Chapter 13
Nanobiotechnology Applications in Special Reference to Fungi

Safiye Elif Korcan and Muhsin Konuk

Abstract Nanobiotechnology is placed in the intersection point of nanobiology, biotechnology, nanotechnology, and biology. This technique approach provides an angle to scientists to imagine new systematic gates to study on. From the point of biological sciences, it is an inspiring area for the studies which has not been created. The fungi can synthesize nanoparticles both inside and outside of their cells. In extracellular synthesis, after growing and obtaining the biomass these cells are incubated in the presence of metal salt solutions. The synthesis of nanobioparticles can be observed easily by looking at the color changes in the cultures. After completing the synthesis, nanoparticles were then subjected to centrifuge in high speed and density gradient. Then they were collected by washing with water or organic solvents like EtOH/MeOH. The main focus of this review is to introduce the application of fungi in the synthesis of nanoparticles biologically.

13.1 Introduction

The word "nano" is used to indicate the dimension of less than 100 nm. A nanoparticle (NP) (nanopowder, nanocluster, or nanocrystal) is an ultramicroscopic particle. Nanoparticles (NPs) have different physical, chemical, electronic, electrical, mechanical, magnetic, thermal, dielectric, optical, and biological characters. Developments of this area present great potential of various sectors like energy, environment, agriculture, and healthcare. Hence, it has been building great expectations not only in the academia but also among the investors, governments, and industries (Jain et al. 2011).

S.E. Korcan
Uşak University, Vocational School of Health Services, Department of Medical Services and Techniques, Uşak, Turkey
e-mail: safiye.korcan@usak.edu.tr

M. Konuk (✉)
Üsküdar University, School of Engineering and Natural Sciences, Molecular Biology and Genetics Department, 34662 Istanbul, Turkey
e-mail: mkonuk@gmail.com

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Table 13.1 Mechanism of nanoparticle biosynthesis using different sources

Biological systems	Possible mechanism
Plant	Secondary metabolites (alkaloids, flavonoids, saponins, steroids, tannins, and other nutritional compounds) act as reducing and stabilizing agents
Algae	Polysaccharides have hydroxyl groups and other functionalities that can play important roles in both the reduction and the stabilization of nanoparticles
Fungi	Reducing enzyme intracellularly or extracellularly and the procedure of biomimetic mineralization
Yeast	Membrane bound (as well as cytosolic) oxidoreductases and quinones
Bacteria	The microbial cell reduces metal ions by the use of specific reducing enzymes like NADH-dependent reductase or nitrate-dependent reductase
Virus	Tobacco mosaic virus (TMV) was used as template for the synthesis of iron oxides by oxidative hydrolysis, co-crystallization of CdS and PbS, and the synthesis of SiO2 by sol-gel condensation. It happened with the help of external groups of glutamate and aspartate on the external surface of the virus. Self-assembled viral capsids of genetically engineered viruses were exploited as biological templates for the assembly of quantum dot nanowires

Moghaddam et al. (2015); Yen and Mashitah (2012)

There are diverse techniques to synthesize different kinds of NPs (Xiangqian et al. 2011). Physical and chemical ones are popular but the use of toxic chemicals greatly limits their biomedical applications. For this reason, improving of reliable, nontoxic, and environmentally friendly methods for synthesis of NPs is very important (Prasad 2014; Prasad et al. 2016, 2017). Research in biotechnology has revealed that there are reliable, eco-friendly processes for synthesis of novel nanomaterials. Biological synthesis of nanoparticles using various biological systems such as yeast, bacteria, fungi, algae, and plant extract has also been in our knowledge (Yen and Mashitah 2012; Prasad et al. 2016).

13.2 Nanoparticle Synthesis Using Microorganisms

In the last decade, the application of green nanotechnology has been investigated as an alternative way to chemical and physical techniques. Green synthesis of nanoparticles can be done by polysaccharide method, tollens method, irradiation method, biological methods, and polyoxometalates method (Sharma et al. 2009). As shown in Table 13.1, biological syntheses of NPs in different biological systems have been reported (Yen and Mashitah 2012). As it is well known, many biological systems accumulate inorganic material inside or outside of the cell to form NPs. Many microbial species can produce metal NPs (gold, silver, goldsilver alloy, selenium, tellurium, platinum, palladium, silica, titania, zirconia, etc.). This kind of syntheses of NPs brings together the nanotechnology and biotechnology.

13.2.1 Advantages of Biological Synthesis of Nanoparticles

(i) Routine methods for synthesing of the metal nanomaterials often need to use of organic solvents and/or high-energy input. In opposition, microbes have evolved to possess molecular machineries to detoxify heavy metals, mainly by operating metal-binding peptides (Park et al. 2016).
(ii) Biological methods for nanoparticle synthesis would help avoiding many of the detrimental features by enabling synthesis at mild pH, pressure and temperature, and at a substantially lower cost (Jain et al. 2011).
(iii) Biological process is also an environmentally friendly way, because, both production and remediation of NPs can be achieved at the same time.
(iv) Diverse NPs, including those that have never been chemically synthesized, can be synthesized biologically (Park et al. 2016).

