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Review article: Bioical factories of metallic nanoparticles

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ABSTRACT

The green synthesis of metallic nanoparticles is an active area of academic and more importantly, “application research” in nanotechnology. A variety of chemical and physical procedures could be used for synthesis of metallic nanoparticles. However, these methods are fraught with many problems including use of toxic solvents, generation of hazardous by-products, and high energy consumption. Accordingly, there is an essential need to develop environmentally benign procedures for synthesis of metallic nanoparticles. A promising approach to achieve this objective is to exploit the array of biological resources in nature. Indeed, over the past several years, plants bacteria and fungi have been used for production of low-cost, energy-efficient, and nontoxic metallic nanoparticles. In this review, we provide an overview of various reports of Biosynthesis of metallic nanoparticles using inactivated plant biomass, living plants, bacteria and fungi. © 2014 Trade Science Inc. - INDIA

KEYWORDS

Bioical factories;
Metallic nanoparticles.

INTRODUCTION

Definition

In nanotechnology, a particle is defined as a small object that behaves as a whole unit in terms of its transport and properties. It is further classified according to size: In terms of diameter, fine particles cover a range between 100 and 2500 nanometers, while ultrafine particles, on the other hand, are sized between 1 and 100 nanometers. Similarly to ultrafine particles, nanoparticles are sized between 1 and 100 nanometers^[8]. Nanoparticles (NPs) are usually considered to be a number of atoms or molecules with a radius $d > 100$ nm. But this definition is somewhat arbitrary. The nanoparticle regime might be best defined as the point

at which the properties of the particles differ from those of the bulk materials^[42].

Their small size allows them to interact with biological macromolecules and pass through most of the cellular machinery unnoticed by the immune system as the macromolecule can act as a shield from any immune response. Furthermore nanoparticles may act as a scaffold that would allow the attachment of other biomolecules, such as antibodies, peptides and even DNA^[56].

SYNTHESIS

The biological production of metal nanoparticles is becoming a very important field in chemistry, biology, and materials science. Metal nanoparticles have been

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produced chemically and physically for a long time; however, their biological production has only been investigated very recently. The biological reduction of metals by plant extracts has been known since the early 1900s; however, the reduction products were not studied. Furthermore, the synthesis of nanoparticles using plant materials, for the most part, has only recently been studied within the last three decades, while the production of nanoparticles using living plants has only been studied in the last half decade^[34].

NPs could be metals, ceramics, polymers and composites and synthesis of nanoparticles can be achieved through several methods such as extensive ball milling, condensation or precipitation (chemical route), drawing glassy materials, self-assembly including biological fabrication, forming materials around/within templates, growth of secondary materials on a crystalline lattice in which the lattice parameter do not match (strained-layer growth), etc. All these procedures are capital, time and labour-intensive and each having its own advantages and disadvantages.

The synthesis and assembly of nanoparticles would benefit from the development of clean, nontoxic and environmentally acceptable “green chemistry” procedures, probably involving organisms ranging from bacteria to fungi and even plants^[33]. Among various biological systems, plants provide an easy and safe green route for the synthesis of various metal nanoparticles^[31].

Formation of metal nanoparticles by inactivated plant biomass

This technology, known as biosorption, emerged in the 1980s and obtained attention because it has shown to be very promising for the removal of contaminants from effluents in an environmentally friendly approach^[12,58].

Ti/Ni nanoparticles can be synthesized by bio-reduction methods, by means of mixtures of aqueous solution of salts of nickel and titanium, using alfalfa treated as biomass source. Single crystalline and multiple twinned types of nanoparticles were produced. The structure, shape and sizes of the alloyed nanoparticles were critically controlled by the sample preparation. The particle size distribution for every pH was bimodal but with the highest percentage of particles with sizes in the quantum dot range^[45].

Stable gold nanoparticles were formed by treating an aqueous HAuCl₄ solution using the plant leaf extracts as reducing agents. The proposed method requires only a few minutes for >90% conversion by using Magnolia and Persimmon leaf broths by increasing the reaction temperature to 95 °C; the reaction rate thus obtained was higher or comparable to the rate of gold nanoparticle synthesis by chemical methods. The particle size ranging from 5 to 300 nm and the shape of the plate and spherical structures could be controlled by changing the reaction temperature and leaf broth concentration^[16].

