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Nano-reduction of gold and silver ions: A perspective on the fate of microbial laccases as potential biocatalysts in the synthesis of metals (gold and silver) nano-particles

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ABSTRACT

Nanoparticles of metals have momentous place in the field of biological as well as pharmaceutical chemistry due to which in the present scenario of the research, this field is of auspicious interest. Synthesis of metal nanoparticles via microbial assistance is a burning field for their green synthesis. In this direction, microbial enzymes play significant role, out of which microbial laccases may also be a talented biocatalyst for the synthesis of metal nanoparticles considering its efficacy and interesting promising biological applications. A very little works are known on the role of microbial laccases in the synthesis of metal nanoparticles but after effective scrutiny of their reported works on the synthesis of gold and silver nanoparticles, its fate as potential biocatalyst in the synthesis of metals nanoparticles is being automatically established. Thus, this perspective commendably appraises the active applicability of microbial laccases in the synthesis of gold and silver nanoparticles by reducing their ions in suitable reaction environment.

Introduction

Now-a-days, synthesis of metal nanoparticles is a promising topic of research interest because of the great medicinal applicability and biotechnological applications of metal nanoparticles. Out of several ways for the synthesis of metal nanoparticles, biological technique is also one of the important and efficient ways. Further, the use of biological sources for the synthesis of metal nanoparticles are biocompatible, inexpensive, nontoxic and environment friendly in compare to the physical as well as chemical methods, thus, researches in the field of metal nanoparticles' synthesis *via* biological routes attained greater attention (Mukherjee et al., 2013; Patra et al., 2015; Ovais et al., 2018a; Mukherjee et al., 2015; Ovais et al., 2018b). In biological techniques, utilizations of microbial sources for the production of metal nanoparticles are of special interest due to the involvements of microbial enzymes in the reaction. A comprehensive review on the biosynthesis of metal nanoparticles was presented by Ovais et al., (2018a) and detailed mechanistic approach was given for it (Ovais et al., 2018a). In the production of metal nanoparticles, extracellular enzymes are known for acting as reducing agents (Subbaiya et al., 2017). Various mechanisms are utilized by microbes including changes in solubility, bio-sorption, metal complexation, extracellular precipitation, toxicity *via* oxidation–reduction, the absence of specific transporters, and efflux pumps (Patra et al., 2014; Mukherjee and Patra, 2017; Ovais et al., 2018a).

This perspective specifically deals with the involvement and efficacy of laccase enzymes in the synthesis of metal (gold and silver) nanoparticles. Laccases [EC 1.10.3.2] are multi-copper comprising oxidoreductases and known for their several biological roles like roles in organic synthesis, medicinal applications, carbohydrate chemistry, food industries, polymer chemistry, biosensor developments and many more (Chaurasia et al., 2016, 2015a, 2015b; Mogharabi and Faramarzi, 2014; Sousa et al., 2021; Bassanini et al., 2021; Mayolo-Deloisa et al., 2020; Chaurasia and Bharati, 2017; Chaurasia et al., 2013a, 2013b; Chaurasia et al., 2014; Sharma et al., 2016; Maurya et al., 2017; Kushwaha et al., 2017), out of which, role in the synthesis of metal nanoparticles is its hidden potential application that is needed to be explored. Since, a very little works are known on laccase catalyzed synthesis of metal (gold and silver) nanoparticles, thus, in best of author's knowledge, there are no any reviews articles on laccase catalyzed metal nanoparticles' synthesis, specifically, on gold and silver nanoparticles synthesis. Therefore;

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authors have discussed here the connections and potential of laccase enzymes for the metal (gold and silver) nanoparticles' synthesis. This perspective objectively establishes the fate and usefulness of laccase in the synthesis of gold and silver nanoparticles by reducing their ionic salts using proper reaction conditions.

Microbes assisted synthesis of gold and silver nanoparticles with potential involvements of their extracellular/intracellular enzymes

Involvements of microbes and associated enzymes in the synthesis of silver and gold nanoparticles have been extensively studied. Herein, in order to get an optimistic picture on the microbial assisted synthesis of such metal nanoparticles, some recent works have been discussed briefly. In the process of microbial assisted reduction of metal ions in their nanoparticles, microbial enzymes play significant roles. Microbes have ability to synthesize the metal nanoparticles *via* intracellular as well as extracellular techniques. In the intracellular method, the microbial cell is comprised of a remarkable ion transport system. Positively charged metal ions are attracted by negatively charged bacterial cell wall. Furthermore, enzymes present in the bacterial cell wall cause the reduction of metal ions into the respective metal nanoparticles while in extracellular approach, reductases secreted by microbial cells cause the bio-reduction of metal ions in to their respective metal nanoparticles (Hulkoti and Taranath, 2014). Different microbial sources have been given in **Table 1** showing roles in the synthesis of gold and silver nanoparticle. This table is based on the information given in a review article of Ovais et al., (2018a) along with new available additional recent examples showing the great role of microbial sources and/or their extracellular and intracellular enzymes in the synthesis of gold and silver nanoparticles.