13.2.2 Advances of Fungal Synthesis of Nanoparticles

The fungi such as *Fusarium oxysporum*, *Colletotrichum sp*. (Shankar et al. 2003), *Trichothecium sp*., *Trichoderma asperellum*, *T. viride*, (Ahmad et al. 2005; Fayaz et al. 2010), *Phanerochaete chrysosporium* (Fayaz et al. 2006), *F. solani* (Ingle et al. 2009), *F. semitectum* (Basavaraja et al. 2008), *A. fumigatus* (Bhainsa and D'Souza 2006), *Coriolus versicolor* (Bhainsa et al. 2009), *Aspergillus niger* (Gade et al. 2008), *Phoma glomerata* (Birla et al. 2009), *Penicillium brevicompactum* (Shaligram et al. 2009), *Cladosporium cladosporioides* (Balaji et al. 2009), *Penicillium fellutanum* (Kathiresan et al. 2009), and *Volvariella volvaceae* (Philip 2009) have been investigated for NPs synthesis. Potential fungal isolates used for the biosynthesis of nanoparticles were given in Table 13.2.

13.2.3 Fungi Are More Advantageous Compared to Other Microorganisms

(a) Mycelial mesh of fungi can flow pressure. Aggregation and other conditions in bioreactors/chambers might be also compared to plant and bacteria.
(b) These are critical to grow and easy to both handle and manufacture. The extracellular reductive protein secretions are high and can be easily managed.
(c) Since the nanoparticles precipitated outside the cell are devoid of unnecessary cellular components, they might be directly used in various applications (Narayanan and Sakthivel 2010).
(d) Since fungi have the advantage of producing very high secreted proteins, this feature might increase nanoparticle synthesis grade.

Table 13.2 Potential fungal isolates used for the biosynthesis of nanoparticles

Fungi	NPs	Shape and location	Min and max particle size (nm)	References
Fusarium oxysporum	Pt	Rectangular, triangular, hexagonal,square,spherical, and aggregates	70–180	Govender et al. (2009); Moghaddam et al. (2015)
	Cd	Spherical, extracellular	9–15	Kumar et al. (2007a, b); Moghaddam et al. (2015)
	Ag	Aggregates, spherical, extracellular	5–50	Ahmad et al. (2003); Kumar et al. (2007a, b); Moghaddam et al. (2015)
	Au	Triangular, spherical, extracellular, or intracellular	2–50	Mandal et al. (2006); Zhang et al. (2011); Moghaddam et al. (2015); Khandel and Kumar (2016)
	$PbCO_3$, $CdCO_3$	Spherical, extracellular	120–200	Sanyal et al. (2005); Li et al. (2011)
	$SrCO_3$	Needlelike, extracellular	10–50	Rautaray et al. (2004); Li et al. (2011)
	CdSe	Spherical, extracellular	9–15	Kumar et al. (2007a, b); Narayanan and Sakthivel (2010)
	CdS	Spherical, extracellular	5–20	Ahmad et al. (2002); Salahuddin and Azamal (2016)
	TiO_2	Spherical, extracellular	6–13	Bansal et al. (2005); Salahuddin and Azamal (2016)
	$BaTiO_3$	Spherical, extracellular	4–5	Bansal et al. (2006); Narayanan and Sakthivel (2010)

(continued)

Table 13.2 (continued)

Fungi	NPs	Shape and location	Min and max particle size (nm)	References
	ZrO_2	Spherical,	3–11	Bansal et al. (2004); Salahuddin and Azamal (2016)
	Si	Quasi-spherical	5–15	Bansal et al. (2005); Narayanan and Sakthivel (2010)
	Bi_2O_3	Quasi	5–8	Uddin et al. (2008); Narayanan and Sakthivel (2010)
	BT	Extracellular	4–5	Bansal et al. (2006); Khandel and Kumar (2016)
	Fe_3O_4	Irregular, quasi-spherical	20–50	Bharde et al. (2006); Khandel and Kumar (2016)
Fusarium oxysporum f. sp. *lycopersici*	Pt	Hexagonal, pentagonal, circular, squares, rectangles Extra- and intracellular	10–100	Riddin et al. (2006); Govender et al. (2009); Moghaddam et al. (2015); Narayanan and Sakthivel (2010)
Fusarium spp.	Zn	Alteration intracellular	100–200	Velmurugan et al. (2010); Moghaddam et al. (2015)
Fusarium solani	Ag	Spherical, extracellular	5–35	Maliszewska et al. (2009a, b); Khandel and Kumar (2016)
Fusarium culmorum	Ag, Au, Pb, Cu	Spherical, extracellular	5–10	Bharde et al. (2006); Khandel and Kumar (2016)
Aspergillus clavitus	Ag	Extracellular	550–650	Saravanan and Nanda (2010); Moghaddam et al. (2015)
	Au	Triangular, spherical and hexagonal, extracellular	24.4	Verma et al. (2011)

(continued)

Table 13.2 (continued)