In previous study^[60] gold nanoparticles were synthesized by using Barbated Skullcup (BS) herb (a dried whole plant of *Scutellaria barbata* D. Don) as the reducing agent. After exposing the gold ions to BS herb extract, rapid reduction of gold ions was observed leading to the formation of gold nanoparticles in solution. Transmission electron microscopy (TEM) micrograph analysis of the gold nanoparticles indicated that they were well-dispersed and ranged in size 5–30 nm.

Formation of metal nanoparticles by living plants

The mechanism of formation of nanoparticles; whether they are formed outside in the media and then translocated to plants or whether they are formed by the reduction of metal salts within the plants itself still needs more clarification^[15]. The reduction of silver ions (Ag⁺) in aqueous solution generally yields colloidal silver with particle diameter in the range of nanometers. Initially, the reduction of various complexes with Ag⁺ ions leads to the formation of silver atoms (Ag⁰), which is followed by agglomeration into oligomeric clusters. These clusters eventually lead to the formation of colloidal Ag particles^[54].

Biosynthesis might have resulted due to different metabolites (like organic acids and quinones in this case) or metabolic fluxes and other oxido-reductively labile metabolites like ascorbates or catechol/protocatechuic acid^[1] as shown in Figures (1,2,3).

Development of biologically inspired experimental processes for the synthesis of nanoparticles is evolving into an important branch of nanotechnology. For example, using the fruit extract of *Emblica Officinalis* (amla, Indian Gooseberry)^[2], using the leaf extract of *Glycine max* (soybean)^[57], using the leaf extract of *Geranium*

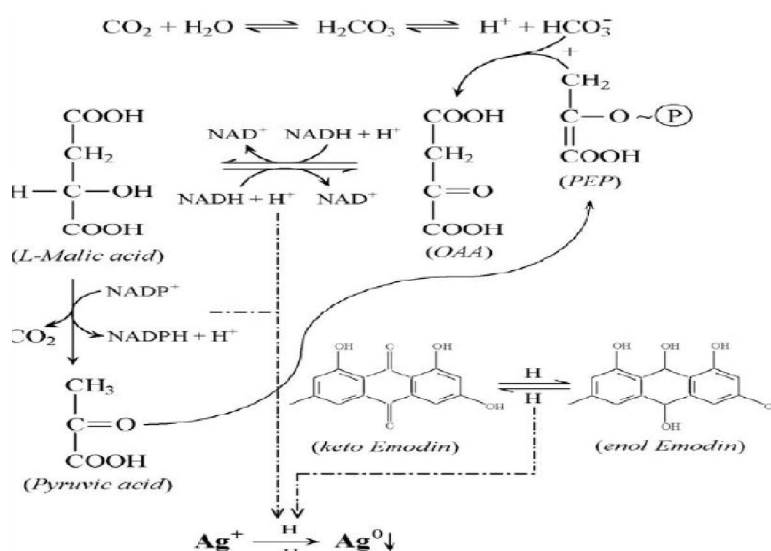


Figure 1 : Mechanism of biosynthesis of Ag nanoparticles using xerophytes

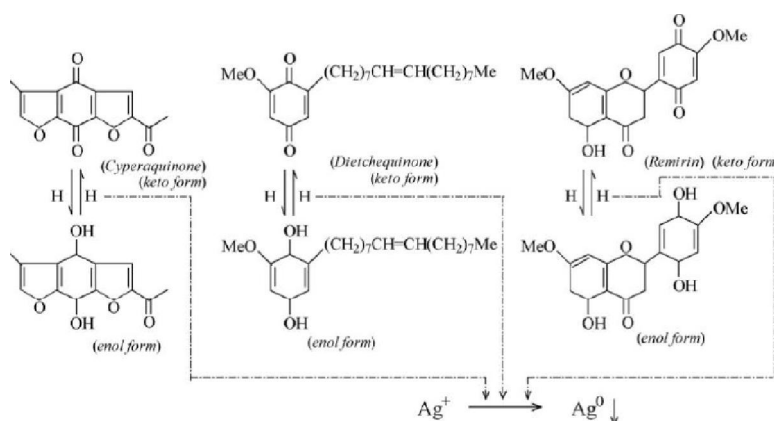


Figure 2 : Mechanism of biosynthesis of Ag nanoparticles using mesophytes

(*Pelargonium graveolens*)^[46] as reducing and protecting agents. In addition to using bacterium for nanoparticles synthesis as *Brevibacterium casei*^[18a] or using *Aspergillus clavatus*^[53] or using mushroom extract of *Volvariella volvacea*^[35].