Gold nanoparticles' synthesis (Arib et al., 2021; Kuan et al., 2018, 2014; Habibi et al., 2016) can be done by involving the chloroauric acid chemical reduction ($HAuCl_4$) and using $NaBH_4$ (sodium borohydride) and/or sodium citrate as the reducing agents (De Souza et al., 2019; Yeh et al., 2012; Grzelczak et al., 2008). Proteins (bio-macromolecules) are the ideal molecules for highly biocompatible gold nanoparticles synthesis that have been already utilized in the synthesis of nanoparticles (Chakraborty and Parak, 2019; Chakraborty and Feliu, 2018; Leng et al., 2016; Yoshimura, 2006). In this direction, in order to produce gold nanoparticles, Arib et al., (2021) first time reported the one step synthesis in which Manganese Superoxide Dismutase (MnSOD) protein plays a main role in the gold salts reduction *via* the use of a Good's buffer (HEPES). They showed that there are three main steps in the enzyme mediated formation of gold nanoparticles from $AuCl_4^-$. First step, involves the enzymes complexation (MnSOD, CAT) (CAT for Catalase) with $AuCl_4^-$ to generate gold clusters while second step includes the enzymes' stalking onto gold clusters and initial reduction of enzyme-metal (Au III) complex from HEPES solution to form Au II and ultimately, enzyme stabilized gold nanoparticles formation occurs from the reduction of Au II ions (Arib et al., 2021).

Koul et al., (2021) comprehensively discussed the microbial mediated nanoparticles biosynthesis regarding the applications in the field of medicine and diagnostics, bioremediation, agriculture, and future prospects along with information on various strategies for the synthesis of microbe assisted nanoparticles. *Escherichia coli, Lactobacillus* sp., *Bacillus cereus, Acinetobacter* sp., *Pseudomonas* sp., *Corynebacterium* sp., and *Klebsiella pneumonia* are the examples of the most explored bacterial species for the silver nanoparticles synthesis (Marooufpour et al., 2019; NVKV Prasad et al., 2011; Iravani 2014). Use of supernatants from cultures/cell-filtrate of *E. coli, Klebsiella pneumonia,* and *Enterobacter cloacae* for the quick production of silver nanoparticles by the reduction of aqueous silver ions was reported by Shahverdi et al., (2007). Extracellular synthesis of spherical silver nanoparticles using *Bacillus cereus* was investigated by Prakash et al., (2011). Enzymatic-reduction-mediated intracellular biosynthesis of quasihexagonal shaped and 5–50-nm-sized gold nanoparticles was demonstrated by Correa-Llantén et al., (2013) using the bacterium *Geobacillus* sp. strain ID17. Biosynthesis of 20–25-nm-sized, well-dispersed gold nanoparticles has been reported by Srinath et al., (2018) using the bacterium *Bacillus subtilis*. Also, there are other many recent examples of microbes assisted synthesis of silver and gold nanoparticles (Clarance et al., 2020; Munawer et al., 2020; Ramos et al., 2020; El Domany et al., 2018; Neethu et al., 2018; Elahian et al., 2017; Bhargava et al., 2016; Rajput et al., 2016; Kitching et al., 2016; Zhang et al., 2016; Eugenio et al., 2016) that have been well covered by Koul et al., (2021).

Lee et al., (2020) also reviewed the recent developments in the field of gold nanoparticles facile biosynthesis and applications in biomedical field. Green materials sources and other parameters determining the gold nanoparticles functionalities have also been discussed in their review. Menon et al., (2017) interestingly, described about the biogenic synthesis of gold nanoparticles. In their review, they explained the role of fungi, algae, bacteria, yeasts, and actinomycetes in such metal nanoparticles synthesis. Different shaped gold nanoparticles formed by different microorganisms perform various functions in diagnosis and therapy or cancer treatment, medicine, as anti-angiogenesis, antimalarial agents, anti -arthritic, and so on **(Fig. 1)** (Menon et al., 2017).