Fungi	NPs	Shape and location	Min and max particle size (nm)	References
Aspergillus fumigatus	ZnO	Spherical and hexagonal, extracellular	1.2–6.8	Raliya (2013); Moghaddam et al. (2015)
	Ag, Ag-Au	Mostly spherical. Extracellular	5–25/15->120	Bhainsa and D'Souza (2006)
Aspergillus oryzae TFR9	$FeCl_3$	Spherical	10–24.6	Binupriya et al. (2010a, b); Raliya (2013); Moghaddam et al. (2015); Siddiqi and Azamal (2016)
Aspergillus oryzae	Ag, Zn, Au	Spherical, extracellular	2.78–5.76	Khandel and Kumar (2016)
Aspergillus oryzae var. viridis	Au	Various shapes Mycelial surface	10–60	Binupriya et al. (2010a, b); Siddiqi and Azamal (2016)
Aspergillus tubingensis	$Ca_3P_2O_8$	Spherical, extracellular	28.2	Tarafdar et al. (2012); Siddiqi and Azamal (2016)
Aspergillus niger	Au	Nanowalls, spiral plates, polydispersed or spherical,	12.8–20	Xie et al. (2007); Bhambure et al. (2009)
	Ag	Spherical, extracellular	3–30	Alani et al. (2012); Moghaddam et al. (2015)
Aspergillus flavus	Ag	Spherical, cell wall surface	8.92–17	Vigneshwaran et al. (2007a, b); Moghaddam et al. (2015)
	TiO_2	Extracellular	12–74	Vigneshwaran et al. (2007a, b); Rajakumar et al. (2012); Raliya et al. (2015); Moghaddam et al. (2015)
Aspergillus clavitus	Ag	Extracellular	100–200	Saravanan and Nanda (2010)
Aspergillus terreus	Ag, Au-Ag	Spherical, extracellular	1–20	Khandel and Kumar (2016)

(continued)

Table 13.2 (continued)

Fungi	NPs	Shape and location	Min and max particle size (nm)	References
A. sydowii	Au	Spherical, extracellular	8.7–15.6	Vala (2015); Siddiqi and Azamal (2016)
A. terreus	Ag	Spherical, extracellular	1–20	Li et al. (2012); Siddiqi and Azamal (2016)
Aspergillus versicolor mycelia	Hg	Alteration. Surface of mycelia	20.5 ± 1.82	Das et al. (2008); Moghaddam et al. (2015)
Alternaria alternata	Ag, Cd	Spherical, extracellular	20–60	Gajbhiye et al. (2009); Khandel and Kumar (2016)
Rhizopus oryzae	Au	Nanocrystalline or triangular, hexagonal, pentagonal, spheroidal, sea urchin-like, 2D nanowires, nanorods. Cell surface	Various 10	Gericke and Pinches (2006); Das et al. (2009); Maliszewska et al. (2009a, b); Das et al. (2010); Moghaddam et al. (2015)
Rhizopus stolonifer	Au	Irregularly (uniform)	1–5	Binupriya et al. (2010a, b); Sarkar et al. (2012); Moghaddam et al. (2015)
	Ag	Quasi-spherical	25–30	
Rhizopus nigricans	Ag	Spherical, extracellular	7–20	Mohammadian et al. (2007); Khandel and Kumar (2016)
Phanerochaete chysosporium	Ag	Spherical, pyramidal, extracellular	50–200	Sanghi and Verma (2009); Khandel and Kumar (2016)
	Au	Spherical, extracellular	10–100	Philip (2009); Moghaddam et al. (2015)
Phyllanthus amarus	Ag	Spherical, extracellular	30	

(continued)

Table 13.2 (continued)

Fungi	NPs	Shape and location	Min and max particle size (nm)	References
Pleurotus sajor-caju	Au, Ag	Spherical, extracellular	20–40	Husseiny et al. (2007); Khandel and Kumar (2016)
				Vigneshwaran and Kathe (2007)
Penicillium fellutanum	Ag	Mostly spherical, extracellular	5–25	Kathiresan et al. (2009); Khandel and Kumar (2016)
Penicillium strain J3	Ag	Mostly spherical	10–100	Maliszewska et al. (2009a, b); Moghaddam et al. (2015)
Penicillium brevicompactum WA2315 (139)	Ag	Spherical, extracellular	58.35 ± 17.88	Shaligram et al. (2009); Khandel and Kumar (2016)
Penicillium brevicompactum	Au	Spherical, triangular and hexagonal Extracellular	10–60	Selvakannan et al. (2004); Khandel and Kumar (2016)
Penicillium citrinum	Ag	Spherical. Extracellular	5–25	Kathiresan et al. (2009); Khandel and Kumar (2016)
P. fellutanum	Ag	Spherical	5–25	Kathiresan et al. (2009); Siddiqi and Azamal (2016)
P. nagiovense AJ12	Ag	Spherical cell-free filtrate	25 ± 2.8	Maliszewska et al. (2014); Siddiqi and Azamal (2016)
P. rugulosum	Au	Spherical, triangular, hexagonal	20–80	Mishra et al. (2012); Siddiqi and Azamal (2016)
Penicillium sp.	Au	Spherical cell filtrate	30–50	Du et al. (2011); Siddiqi and Azamal (2016)

(continued)

Table 13.2 (continued)