Silver nanoparticles were successfully synthesized from AgNO_3 through a simple green route using the latex of *Jatropha curcas* as reducing as well as capping agent^[14].

In previous study^[44], nano-sized Ag particles were synthesized using novel *C. zeylanicum* bark powder (CBP) and extract (CBPE) was succeeded. Also, Silver nanowires (AgNWs) with diameters in the range of 40-60 nm and lengths up to tens of micrometers can be synthesized by using the broth of *Cassia fistula* leaf as reductant and capping agent without using any chemical reagent or surfactant templates^[27] as shown in Figure 4.

This environmentally friendly method of biological silver nanoparticles production provides rates of synthesis faster or comparable to those of chemical methods and can potentially be used in various human contacting areas such as cosmetics, foods and medical applications^[49].

Formation of metal nanoparticles by bacteria

Until now, a wide range of prokaryotes as prospective nanoparticle synthesizers have been witnessed. One major advantage of having prokaryotes as nanoparticle synthesizers is that they can be easily modified using genetic engineering techniques for over expression of specific enzymes, apart from the ease of handling^[21]. Bacterial cells are constantly exposed to stressful situations and an ability to resist those stresses is essential for their survival. The ability of microorganisms to grow in the presence of high metal concentrations

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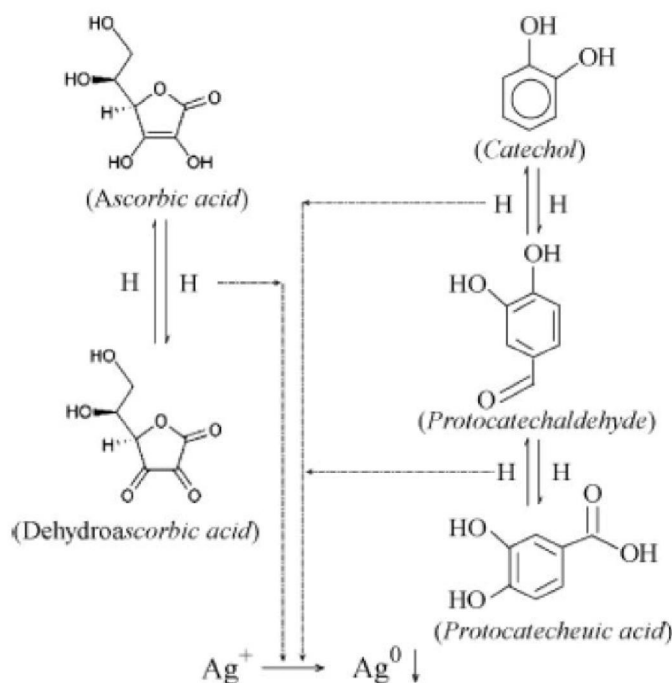


Figure 3 : Mechanism of biosynthesis of Ag nanoparticles using hydrophytes

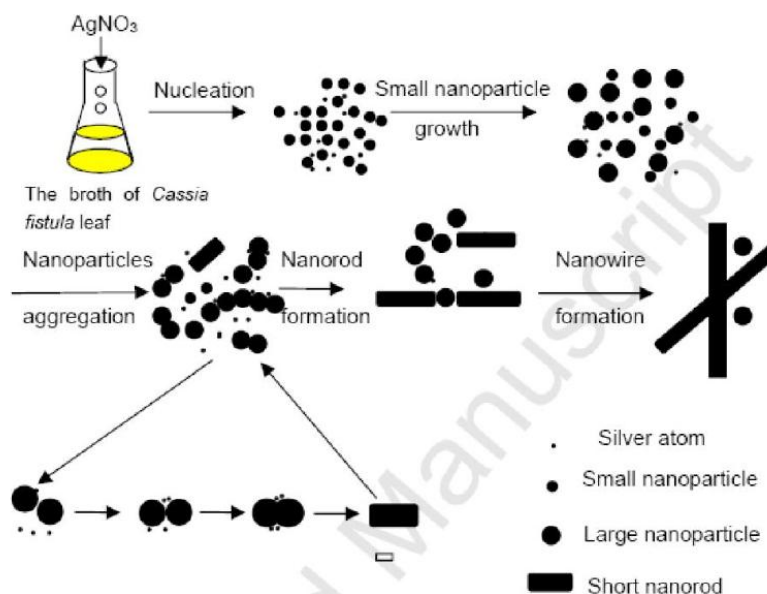


Figure 4 : Schematic illustration of the growth mechanism of AgNWs

might result from specific mechanisms of resistance. Such mechanisms include: efflux systems; alteration of solubility and toxicity by changes in the redox state of the metal ions; extracellular complexation or precipitation of metals; and the lack of specific metal transport systems^[51].