In a review article of Ovais et al., (2018a), nice discussions on the microbial enzyme based synthesis of metal nanoparticles have been performed considering the various important points. They included the points based on the biosynthesis of metal nanoparticles by microorganisms, bacteria, and cyanobacteria, myco-synthesis, algae as biosynthesis factories, mechanisms, involvements of extracellular and intracellular enzymes in metal nanoparticle synthesis, and others. In the production of metal nanoparticles, extracellular microbial enzymes are known to act as reducing agents (Subbaiya et al., 2017). **Fig. 2** nicely demonstrates the role of microbial enzymes (NADH and NADH-dependent) in gold and silver metal nanoparticles' synthesis (Ovais et al., 2018a). Bacterial and fungal cells along with the sugars molecules play an important role in the intracellular mechanism of metal bio-reduction. Chiefly, the interactions of intracellular enzymes and positively charged groups are used in metallic ions' gripping from medium and the subsequent reduction inside the cell (Thakkar et al., 2010; Dauthal and Mukhopadhyay, 2016).

There are many other noteworthy works covering the microbial assisted synthesis and microbial based other studies on gold and silver nanoparticles that can be studied for more details and further enhancement of information (Lengke et al., 2007; Patel et al., 2015; Satapathy and Shukla 2017; Sonker et al., 2017; Bakir et al., 2018; Zhang et al., 2011; AbdelRahim et al., 2017; Maceda et al., 2018; Vijayaraghavan et al., 2011; Camas et al., 2018).

Microbial laccase in the synthesis of metals (Gold and silver) nanoparticles

Different microbial systems have been applied for the study of the synthesis of various metal nanoparticles (Ovais et al., 2018a; Vetchinkina et al., 2018) but a very little works are known on the potential involvement of laccase in the synthesis of metal nanoparticles. On the basis of the reported works on the laccase assisted synthesis of gold and silver nanoparticles, we can establish the fix position of laccase in this field. A general schematic representation about the possible methodology involved in synthesis of metal (gold and silver) nanoparticles from their respective ionic salts have been given in Fig. 3. This figure shows that in the presence of effective reductive biocatalysts (i.e. laccase in this case) and suitable conditions like substrate concentration, pH and temperature, metal nanoparticles can be easily synthesized. The most of the reports on laccase catalyzed metal nanoparticle synthesis are based on the synthesis of gold and silver nanoparticles, so, suitable methodologies and mechanistic way for the synthesis of gold and silver nanoparticles are interestingly discussed in this perspective. Microbial laccases involved in the synthesis of gold and silver nanoparticles are

Table 1
List of some important microbial sources (sources of extracellular and intracellular enzymes) used in the synthesis of metal nanoparticles.