Fungi	NPs	Shape and location	Min and max particle size (nm)	References
Trichoderma viride	Ag	Spherical, rod-like. Extracellular	2–100	Mukherjee et al. (2008); Fayaz et al. (2009a, b); Fayaz et al. (2010a, b); Moghaddam et al. (2015)
Trichoderma asperellum	Ag	Nanocrystalline or spherical. Extracellular	13–18	Mukherjee et al. (2008); Moghaddam et al. (2015)
Trichoderma reesei	Ag	Extracellular	5–50	Vahabi et al. (2011)
Trichoderma Koningii	Au	Small spheres to polygons. Cell-free filtrate	10–40	Maliszewska et al. (2009a, b); Maliszewska (2013); Siddiqi and Azamal (2016)
Trichoderma harzianum	Cu, Ag	Spherical. Extracellular	20–35	Gajbhiye et al. (2009); Khandel and Kumar (2016)
Tricholoma crassum	Au	Spherical. Extracellular	8.62–9.12	Sawle et al. (2008); Khandel and Kumar (2016)
Pleurotus sajor-caju	Ag	Spherical extracellular	30.5	Vigneshwaran and Kathe (2007)
Volvariella volvaceae	Au-Ag	Triangular,spherical, hexagonal extracellular,	20–150	Philip (2009); Thakkar et al. (2010); Moghaddam et al. (2015)
Cladosporium cladosporioides	Ag	Mostly spherical or hexagonal. Extracellular	10–100	Balaji et al. (2009); Khandel and Kumar (2016)
Cylindrocladium floridanum	Au	Spherical. Extracellular	19.5	Zhang et al. (2012); Khandel and Kumar (2016)
Cochliobolus lunatus	Ag	Spherical. Extracellular	5–10	Khandel and Kumar (2016)

(continued)

Table 13.2 (continued)

Fungi	NPs	Shape and location	Min and max particle size (nm)	References
Cochlibolus lunatus	Cu, Al	Quasi- spherical. Extracellular	3–21	Salunkhe et al. (2011); Raheman et al. (2011)
Hypocrea lixii	Cu	Spherical. Extracellular	24.5	Deplanche et al. (2010); Khandel and Kumar (2016)
Phoma sorghina	Ag	Rod shaped. Extracellular	120–160×30–40	Raheman et al. (2011)
Pestalotia sp.	Ag	Spherical extracellular or intracellular	10–40	Raheman et al. (2011)
Coriolus versicolor	Ag	Extra- and intracellular. Spherical	25–491	Sanghi and Verma (2009); Moghaddam et al. (2015)
Verticillium sp.	Fe_3O_4	Extracellular. Cubo-octahedral, quasi-spherical	20–400	Bharde et al. (2006); Moghaddam et al. (2015)
	Au	Spherical. Cell wall, cytoplasmic membrane amd ıntracellular	20	Mukherjee et al. (2001); Ramanathan et al. (2013)
Verticillium luteoalbum	Ag	Spherical. Extracellular	12–22	Bawaskar et al. (2010); Fayaz et al. (2009a, b); Khandel and Kumar (2016)
	Au	Spherical. Extracellular	12–15	
Yarrowia lipolytica	Au	Hexagonal, triangular, extracellular	15	Agnihotri et al. (2009); Pimprikar et al. (2009)

(e) Fungal mycelia provide higher surface area than bacteria and this advantage could be used to support the interaction of metal ions and fungal agents. This is enhancing the conversion of ions to metallic nanoparticles.
(f) Fungi also have the advantage to ease the downstream processing when extracellular nanoparticles are produced.
(g) Scalability is another factor for consideration of commercial production of nanoparticles. This gives fungi the edge as the chassis of choice for long-term development as they might be easily used in large-scale reactors (Pantidos and Horsfall 2014).

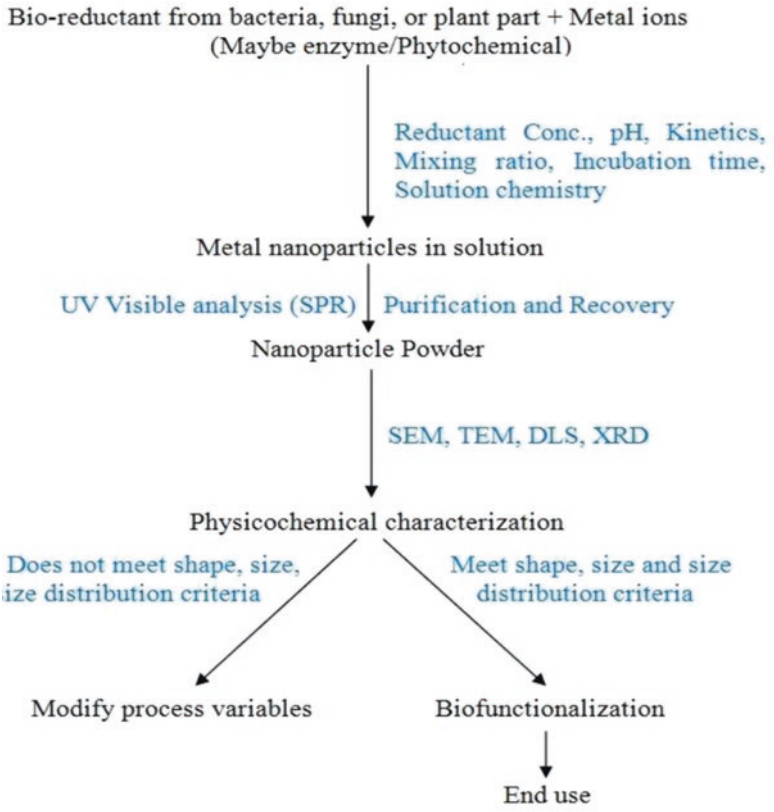

Fig. 13.1 Generalized flow chart for the biosynthesis of metallic nanoparticles (Rath et al. 2014; Punjabi et al. 2015)

13.3 Biosynthesis of Nanoparticles by Fungi

Researchers paid attention in recent years that the novel field of nano-biosynthesis of metal nanoparticles called "myconanotechnology." This new field is at the interference of nanotechnology and mycology combination which is interesting as a new applied science with a substantial potential due to the wide range of diversity of fungi. The fungal systems have already been used for the biosynthesis of metal nanoparticles of silver, gold, zirconium, silica, titanium, iron (magnetite), and platinum as well as ultrafine oxide nanoparticles, such as Sb_2O_3 and TiO_2. A generalized flow chart for the biosynthesis of metallic nanoparticles is shown in Fig. 13.1.

