the ambient environmental conditions. Consequently the establishment and optimization of nanomaterial could be achieved much simply. Nanotechnology has become a progressing area, hence there is growing need to search the eco-friendly and cost effective procedures for synthesis of nanomaterials. Exploring the basic mechanism of biogenesis of NPs has become an investigative issue, which can be regarded as potent eco-friendly nano factories. Nanotechnologists have perceived siliceous materials by diatoms, magnetite particles by magneto-tactic bacteria and calcium layers by S-layer bacteria. Several biological applications like bio-mineralization, bioleaching and bioremediation enable the better understanding of metal microbe interaction.

All biological methods have the advantages of being more stable and ecofriendly. Although the biological methods of synthesis are common presently, but there is still need to optimize conditions of synthesis and understanding the synthesis mechanism with efficient downstream processing techniques [7].

1.2 Microbial Synthesis of Metal Nanoparticles
1.2.1 Biosynthesis of nanoparticles by viruses
Biomolecules like fatty acids and amino acids could act as a template for the production of semiconductor nanocrystals [8]. The synthesis of eco-friendly and inorganic nanostructures has been carried out by biological templates of protein cages[9], DNA[10], bio-lipid cylinders [11] and bacterial rapidosomes [12]. Genetically engineered viruses and (Self-assembled) viral capsids were utilized in fabrication process of quantum dots and nanowires [13]. Iron oxide NPs were also synthesized by oxidative hydrolysis in the presence of tobacco mosaic virus (TMV). M13 bacteriophages expressed the Pviii fusion protein which worked as nuclei for the accumulation of ZnS and CdS nanostructures [13].

1.2.2 Yeast mediated synthesis of nanoparticles
Generally, yeast mediated synthesis of semiconductor NPs has been also observed. *Candida glubrata* detoxified metal ions by generating metal–thiolate complexes with phytochelatins[14], and produced the intracellular spherical and mono-dispersed quantum crystallites of CdS [15]. Similarly intracellular formulation of Gold nanoparticles (GNPs) was reported in a pH dependent manner reduction of gold ions take place [14]. At low pH 2.0 production of triangular and hexagonal gold crystals was observed owing to the nucleation on the cell boundary[16]. A silver tolerant strain of yeast MKY3 was reported to produce extracellular hexagonal SNPs [14]. Antimony oxide (Sb_2O_3) NPs exhibiting the characteristics of semiconductor were produced by S. cerevisiae at ambient conditions. This was possibly due to the radial tautomerization by membrane bounded pH-dependent oxidoreductases[17].

1.2.3 Actinomycete mediated synthesis of nanoparticles
Actinomycetes have been identified for the synthesis of intracellular as well as extracellular NPs. An extracellular synthesis of mono-dispersed and spherical GNPs was detected thorough the *Thermomonospora* sp[18]. A novel extremophilic actinomycete. *Rhodococcus* sp. was investigated for intracellular biosynthesis of metallic NPs on inner side of cell wall and cytoplasmic membranes. Cytoplasmic membrane contained more particles than on the cell wall which indicates the presence of enzyme [16]. Previously actinomycetes were distinguished as the primary source of secondary

metabolites, but these findings would take a lead in sorting of more actinomycetes strains for the formulation of nanostructures [17].

1.2.4 Algae mediated synthesis of nanoparticles

There are few reports on use of microscopic algae for the metallic NPs. Recently, in a study _Chlamydomonas reinhardtii_ was used for the controled biosynthesis of SNPs. Another investigation explored an organized way to explore the process of metallic NPs by _Sargassum wightii_ [19]. That was first report about the use of marine alga for the synthesis of relatively stable GNPs. Extremely stable GNPs (8-12nm) with high density were formulated following the reduction of gold ions. Certainly, at agitating condition bio-reduction of 95% of $AuCl_4^-$ ions take place within 11-12 hours. The synthesis procedures have been expanded to nanostructures of platinum and palladium by using their metallic chloride [20].