S.No.	Microbial Source	Metal	Shape	Size (nm)	Refs.
1	Coprinus comatus	Gold	-	<100	Naeem et al., (2021)
2	Fusarium solani ATLOY – 8	Silver	Needle and flower like structures with spindle shape	40–45	Clarance et al., (2020)
3	Cladosporium sp.	Gold	Spherical	5–10	Munawer et al., (2020)
4	*Penicillium polonicum* ARA 10	Silver	–	10–15	Neethu et al., (2018)
5	*Bacillus subtilis*	Gold	-	20-25	(Srinath et al., 2018)
6	*Pleurotus ostreatus*	Gold	Uneven in a spherical shape	10–30	El Domany et al., (2018)
7	*Rhodotorula glutinis*	Silver	Spherical	15.45	Cunha et al., (2018)
8	*Candida glabrata*	Silver	Spherical	2–15	Jalal et al., (2018)
9	*Phenerochaete chrysosporium*	Silver	Spherical-Oval	34–90	Saravanan et al., (2018)
10	*Aspergillus terreus*	Silver	Spherical	16–57	Singh and Vidyasagar (2018)
11	*Trichoderma harzianum*	Gold	Spherical	32–44	Tripathi et al., (2018)
12	*Trametes trogii*	Silver	Spherical- Ellipsoidal	5–65	Kobashigawa et al., (2019)
13	*Pichia* pastoris	Silver	Spherical	70–180	Elahian et al., (2017)
14	*Rhizopus oryzae*	Gold	Flower like	43 ± 19 nm	Kitching et al., (2016)
15	Cladosporium oxysporum AJP03	Gold	Quasi-spherical	72.32 ± 21.80	Bhargava et al., (2016)
16	*Fusarium oxysporum*	Silver	–	10–20	Rajput et al., (2016)
17	Magnusiomyces ingens LH-F1	Gold	Mixture of sphere, plates (triangle, hexagon, pentagon), and irregularshaped nanoparticles	80.1 ± 9.8 nm	Zhang et al., (2016)
18	Yeast strains	Ag/AgCl	crystalline structure	2–10	Eugenio et al., (2016)
19	*Actinobacter*	Silver	Spherical	13.2	Wypij et al., (2016)
20	*Acinetobacter*	Gold	Spherical-triangular-polyhedral	19	Wadhwani et al., (2016)
21	*Klebsiella pneumonia*	Gold	Spherical	10–15	Prema et al., (2016)
22	*Ureibacillus thermosphaericus*	Gold	–	50–70	Juibari et al., (2011)
23	*Shewanella Oneidensis*	Gold	Round	12	Suresh et al., (2011)
24	*Neurospora crassa*	Gold-Silver, Gold	Round	20–50	Castro-Longoria et al., (2011)
25	*Brevibacterium casei*	Silver and Gold	–	10–50	Kalishwaralal et al., (2010)
26	*Corynebacterium glutamicum*	Silver	Irregular	5–50	Sneha et al., (2010)
27	*Bacillus cereus*	Silver	Round	4–5	Babu and Gunasekaran (2009)
28	*Yarrowia lipolytica*	Gold	Triangles	15	Agnihotri et al., (2009)
29	*Trichoderma viride*	Silver	–	2–4	Fayaz et al., (2009)
30	*Bacillus licheniformis*	Silver	–	50	Kalimuthu et al., (2008)
31	*E. coli*	Gold	Hexagonal, Triangle	20–30	Du et al., (2007)
32	*Rhodopseudomonas capsulate*	Gold	Round	10–20	He et al., (2007)
33	*Pseudomonas aeruginosa*	Gold	–	15–30	Husseiny et al., (2007)
34	*Aspergillus flavus*	Silver	Round	8.92	Vigneshwaran et al., (2007)
35	*Sargassum wightii*	Gold	Planar	8–12	Singaravelu et al., (2007)
36	*Plectonema boryanum*	Gold	Cubic	<10–25	Lengke et al., (2006)
37	*Aspergillus fumigatus*	Silver	Round	5–25	Bhainsa and D'souza (2006)
38	*Phaenerochaete chrysosporium*	Silver	Pyramidal	50–200	Vigneshwaran et al., (2006)
39	*Fusarium oxysporum*	Alloy of gold-silver	Round	8–14	Senapati et al., (2005)
40	*Verticillium* sp.	Silver	Round	25–32	Senapati et al., (2004)
41	*Rhodococcus* sp.	Gold	Round	8–12	Ahmad et al., (2003)

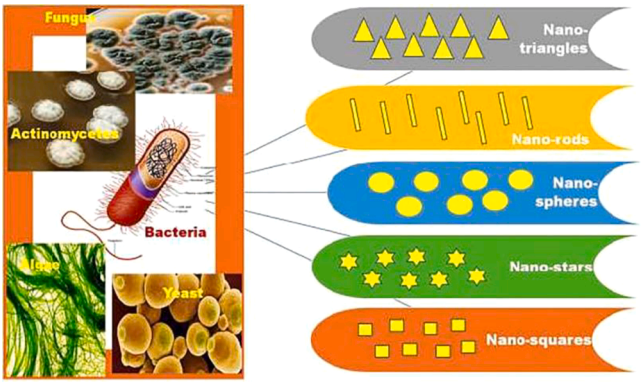

Fig. 1. Different shaped gold nanoparticles formed from different microbial sources (Menon et al., 2017).

shown in Table 2 along with the main findings and characterization techniques involved.

Laccase assisted synthesis of gold nanoparticles

Ovais et al., (2018a) provided a mechanistic approach on the biosynthesis of metal nanoparticles through microbial enzymes. For biological applications, microbes act as potential bio-factories for the reduction of gold, silver, cadmium, gold-silver alloy, selenium, silica, magnetite, titania, platinum, palladium, and other metals to their subsequent nanoparticles for biological applications (Narayanan and Sakthivel 2010). Using many bio-reduction processes, these metal nanoparticles are synthesized by microbes either extracellularly or intracellularly. In their review, they have discussed about the role of various microorganisms in the synthesis of different metal nanoparticles. In a study, AuNPs (10–100 nm in particle size) were formed after incubation of Phanerochaete chrysosporium in an ionic Au^{3+} solution. As the extracellular reducing agent, laccase enzyme was used while for the intracellular reduction of Au^{3+} ions, ligninase enzyme was found to be responsible (Sanghi et al., 2011).