As happens in all cells, microbial cells also need metal ions primerly as cofactors. Metal/metal ions can interact with fungi in various ways and rely on the type of metal, organism, and environment. They accomplish toxic effects in some ways, like inhibiting the enzymes. Microorganisms have the ability to survive at high concentrations of toxic metals. The adaptation of fungi exposed to heavy metal ions has

been examined to increase the tolerance of fungi. Therefore, microbial cells have evolved the ability to manage proper metal-protein interactions (Tottey et al. 2005; Kang et al. 2008; Anahid et al. 2011; Park et al. 2016). Microorganisms have diverse mechanisms of developing nanoparticles. Silver nanoparticle synthesis was suggested as a defensive mechanism of cells for silver. Ahmad et al. (2003) reported that NADH-dependent enzymes are responsible for the biosynthesis of nanoparticles. The reduction mechanism seems to be initiated by electron transfer from the NADH by NADH-dependent reductase as electron carrier.

Two mechanisms have been suggested for heavy metal tolerance/detoxication in fungi:

1. Extracellular (chelation and cell wall binding) separation
2. Intracellular physical separation of metal by binding to ligands (peptides or others) to prevent them from metal sensitive cellular targets.

During the intracellular synthesis of gold nanoparticles (A), the gold metal ions firstly bind on the fungal cell surface, through electrostatic interaction force which is generated due to opposite charges present on the metal ion surface and fungal cell surface. After that, absorbed metal ions are reduced by enzymes of the fungal cell wall. This is the result of the positively charged groups of these enzymes and this leads to the aggregation and formation of metal nanoparticles. In case of extracellular synthesis of silver nanoparticles (B) due to the nitrate reductase presents in the cell of fungi. This enzyme reduces the silver metal ions into silver nanoparticles. This finally results to the formation of highly stable silver nanoparticles (Fig. 13.2) (Khandel and Kumar 2016).

Biogenic synthesis of metal nanoparticles engages bioreduction of metal salts to elemental metals. This might be stabilizing the organic molecules present in the microorganisms such as fungi and bacteria. The other way of producing metal nanoparticles is biosorption. In this way, metal ions in the aqueous medium are stuck to the organisms' cell wall surface (Siddiqi and Azamal 2016).

Extracellular mechanisms are mainly intimated in the avoidance of metal entry. In this mechanism, different organic molecules, which do not belong to the cell wall matrix, are excreted by the fungal cell to chelate metal ions. This binding is called biosorption. In general, surface of the cell surface is negatively charged due to the presence of several anionic structures, such as glucan and chitin. This feature gives microorganisms the ability to bind metal cations (Anahid et al. 2011). Chelating agents can be organic or inorganic compounds and capable to bind to metal ions to forming complex ringlike structure called "chelates." Chelating agents have "ligand"-binding atoms which form either two or one and one coordinate or two coordinate covalent linkages in the case of bidentate chelates. Mainly, S, N, and O atoms function as ligand atoms in the form of chemical groups like –SH, −S-S, $-NH_2$, =NH, −OH, $-OPO_3H$, or >C=O. Bidentate or multidentate ligands form ring structures that include the metal ion and the two ligand atoms attached to the metal (Andersen 1999).

Siderophores are small, high-affinity iron-chelating compounds secreted by microorganisms such as bacteria and fungi. It was reported that most fungi produce

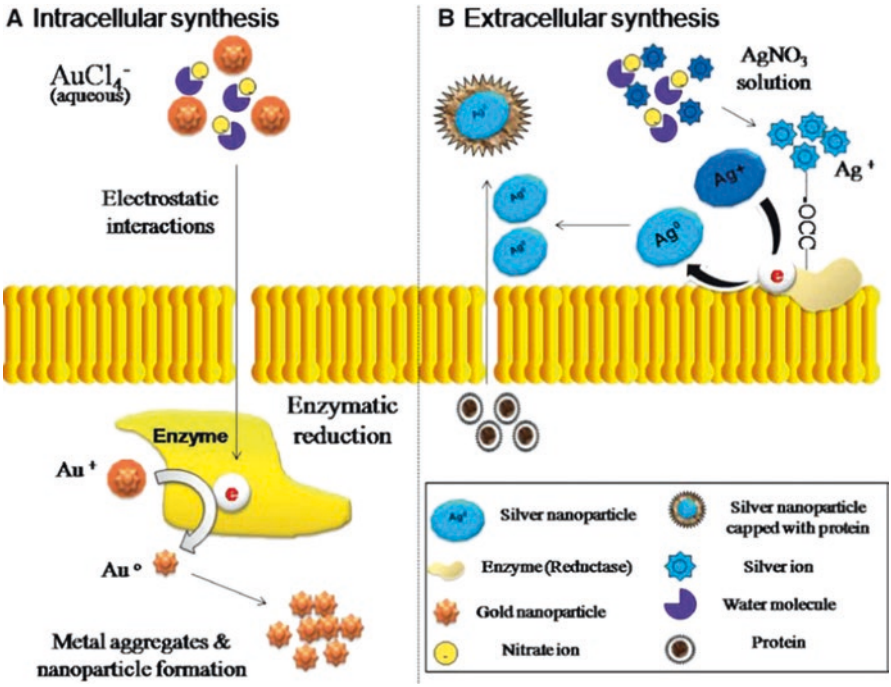

Fig. 13.2 Mechanism of intracellular and extracellular synthesis of gold (Au) and silver (Ag) nanoparticles through fungi (Khandel and Kumar 2016)