Microorganisms are paramount for metal cycling and mineral formation in Earth surface environments. Metal cycles are driven by microorganisms, because some metal ions are essential for microbial nutrition,

others are oxidized or reduced to obtain metabolic energy, while in particular heavy metal ions, e.g., Hg^{2+} , Cd^{2+} , Ag^+ , Co^{2+} , CrO_4^{2-} , Cu^{2+} , Ni^{2+} , Pb^{2+} , Zn^{2+} , also cause toxic effects^[38]. To counter these effects, microorganisms have developed genetic and proteomic responses to strictly regulate metal homeostasis^[32].

Metallophilic bacteria, such as the Gram-negative β -proteobacterium *Cupriavidus metallidurans*, harbor numerous metal resistance gene clusters enabling cell detoxification via a number of mechanisms such as

complexation, efflux, or reductive precipitation. Hence metallophilic bacteria thrive in environments containing high concentrations of mobile heavy metal ions, such as mine waste rock piles, efflux streams of metal processing plants, and naturally mineralized zones.

Microbial resistance against heavy metal ions has been exploited for biological metal recovery via reduction of the metal ions or formation of metal sulfides^[28].

Sulphate-reducing bacteria have been cited in the literature as excellent models for metal bioremediation. Metals are removed from solution either by precipitation, where the metal ion becomes complexed with the sulphides – produced from sulphate metabolism in the dissimilatory sulphate reduction pathway – forming an insoluble metal-sulphide^[37] and/or via metal-hydrogenase activity, where the metal-ion becomes reduced to a lower, often less toxic oxidation state, due to the catalytic action of the redox, hydrogenase enzymes^[24]. It is well documented that SRB contain a variety of hydrogenase enzymes both cytoplasmic and periplasmic, either free or membrane bound capable of hydrogen uptake or hydrogen evolution^[26].

Two different hydrogenase enzymes from sulphate-reducing bacteria are responsible for the bioreductive mechanism of platinum into nanoparticles. A mixed consortium of SRB was capable of reducing Pt(IV) to Pt(0) via the intermediate cation Pt(II) in a two-step two-electron reduction mechanism involving two different hydrogenase enzymes.

First, a cytoplasmic hydrogenase, that was oxygen sensitive, was not inhibited by Cu(II), required no exogenous electron donors and produced hydrogen (and excess electrons) from metabolite oxidation and/

or Pt (IV) reduction. Second, a periplasmic hydrogenase that was oxygen-tolerant/protected, was inhibited by Cu(II) and used the endogenously formed hydrogen donors (and Pt (II) ions) to form Pt (0) nanoparticles^[40] as shown in Figure 5.

Low-cost green and reproducible microbes (*Lactobacillus* sp. and *Sachharomyces cerevisiae*) can mediate biosynthesis of CdS nanoparticles performed akin to room temperature in the laboratory ambience^[36] as shown in Figure 6.

Bacteria *R. capsulata* is capable of producing gold nanoparticles extracellularly and the gold nanoparticles are quite stable in solution. Bacteria *R. capsulata* are known to secrete cofactor NADH- and NADH dependent enzymes that may be responsible for the bioreduction of Au (3+) to Au (0) and the subsequent formation of gold nanoparticles.

The reduction seems to be initiated by electron transfer from the NADH by NADH-dependent reductase as electron carrier. Then the gold ions obtain electrons and are reduced to Au (0)^[47] as shown in Figure 7.

Phototrophic bacteria are ubiquitous in fresh and marine water, soil, wastewater, and activated sludge. They are metabolically the most versatile among all procaryotes: anaerobically photoautotrophic and photoheterotrophic in the light and aerobically chemoheterotrophic in the dark, so they can use a broad range of organic compounds as carbon and energy sources^[20].