A quick and ecofriendly method for the bio-synthesis of well dispersed gold nanoparticles was developed by Li et al., (2017) using laccase from *Trametes versicolor* as reducing as well as stabilizing reagent. For the purpose of gold nanoparticles synthesis, they purified the laccase, methodology of which is briefly described here. They dissolved laccase (10.0 mg) in 1.0 mL sodium acetate buffer (10.0 mmol L^{-1}, pH 5.5) and centrifuged it. DEAE-SephadexA-50 was used as anion-exchange column (previously equilibrated with buffer) at 4 °C and supernatant was applied to it. Elution of laccase was done with 60.0 mmol L^{-1} ammonium sulfate and de-salted by sodium acetate buffer (20.0 mmol L^{-1}, pH 5.5). They added the solution of purified laccase (180.0 μL, 0.575 mg mL^{-1}) to a solution containing 164.6 μL of 24.3 mmol L^{-1} $HAuCl_4$ and 50.0 μL of 1.0 mol L^{-1} NaOH, and adjusted the volume to 1.0 mL with ultrapure water. Under the ambient condition with mild stirring, they incubated the mixture for 60 min. Lastly, in order to remove unbound laccase enzyme, they purified the synthesized gold nanoparticles *via* double centrifugation (14,000 rpm for 45 min at 4 °C). They also studied the parameters affecting the formation of gold nanoparticles by reducing $HAuCl_4$ with laccase through UV–Vis spectroscopy. Alkaline condition was the favorable condition for the synthesis and formation of gold nanoparticles. With the rising sodium hydroxide (NaOH), intensities of the surface plasmon resonance band continuously increased and peaked at 50.0 mmol L^{-1}. However, upon further increase in NaOH concentration, there was not change in the intensities of the band and thus, they selected 50.0 mmol L^{-1} NaOH for subsequent synthesis. Further, there was increase in the yield of gold nanoparticles with rise of $AuCl_4^-$ concentration from 0 to 4.0 mmol L^{-1}, and up to 4.0 mmol L^{-1} and thus, 4.0 mmol L^{-1} concentration was accordingly used for the subsequent synthesis. They selected the concentration of laccase (103.5 μg mL^{-1}) after the examination of the

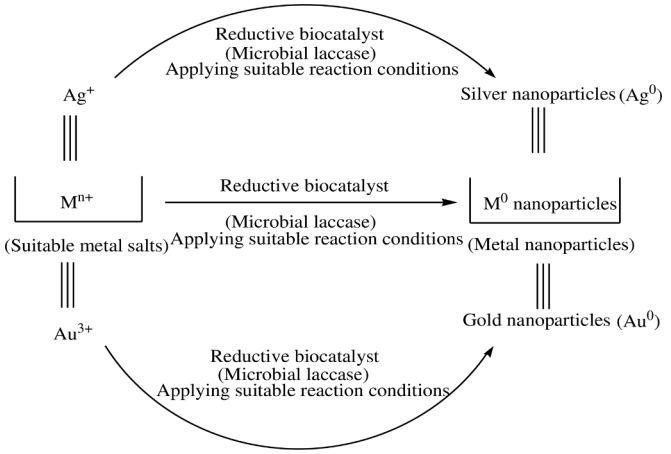

Fig. 3. A general schematic representation of the possible route for the synthesis of metal nanoparticles (gold and silver nanoparticles) with the help of suitable reductive biocatalysts.

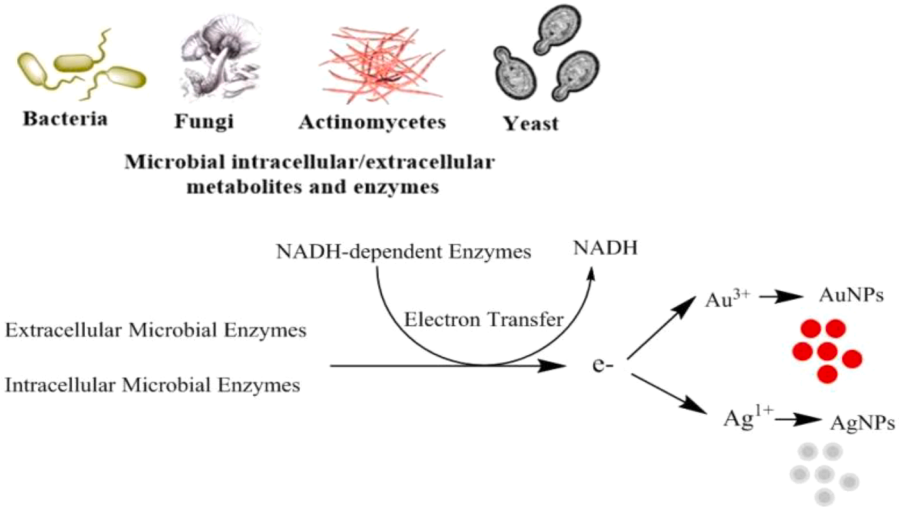

Fig. 2. Involvement of microbial enzymes in the gold and silver metal nanoparticles' synthesis (Ovais et al., 2018a).