1.2.5 Fungal mediated synthesis of nanoparticles

The bioaccumulation of metals and metal tolerance ability makes the fungus as potential candidate in biological production of metallic NPs. The complex process of metals accumulation renders through different mechanisms including physicochemical and biological processes which might be involved in extracellular adhering with metabolites (metabolism-dependent accumulation). A rapid extracellular synthesis of stabilized metal NPs was observed, when _Fusarium oxysporum_ was used as source of enzyme [20]. In contrast to intracellular, extracellular synthesis have more advantages due to easy downstream processing techniques[21]. Moreover intracellular synthesis would require advanced instruments to extract NPs from the biomass. The intracellular SNPs (2–25 nm) synthesis was also described within _Verticillium_ with the metallic deposits clearly affiliated to the cell membrane[22]. Extracellular synthesis of SNPs can also be accomplished by the fungus _Phoma_ using cell extract with aqueous solution of silver nitrate [23].

Fusarium oxysporum has the ability to reduce the silver nitrate solution by nitrate reductase that formulated SNPs. Capping-proteins released by fungus provides the stability and prevent the NPs from aggregation [24]. A rapid photo-biological method for the generation of SNPs (10–60 nm) was reported by Mohammadian et al, (2007) using various strains of _F. oxysporum_. There is a great deal of research for the synthesis of SNPs by using _F. semitectum, F. solani_ [25]. _Cladosporium cladosporioides_[26] and _Trichoderma asperellum_[27]. Extracellular polydispersed and spherical SNPs having dimensions of 4–100 nm was obtained, when the capping ligands of proteins was used for stability [28]. However, amount of cofactor like NADH can play a key role for synthesis of highly stabeled alloy NPs of gold-silver with various compositions. [29].

To elucidate the mechanism of synthesis for nanoscale materials, invitro production of SNPs was done by using enzyme NADPH-dependent nitrate reductase and a capping agent phytochelatin from a fungus _Fusarium oxysporum_ [30]. Enzymes particularly involved in selective bioleaching of silicates from zirconia was identified as responsible agent for synthesis process. Extracellular protein-mediated hydrolysis of aqueous solution of K_2ZrF_6 creates zirconia NPs after exposing with _Fusarium oxysporum_ at room temperature[31]. The effect of temperature and concentration of salt hexachloroplatinic acid (H_2PtCl_6) and pH in synthesis of NPs was appreciated through statistical technique Response surface methodology (RSM) [21].

Few fungal strains has also produced various metal NPs of oxides and metal sulphide. _Candida glabrata_ produced intracellular NPs of CdS, when culture was exposed to Cd^{2+} ions. Similarly, PbS nanocrystalls were produced intracellularly [32]. Investigations have revealed that _S. cerevisiae_ can also synthesize NPs of titanium oxide (TiO_2). _Verticillium_ and _F. oxysporum_ extracellularly produced iron oxide NPs (magnetite), when cell free extracts was exposed to salts ferrous salts and ferric one-to-one at room temperature [33].

1.2.6 Bacterial mediated synthesis of nanoparticles

Bacteriogenesis of NPs could be achieved by extracellular as well as intracellular. Microbial resistance to heavy metals is the ability to detoxify chemicals due to ion efflux from special membrane-proteins, functioning as chemiosmotic cation (proton anti-transporters) and ATPase (energy-dependent). Alteration in solubility is another mechanism of metal resistance [34]. Consequently, detoxification of

metal ions are the results of precipitation and reduction from soluble, toxic inorganic ions to insoluble and non-toxic metallic nanoclusters. Detoxification of metals by microbes can also be achieved by precipitation, biosorption, extracellular complexation, and intracellular bioaccumulation. With reference to commercial applications the extracellularly produced NPs have considerable importance. However, polydispersity remain as major concern. In order to achieve monodispersity there is still need to optimize the procedures in biological and microbial synthesis [35].

Biogenic NPs have applications in bioreactors as catalysts and retained for continuous use. In the recent years bacteria has been applied for the process of deposition in mineral ores[36]. The accumulation of gold by *Pedomicrobium* has been reported in the Alaskar placer [37]. The reduction of water soluble Au^{+3} to Au^0 produced the GNPs of 5–25 nm with octahedral structure. The *Geobacter ferrireducens* precipitated the gold in periplasmic space via reducing the Fe (III) [38]. Similarly, *Shewanella algae* mesophilic iron (III)-reducing strain formulated GNPs in periplasmic space [8].