hydroxamate-type siderophores, but there is only little information regarding the production of catecholate-type compounds by fungi (Gadd 1999; Renshaw et al. 2002; Haselwandter and Winkelmann 2002). However, the output of catecholate-type chelating compounds has recently been depicted in wood-rotting fungi (Arantes and Milagres 2006). Whether these compounds are true or not is unknown, since siderophores are debatable due to their role in iron transport (Renshaw et al. 2002).

The presence of unspecific metal-chelating compounds such as organic acids was also examined in the fungal cultures as the low pH of the culture filtrates proposes the production of these acids. Oxalic, citric, and succinic acids are common metabolites produced by several mycorrhizal fungi. Their production is associated with the solubilization of insoluble metal-containing compounds (Fomina et al. 2005). It is known that depending on the concentration of these organic acids, they can react with CAS reagent in the same form as true siderophores and cause color changes in the mixtures.

The biosynthesis of metal nanoparticles by the fungi has also been reported. In the colorimetric examinations, the filtrate color changes from almost yellow to brown. This is a clear indication of the silver nanoparticles production in the reaction mixture (Juraifani and Ghazwani 2015). This result has also indicated that

organic acids can play an important role in the transport and metabolism of metals in some microorganisms (Carson et al. 1992; Machuca et al. 2007).

Chelating compounds was determined by the Schwyn and Neilands (1987) spectrophotometrically using the Chrome Azurol S (CAS) reagent containing Fe(III) Absorbance at 630 nm after 1 h of incubation at room temperature. Percentages of compounds were calculated by subtracting the sample absorbance from the reference; and values >10% were considered as positive. They also investigated and developed the measurement in solid medium using the CAS agar-plate assay. This also depended on the color during the incubation period.

Biosynthesis of metal nanoparticles involves in bioreduction of metal salts to elemental metal. This might stabilize the organic compounds already present in the microorganisms. Sneha et al. (2010) exhibited the gold or silver ions were first captured on the surface of the fungal cells via electrostatic interaction between the ions and negatively charged cell wall from the carboxylate groups in the enzymes. This condition clearly indicates that metal ions are first sticks on the surface or inside of the microbial cells then reduced to nanoparticles in the presence of the related enzymes (Benzerara et al. 2010; Li et al. 2011). The reduction process takes place on the surface by the enzymes found in the cell wall (Mukherjee et al. 2001). Microorganisms affect the NP formation in two distinctive ways. First way, they could modify the composition of the solution in order that the solution becomes more supersaturated than its previous phase. Second way, microbes could impact the mineral formation through the organic polymers production (Benzerara et al. 2010; Li et al. 2011).

Some phenolic compounds such as naphthoquinone and anthraquinones show excellent redox properties and can act as electron shuttle in silver reduction. Specific extracellular enzymes act on a specific metal (Medentsev and Alimenko 1998; Bell et al. 2003; Siddiqi and Azamal 2016). For instance, nitrate reductase is essential for ferric ion reduction. Nitrate reductase system might be responsible for the bioreduction and formation of silver nanoparticles (Kumar et al. 2003). Similarly, a number of studies with *Fusarium oxysporum* demonstrated that the reduction of silver ions happens in the presence of a nitrate-dependent reductase and a shuttle quinone for extracellular process (Durán et al. 2005). These findings suggested that metal ion reduction needs not only the enzyme but also an electron shuttle (Durán et al. 2005).

NADH and NADH-dependent nitrate reductases are important factors in the biosynthesis of metal NPs. This enzymes catalyze NAD(P)H reduction of nitrate to nitrite. Eukaryotic assimilatory nitrate reductase (NR) catalyzes the following reaction:

$$\mathrm{NO}^{-3} + \mathrm{NADH} \rightarrow \mathrm{NO}^{-2} + \mathrm{NAD}^{++}\mathrm{OH}^{-}$$
$$\Delta G = -34.2\,\mathrm{kcal/mol}\left(-143\,\mathrm{kJ/mol}\right); \Delta E = 0.74\,\mathrm{V}$$

Two forms of the enzyme, NAD(P)H-bispecific forms (EC 1.6.6.2) and NADPH-specific forms (EC 1.6.6.3), are found in fungi. Campbell (1999) suggested that NR could also contribute to iron reduction in vivo since it catalyzes NADH ferric citrate

reduction. *Fusarium oxysporum* MT 811 is able to reduce nitrates and nitrites to N_2. Fungal NR is similar to the bacterial enzyme that contains copper in their active site. The reduction of NO to N_2 is catalyzed by cytosolic and mitochondrial NORases (cytochrome P450). Its synthesis is specifically induced by nitrate and nitrite but repressed under aeration (Takaya et al. 1999).