Table 2
Lists of microbes used as sources of laccase enzymes for the synthesis of gold and silver nanoparticles as per available literature along with other information.

S.No.	Microbes (Source of laccase enzyme)	Type of laccase used (Purified/ semi-purified/ crude)	Synthesized metal nanoparticles	Materials used for the synthesis of metal nanoparticles	Shape/ Dispersion	Size (nm)	Techniques used for characterization	Refs.
1	*Trametes versicolor*	Purified laccase	Gold	Purified laccase (0.575 mg mL^{-1})+ $HAuCl_4$(24.3 mmol L^{-1})+ NaOH (1.0 mol L^{-1})	Spherical/ well dispersed	10.10-13.54	UV–Vis absorption spectra, XRD spectrum, TEM image, HRTEM image, SAED pattern, Particle size distribution	Li et al., (2017)
2	*Pleurotus ostreatus*	Partially purified laccase	Gold	Laccase (417 IU/mg)+ $HAuCl_4$ (10 mg/1 ml)	Highly mono dispersed	22–39	UV–Vis spectroscopy, DLS, TEM	El-Batal et al., (2015)
3	*Paraconiothyrium variabile*	Purified laccase	Gold	Laccase (73 U)+$HAuCl_4$ (0.6 mM)	Well dispersed	71–266	UV–Vis spectroscopy, SEM, TEM, Energy Dispersive X-ray (EDX)	Faramarzi and Forootanfar (2011)
4	*Lentinus edodes*	Crude laccase	Silver	$AgNO_3$ solution (30 ml, 1 mM)+ Crude laccase (12 ml)	Walnut shape	50–100	UV–Vis spectroscopy, SEM	Lateef and Adeeyo (2015)
5	*Trametes versicolor*	Semi-purified laccase	Ag@AgCl	Semi-purified laccase (aqueous solution of 200 UL^{-1})+$AgNO_3$ (1 mmol L^{-1})	Spherical shape	<100	UV–Vis spectroscopy, X-ray diffraction studies, particle size analysis, TEM, FTIR and SEM	Durán et al., (2014)

concentration of laccase from 2.9 to 115.0 μg mL^{-1}. Result suggests that gold nanoparticles could be easily synthesized at room temperature. Also, this developed method is promising for the gold nanoparticles' rapid synthesis. Prepared gold nanoparticles showed an uniform spherical shape, excellent storage stability and narrow size distribution and act as an effective catalyst in the borohydride reduction of 4-nitrophenol (Li et al., 2017). Fig. 4 (Li et al., (2017)) provides a quick look information on the characterization of synthesized gold nanoparticles *via* different techniques viz. UV–Vis absorption spectra (UV–Vis-Ultra Violet-Visible), XRD spectrum (XRD-X-Ray diffraction), TEM image (TEM-Transmission Electron Microscopy), HRTEM image (HRTEM-High Resolution Transmission Electron Microscopy), SAED pattern (SAED-Selected Area Electron Diffraction), and Particle Size Distribution. A single but strong SPR (surface plasmon resonance) band was found at 518 nm for the synthesized gold nanoparticles in UV–Vis spectroscopy (Fig. 4A). Four prominent Bragg reflections at 2θ values of 38.1, 44.3, 64.5, and 77.6°, which corresponded to (111), (200), (220), and (311) lattice planes of the face-centered cubic (fcc) structure of gold was found in XRD pattern indicating the formation of crystalline gold in the specimen (Fig. 4B). The TEM (Fig. 4C) and HRTEM (Fig. 4D) images of the synthesized gold nanoparticles showed uniform composites with spherical morphology and good dispersion. Inter-fringe spacing was 0.23 nm close to the inter-plane distance of the (111) plane in the fcc gold as clear from HRTEM image. Nano-crystalline nature and fcc type's structure were further confirmed by SAED pattern (Fig. 4E) of gold nanoparticles, which was in accordance with the XRD result. Zetasizer (Fig. 4F) was used for analyzing the size of nanoparticles that was in the range of 10.10 to 13.54 nm with an average ~12.24 nm (Li et al., 2017).