Gram-negative bacteria protect themselves from toxic substances through vesicles like lipopolysaccharides (LPS), proteins and phospholipid. *Escherichia coli* DH5α mediated synthesis has been illustrated by reduction of chloroauric acid to Au^0 (GNPs). Cell-bound NPs have anticipating applications in understanding the direct electrochemistry of hemoglobin and other blood proteins [39]. Remarkably, *Rhodobacter capsulatus* a photosynthetic bacterium was also identified as reducing agent of trivalent aurum in log phase. NADH-dependent enzymes and carotenoids engrafted in cell membrane were recognized for participation in bio-reduction [40]. Broadly, intracellular synthesis of SNPs is being concerned with cell surfaces. As in case of *Pseudomonas stutzeri* AG259 the crystallites of silver sulfide (Ag_2S) were located in periplasmic spaces with equilateral, monoclinic, triangular, and hexagonal in shape [41]. In the fabrication of SNPs, silver-binding proteins provides a site that facilitated the nucleation [43].

Recently, a *Bacillus* species was noticed to reduce metallic silver ions to atomic silver [42]. This accumulation of silver on cell wall has been reflected as a resistance process assisted through periplasmic proteins[42]. Klaus and coworkers (1999) have revealed the organization of SNPs of distinct shape and well-defined sizes within the periplasmic space of the bacteria, when *Pseudomonas stutzeri* AG259 was treated with saturated solution of $AgNO_3$. Similarly, Corynebacterium sp. (SH09) synthesized intracellular SNPs after the incubation of dried cells and diamine silver complex $[Ag(NH_3)_2]^+$ at 60 °C for 72 hours. [43]. When *Lactobacillus* (common bacteria of butter milk) was exposed to metal ions, metallic NPs was detected within the bacterial cells [44].

Interestingly, Alloy NPs were formulated when lactic acid bacteria (whey) was exposed with metallic ions in mixed state [45]. *S. oneidensis* MR-1 was revealed to form nanocrystals of Pb inside the cell membrane and on the cell wall[46]. Moreover, *Desulfosporosinus sp.* converted hexavalent form of uranium U(VI) into tetravalent U(IV) uraninite precipitates. The uraninite precipitates might be instrumental in suppressing the contaminants of soluble radionuclides in soils and transforming the soluble sediments to insoluble form[47]. Magnetic NPs could be synthesized by magnetotactic bacteria and may contain iron sulfide or iron oxide or both.

For differentiation from other types like artificially produced magnetic particles (AMPs) these may be distinguished as bacterial magnetic particles (BacMPs). Within the bacterial cells these (BacMPs) are adjusted in lines and facilitate them as biological compass needles to assist the bacterial movement in the Earth's geomagnetic field along gradients of oxygen in aquatic environments[48]. Organic membranes of BacMPs consisted of proteins and phospholipids are supportive in Magnetotactic bacterial dispersal in aqueous environment. Magnetotactic bacteria inhabit marine and fresh water sediments and synthesized intracellular membrane-bound magnetite[49], pyrrhotite [50], ferromagnetic iron sulfide and greigite (Fe_3S_4) [51].

A study demonstrated that assembly of magnetotactic bacteria can be manipulated through micro-electromagnets in body fluid [52]. Intracellular biosynthesis of magnetic nanocrystals of magnetite (Fe_3O_4) was found to be exhibited by various bacteria including *Magnetospirullum magnetotacticum[53]*, *Aquaspirillum magnetotacticum*[37] and *M. magnetotacticum* MS-1 [52]. The semiconductor nanocrystals of cadmium sulphide (CdS) were intracellularly manufactured by various bacteria including *Klebsiella pneumonia* [54], *Clostridium thermoaceticum* [55]and *E. coli* [56]. It was noticed that CdS nanocrystals were precipitated by the action of cysteine desulfhydrase which caused desulfhydration of cysteine. These bio-mediated semiconductor NPs of CdS exhibited optical and photoactive properties and showed

spherical and elliptical shapes. In another experiment spherical NPs of ZnS were biologically produced by microbes belonging to *Desulfobacteriaceae* [57]. The NPs that were synthesized inside cells require additional protocols and downstream processing steps like treatment with suitable detergents or ultrasound treatment [48].