Morozkina et al. (2005) reported that NRases from *F. oxysporum* mycelia grown aerobically and anaerobically differ in molecular weight, activity in several mineral sources of nitrogen, and optimum temperature. This shows that NRase probably exists in two different forms which function under both aerobic and anaerobic conditions. NRase of *F. oxysporum* grown is inhibited by ammonium ions under aerobic conditions. NRase from the anaerobically grown mycelium had low sensitivity to ammonium ions. *F. oxysporum* has also been shown to produce cadmium sulfide (CdS), lead sulfide (PbS), zinc sulfide (ZnS), and molybdenum sulfide (MoS) nanoparticles, when the appropriate salt is added to the growth medium (Ahmad et al. 2002).

When NR assay was carried out by the reaction of nitrite with 2,3-diaminonaphthalene, it could initiate NP formation by many fungi including *Penicillium* species. However, the exact mechanism of the formation of nanoparticles is yet to be elucidated. Some *Aspergillus flavus* proteins are responsible for synthesis of silver nanoparticles. It was reported that the synthesis procedure takes place in two steps. In the first one, reduction process of bulk silver ions into silver nanoparticles occurs, and in the next step, synthesized nanoparticles are capped. The protein-nanoparticle interactions could play very meaningful role such as providing stability to nanoparticles (Fig. 13.3) (Jain et al. 2011). However, this interaction between protein and nanoparticles is still not completely understood. Understanding the protein-nanoparticle interactions would lead us to form future "nano-factories."

Intracellular metal trafficking systems (IMTS) work to reduce the metal loading in the cytosol. In the IMTS, metal transport proteins might involve in metal tolerance. This could be either by expelling toxic metal ions from the cytosol out or letting the metals into vacuolar systems (Anahid et al. 2011). Some microorganisms could accumulate and detoxify heavy metals owing to various reductase enzymes. These enzymes are able to reduce metal salts to metal nanoparticles with a narrow size and less polydispersity. The size of the NPs is related to their nucleating activities. In accordance to the location where nanoparticles are formed, they can be classified into intracellular and extracellular NPs (Mann 2001). *Trichothecium* sp., *Verticillium luteoalbum*, and *Phoma* sp. have been explored for intracellular gold and silver nanoparticle synthesis. Vigneshwaran et al. (2007a, b) reported the accumulation of silver nanoparticles on the surface of its cell wall in *Aspergillus flavus*. The intracellular formation and accumulation of NPs are composed of transporting metal ions into the microbial cell in the presence of enzymes (Zhang et al. 2011). An intracellular synthesis of NPs needs additional steps such as ultrasound treatment or usage of suitable detergents to release the synthesized nanoparticles (Babu and Gunasekaran 2009; Das et al. 2014).

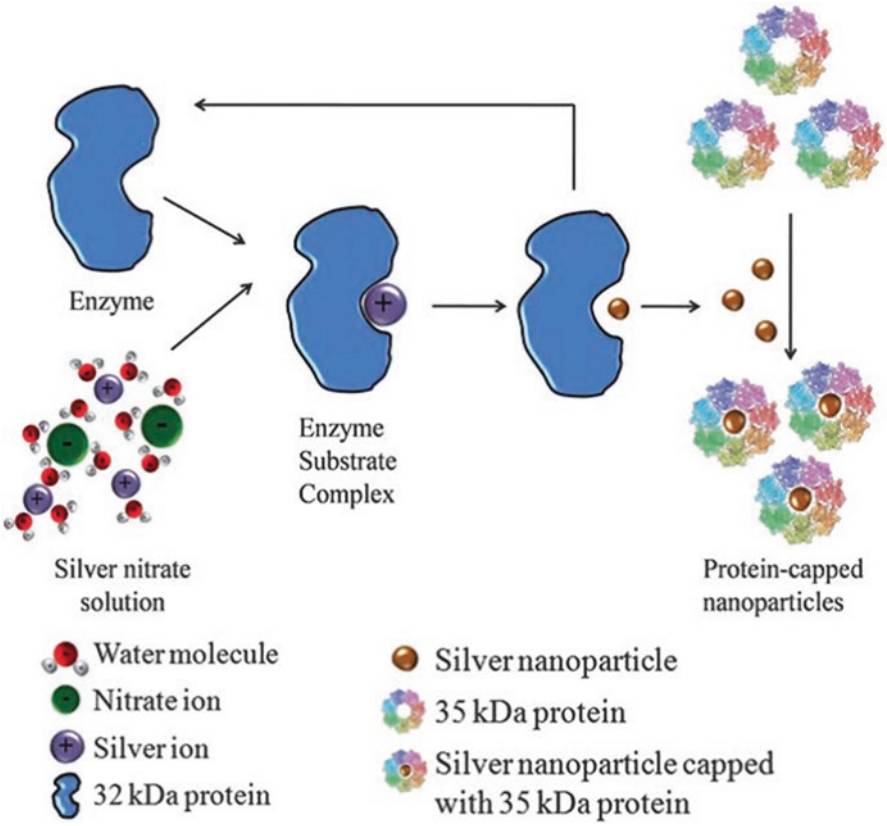

Fig. 13.3 Mechanism showing the role of extracellular proteins in the synthesis of silver nanoparticles (Jain et al. 2011)

Extracellular biosynthesis is cheap and it requires simpler processes. This favors large-scale production of NPs to examine its potential applications. Because of this possible advantage, many studies have been focussed on synthesis of metal nanoparticles outside of the cells (Durán et al. 2005; Das et al. 2014).