Using solid state fermentation, El-Batal et al., (2015) optimized the fungal laccase production from local isolate of *Pleurotus ostreatus* and studied the various aspects along with the use of laccase in the synthesis of gold nanoparticles. Partial purification and characterization were done by them for the synthesis of gold nanoparticles. For attaining 80% saturation, addition of ammonium sulfate was done in the cell free filtrate and then, they kept the flask at 4 °C for 48 h and centrifuged it (2415 g for 15 min at 4 °C). They discarded the supernatant and dissolved the pellet in a citrate phosphate buffer (50 ml, 1 mM, pH 5). For removing the low molecular weight substances and other ions that may interfere with the activity of enzyme, dialysis was performed to desalt the precipitate as per report (Janani et al., 2011). They quantified the protein concentration using Bradford assay with bovine serum albumin (standard) (Bradford 1976). They prepared gold nanoparticles as previously described (El-Batal et al., 2012), briefly, to 3 ml of laccase enzyme, containing 417 IU/mg, 0.1 ml of tetrachloroauric acid with concentration of (10 mg/1 ml) was added, (49% purity). Using magnetic stirrer, they stirred the reaction mixture and in 90 min, the change in color from yellow color of the solution to pink and then, violet indicated the formation of gold nanoparticles as observed visually as well as using UV-Visible spectrophotometer. They confirmed the formation of gold nanoparticles by the violet color formation after 90 min at room temperature giving significant peak at 550 nm. Highly mono dispersed gold nanoparticles with size range of 22–39 nm was shown by the size distribution of the formed gold nanoparticles using DLS (Dynamic Light Scattering) and TEM imaging of gold nanoparticles. They also studied the effects of temperature, gamma radiation and different volumes of $HAuCl_4$ on gold nanoparticles synthesis. When laccase was incubated in $HAuCl_4$ presence at different temperature, there was increase in the absorbance upon increase in temperature showed the greater concentration of formed gold nanoparticles. Further, during the study on the effect of gamma radiation on gold nanoparticles production, production of GNPs was found to be increased upon enhancing the dose of radiation and it was noticed that production of gold nanoparticles was maximum at 5 kGy. They found the highest concentration of gold nanoparticles at the best volume (0.3 mL) of $HAuCl_4$ (El-Batal et al., 2015).

Faramarzi and Forootanfar (2011) purified the laccase from ascomycete, *Paraconiothyrium variabile* and used it for the study of the synthesis of gold nanoparticles (AuNPs) along with the characterization of the properties of produced nanoparticles of gold. They purified the laccase from *P. variabile* by using as per previous report (Forootanfar et al., 2011).They purified it at four steps of ammonium sulfate precipitation, anion exchange chromatography on Q-Sepharose XL column and gel filtration chromatography by Sephadex G-100 column after ammonium sulfate precipitation of active fraction from anion exchange step and then, this purified laccase was used for the gold nanoparticle's biosynthesis. A peak at 530 nm related to surface plasmon absorbance of gold nanopartciles was shown by UV–Vis spectrum of produced AuNPs. This represents the formation of AuNPs after 20 min incubation of $HAuCl_4$ (0.6 mM) in the presence of 73 U laccase at 70 °C. They found the well dispersed nanoparticles based on their TEM image (range 71–266 nm) and further, structure of gold nano-crystals was confirmed by the pattern of energy dispersive X-ray of AuNPs. Au^{3+} undergoes reduction to Au° by incubation of the pure laccase in the presence of chloroaurate ions at different temperatures. Laccase from P. variabile acts as reductive agent for the synthesis of AuNPs. Larger gold particles were formed due to the aggregation of nanoparticles above the critical concentration of $HAuCl_4$. Decrease in the time for the formation of nanoparticles was found from 5 h to 20 min by increase in the incubation temperature from 30 °C to 70 °C and large nanoparticles production was attained within few minutes at 80 °C. They also observed that within the range of 30–60 °C, the particle size and the distribution of the obtained