The synthesis of metallic NPs by microbes and location of reducing agents are interlinked. Extracellular establishment of metallic NPs is possible after the secretion of specific reductive enzymes involved in reduction of metal ions. The extracellarly synthesized NPs have more applications in different fields like bio imaging, electronics, sensor technology and in optoelectronics than intracellular NPs. During an investigation *P. aeruginosa* (ATCC 90271) was used to synthesize extracellular GNPs of particle size 5-40nm [58].Dried cells of *Aeromonas sp.* SH10 reduced the silver nitrate to highly stable uniform size SNPs[59].

A rapid synthesis of SNPs was observed, when the cell filtrate of *Enterobacteriaceae* family (*Klebsiella pneumonia*, *E. coli*, and *Enterobacter cloacae*) was given time to react the silver nitrate solution. The reduction process was suppressed by the addition of piperitone (inhibitor for nitrate reductase) which proved the direct participation of nitro reductase family in the route of reduction. Likewise, the extracellular synthesis of SNPs was also carried out by using *B. licheniformis* [60]. Biogenesis of homogenous SNPs was also detected in cellulose membranes of *Acetobacter xylinum,* when bacterial culture was given exposure to the solution containing Ag^+ ions and tri-ethanol-amine (Ag^+-TAE) [61].

Biogenesis of SNPs was also reported using a silver-resistant bacterium *Morganella* species that was isolated from the gut of an insect [62]. A photosynthetic bacterium *Rhodopseudomonas palustris* produced extracellular nanocrystals of CdS with spherical morphology as demonstrated by Bai et al [61]. *Klebsiella aerogenes* was perceived to synthesize spherical crystallites of CdS. Energy dispersive X-ray spectroscopy (EDS) revealed that both sulfur and cadmium was in equal quantity. The extracellular production of CdS nanocrystals at room temperature by purple non-sulfur bacteria, [61]*R. palustris* [63], *K. aerogenes* [64], *R. sphaeroides* and *G. xylinus* has been described. After precipitation, *Gluconoacetobacter xylinus* CdS NPs were accumulated on cellulose nanofibers of bacteria [65].

 Intriguingly, it has been demonstrated that bacteria can perform catalytic function due to reduction potential, electrochemical energy, and shedding the electron in vicinity in such a potency that they can precipitates magnetite [43].The production of extracellular magnetite NPs by *Actinobacter* sp a non-magnetotactic aerobic bacterium has also been reported by Bharde et al, (2005). Extracellular generation of magnetite NPs has been also executed by some non magnetotactic bacteria e.g. *Geobacter metallireducens* (isolated from bottom of river) in the presence of acetate and under anaerobic environment produced the ultrafine magnetite NPs through reduction of ferric oxide [63].

2. Conclusion

Nano biotechnology has emerged as an interdisplinary field of science and has developed new safe and ecofriendly pathways for synthesis of metal nanomaterials. The growing exposure of biological process toward the green synthesis has directed to develop the cost effective and eco-friendly approaches for synthesis of nontoxic nanoparticles. Because other methods may involve the use of hazardous materials. Therefore microbial synthesis of nanomaterials is cost effective, clean, sustainable and environment friendly approach. Microorganisms are the efficient source and they can be regarded as potential bio factories for the green synthesis of nanoparticles. However there is still need to optimize the synthesis rate and downstream processing techniques. While elucidation of mechanisms involved in synthesis of nanomaterials also needs to be explored further in order to achieve controlled sized nanoparticles and monodispersity. Effect of different environmental conditions and combinatorial factors are essential to observe for the synthesis of NPs with vast applications in medicine, chemistry, electronics and agriculture. The surface chemistry of biogenic nanoparticles should be analyzed properly to explore the application of nanomaterials. The shift from bacteria to fungi as a means of developing natural "nanofactories" has the added advantage that downstream processing and handling of the biomass would be much simpler.

3. References

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