13.4 Factors Affecting Biosynthesis of Metal Nanoparticles

Major parameters (include temperature, pH, the presence of specific enzymes, type of biomass, exposure time to substrate, and the substrate concentration) affect the physical and chemical characters of nanoparticles.

pH is an important factor for shape of nanoparticles. Gericke and Pinches (2006) demonstrated the change in the shape of NPs with the variation of pH. Similarly, Davis and Ogden (1997) discovered that reduction of metal ions were highly sensitive to pH. Dhillon et al. (2012) reported that the movement of ions and activity of microbial biomass were controlled by variation in temperature. It could be also suggested that temperature plays an important role on the growth of organism as well as on metal uptake by the surrounding environment. In addition to temperature and pH, concentration of metal ions and type of enzyme also influence the synthesis of metal nanoparticles. The concentration of reactants decides the rate of reaction and also affects the size and shape of the synthesized particles. According to the study carried out by Gericke and Pinches (2006), synthesis of nanoparticles at different time intervals and their influence on synthesis process were also studied. It was found that incubation time increases the shape and size of nanoparticles. It has been also reported that with increase in the incubation time, the synthesis of nanoparticles also increases (Khandel and Kumar 2016).

13.5 Characterization of Metal Nanoparticles

After the biosynthesis of metal nanoparticles, characterizations of the nanoparticles are also an important step for the identification (size, shape, chemical composition, surface area, and dispersity). For the characterization of nanomaterials, different techniques are employed. These techniques are divided into two categories.

13.5.1 Determination of the Size, Shape, and Conformity of the Nanoparticles Synthesized

This includes mainly X-ray Diffraction (XRD), both Scanning electron microscopy (SEM), and Transmission electron microscopy (TEM), Dynamic light scattering (DLS), and Atomic force microscopy (AFM) analysis.

13.5.2 Functional Group Identification of Synthesized Nanoparticles

Involves in UV-visible spectroscopic analysis, energy dispersive spectroscopy (EDS), and Fourier transforms infrared spectroscopy (FTIR) analysis techniques (Khandel and Kumar 2016).

Table 13.3 Application of fungus-mediated synthesis of metal nanoparticles

NPs	Fungi	Application
Ag	*Alternaria alternata*	Enhancement in antifungal activity of fluconazole against *Phoma glomerata* and water quality monitoring
	Aspergillus clavatus	Antimicrobial activity
	A. niger	Antibacterial activity. Wound healing activity
	Aspergillus sp.	Antimicrobial activity
	Aspergillus tubingensis	44% inhibition of Syncitial virus infection
	Colletotrichum gloeosporioides	Antifungal activity
	Fusarium acuminatum	Antibacterial activity
	F. oxysporum	Textile fabrics
	F. solani	Textile fabrics
	Lecanicillium lecanii	Textile fabrics
	Macrophomina phaseolina	Antimicrobial properties against multidrug-resistant bacteria
	Neurospora oryzae	Only 1–10 nm nanoparticles attached to virus restraining virus from attaching to host cells. HIV
	Penicillium oxalicum	Catalytic activity
	Penicillium sp.	Antibacterial activity against MDR *E. coli* and *S. Aureus*
	Phytophthora infestans	Antimicrobial activity
	Pleurotus ostreatus	Antimicrobial activity
	Raffaelea sp.	Antifungal activity
	Trichoderma crassum	Antimicrobial activity
	T. viride	Vegetable and fruit preservation
Au	*Aspergillus japonicus AJP01*	Catalytic activity
	A. niger	Toxic to mosquito larvae
	Rhizopus oryzae	Water hygiene management
Cds	*Saccharomyces pombe*	Electric diode
	F. oxysporum	Live cell imaging and diagnostics
Carbon nanotubes sensors	*F. oxysporum*	Developed for glucose, ethanol, sulfides, and sequence-specific DNA analysis
Carbon nanotubes with enzymes	*Phoma glomerata*	Establish a fast electron transfer from the active site of the enzyme through the CNT to an electrode, in many cases enhancing the electrochemical activity of the biomolecules

Siddiqi and Husen (2016)

13.6 Applications of Nanobioparticles in Fungi

Owing to their great properties, nanoparticles have significant application in many fields such as cosmetics, catalysts, lubricants, fuel additives, paints, agrochemicals, food packaging, textile engineering, electronics, optics, environmental sensing, nanomedicine, drug and gene delivery agents, biodetection of pathogens, tumor destruction via heating (hyperthermia), magnetic resonance imaging, and phagokinetic studies (Prasad et al. 2014, 2016, 2017; Aziz et al. 2016; Siddiqi and Azamal 2016). Fungus-mediated synthesis of metal nanoparticles is getting much attention due to their extensive application in various sectors (Table 13.3).

13.7 Conclusion

The synthesis of functional nanoparticles by using microorganisms has taken a big concern in recent years. Microorganisms could alter the oxidation state of the metals. These microbial processes provide us new opportunities to synthesize metal nanomaterials biologically. On the contrary to chemical and physical methods, microbic synthesis of nanomaterials can be achieved under optimal environmental conditions in aquatic media. This approach became one of the sustainable development tools for the green bionanotechnological researches.

The mechanism of the biosynthesis has not been clear yet, but we can easily say that it is an enzyme-dependent occurrence for microorganisms. For this reason, we need to determine and characterize the specific enzymes and enlighten the pathways involved in these processes. It is strongly believed in that this area of science is very promising for the future of medicine and other health sciences.

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