Phototrophic bacteria *Rhodospseudomonas palustris*, a typical purple non-sulfur bacterium, reported to synthesize CdS nanocrystals at room temperature through a single step process. C-S-lyase, an intracellu-

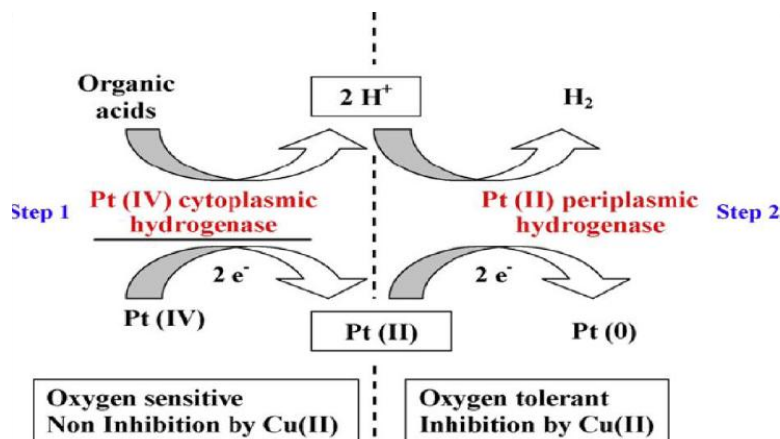


Figure 5 : Suggested mechanism for the double two-electron bioreduction of Pt (IV) into nanoparticles via an intermediary Pt(II)

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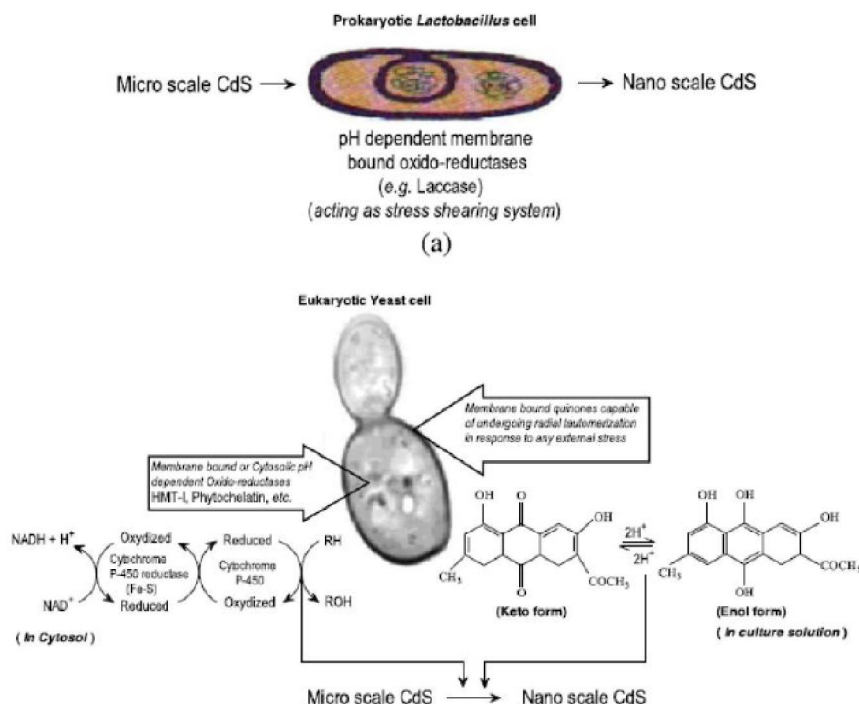


Figure 6 : Schematics for the biosynthesis of n-CdS using (a) Lactobacilli and (b) yeast (*Saccharomyces cerevisiae*)

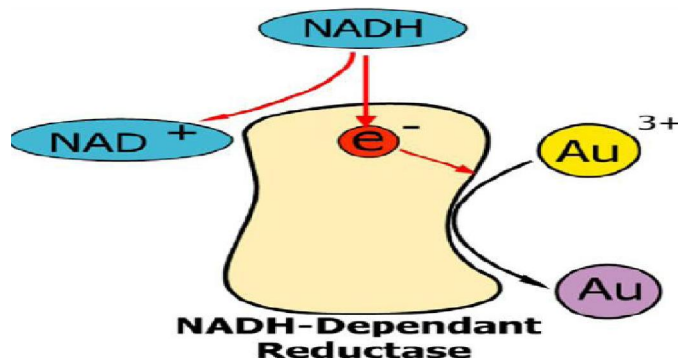


Figure 7 : Scheme illustrates possible mechanisms of gold ions bioreduction

lar enzyme located in the cytoplasm, was responsible for the formation of nanocrystals^[4].

S. algae cells were proposed to deposit platinum nanoparticles at room temperature and neutral pH. The resting cells of *S. algae* cells were able to reduce 1mM aqueous PtCl₆²⁻ ions into elemental platinum at 25 °C and pH 7 within 60 min in the presence of lactate as the electron donor^[59].

Production and structural characterization of crystalline silver nanoparticles from *Bacillus cereus* isolate. The free amine and carbonyl groups present in the bacterial protein could possibly perform the function for the formation and stabilization of silver nanoparticles^[11]. Stabilization of the AgNP by surface-bound proteins is a possibility. Mechanism leading to the reduction of metal ions.

Biomining of particulate Au in metallophillic bacterium *Cupriavidus metallidurans* CH34 is considered to be a result of Au-regulated gene expression leading to the energy-dependent reductive precipitation of toxic Au-complexes leading to the formation of Au (I)-C-compounds and nanoparticulate Au⁰^[39].

The enzyme involved in the synthesis of nanoparticles may be the nitrate reductase present in *B. licheniformis*. This enzyme is induced by nitrate ions and reduces silver ions to metallic silver^[52]. Various types of naturally synthesized nanoparticles by different strains of bacteria are summarized in TABLE 1.

Formation of metal nanoparticles by fungi

Both bacteria and fungi have shown ability to reduce metal ions to form metallic nanoparticles. How-

TABLE 1 : Summary of various types of naturally synthesized nanoparticles by different strains of bacteria

Bacterial Species	Nanoparticle	References
<i>Escherichia coli</i>	Platinum	[3]
<i>Aeromonas hydrophila</i>	ZnO	[17]
<i>Bacillus megaterium</i>	Silver	[41]
<i>Shewanella oneidensis</i>	Silver sulfide	[50]
<i>Bacillus amyloliquifaciens</i>	Cadmium sulfide	[48]
<i>Pseudomonas aeruginosa</i>	Silver	[23]
<i>Brevibacterium casei</i>	Silver and Gold	[18b]

ever, it would be advantageous if a fungus is used for the development of a process keeping in mind handling of the biomass and down stream processing of the nanoparticles^[43].

Even though gold/silver nanoparticles have been synthesized using prokaryotes such as bacteria, and eukaryotes such as fungi, the nanoparticles grow intracellularly. The use of specific enzymes secreted by organisms such as fungi in the extracellular synthesis of nanoparticles is exciting for the following reasons. The synthesis of nanoparticles in solution would be of importance in homogeneous catalysis and other applications such as non-linear optics^[5a].

The nanoparticles may be immobilized in different matrices or in thin film form for optoelectronic applications. this being impossible to achieve if the nanoparticles were bound to the biomass^[25a].

The use of biosource such as fungi can catalyze specific reactions leading to inorganic nanoparticles is a modern and rational biosynthesis strategy that can alternate to other physical and chemical methods. Extracellular secretion of the microorganisms offers the advantage of obtaining large quantities in a relatively pure state, free from other cellular proteins associated with the organism and can be easily processed by filtering of the cells and isolating the enzyme for nanoparticles synthesis from cell-free filtrate^[19a]. Various types of naturally synthesized nanoparticles by different types of fungi are summarized in TABLE 2.

Functionalized silver nanoparticles can be extracellularly biosynthesized by strains of *Cladosporium cladosporioides* fungus^[6]. Also, *Aspergillus fumigatus* has shown potential for extracellular synthesis of fairly monodispersed, silver nanoparticles in

TABLE 2 : Summary of various types of naturally synthesized nanoparticles by different types of fungi

Fungal species	Nanoparticle	References
<i>Ganoderma lucidum</i>	Silver	[19b]
<i>Aspergillus terreus</i>	Silver	[25b]
<i>actinomycete Streptomyces</i>	Gold	[5b]
<i>Penicillium brevicompactum</i>	Gold	[29]
<i>Paraconiothyrium variabile</i>	Gold	[10]
<i>Neurospora crassa</i>	Silver, Gold	[7]
<i>Aspergillus clavatus</i>	Silver	[53]

the range of 5–25 nm^[22].

Non-pathogenic fast growing fungus *Trichoderma viride*, which habited in dead organic materials, was used for extracellular biosynthesis of silver nanoparticles around 2–4 nm. in size^[30].

CONCLUSION

The synthesis of nanoparticles by bio-organisms may support us with green treasures of nanoparticles in safe and economic way.

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