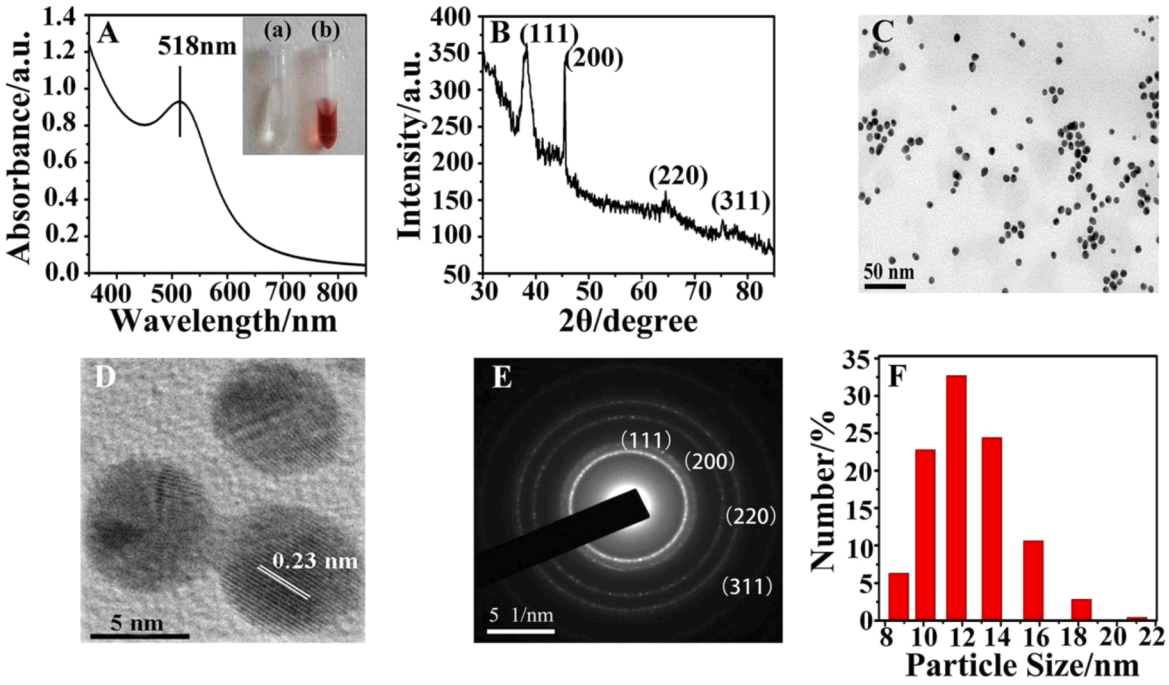

Fig. 4. Different ways of characterization of gold nanoparticles done by Li et al., (2017) (A) UV–Vis absorption spectra of laccase-synthesized gold nanoparticles. Inset shows (a) the control sample (the solution containing NaOH 50.0 mmol L^{-1}, $AuCl_4^-$ (4.0 mmol L^{-1}), and laccase (103.5 μg mL^{-1}) was incubated at ambient temperature for 0.0 min) and (b) gold nanoparticles (Incubation of the same solution was done at ambient temperature for 60.0 min); (B) XRD spectrum of gold nanoparticles; (C) TEM image of gold nanoparticles; scale bar: 50 nm; (D) HRTEM image of gold nanoparticles displaying lattice separation; scale bar: 5 nm; (E) SAED pattern of gold nanoparticles; scale bar: 5 nm^{-1} and (F) particle size distribution of gold nanoparticles.

nanoparticles were inversely reliant on the temperature. Average particle size was increased (124 nm) at 70 °C and in comparison with performing the process at 60 °C, there was narrowed particle size distribution. Overall, 70 °C was found as the optimum temperature (Faramarzi and Forootanfar, 2011).

Purified laccase from *T. versicolor* used by Li et al., (2017), partially purified laccase from *P. ostreatus* used by El-Batal et al., (2015) and purified laccase from *P. variabile* used by Faramarzi and Forootanfar (2011) for the synthesis of gold nanoparticles revealed the efficacy of this enzyme as reductive biocatalyst. Purified, semi-purified or crude laccases obtained from the suitable sources present effective capability in the synthesis of gold nanoparticles which are being proved from various characterization techniques like UV–Vis spectroscopy, XRD, FT-IR (Fourier transform infrared spectroscopy), DLS, SEM (Scanning Electron Microscopy), TEM etc.

Laccase assisted synthesis of silver nanoparticles

There are also a few efficient reports on the laccase assisted synthesis of silver nanoparticles. Lateef and Adeeyo (2015) report the multi-step mutagenesis of *Lentinus edodes* towards optimization of the production of laccase and novel role of laccase in the biosynthesis of AgNPs (silver nanoparticles). They used the crude laccase for the synthesis of AgNPs. The 250 ml fermentation medium obtained having 40.0 g/L of glucose, 1.1 g/L of yeast extract, 2.0 g/L of peptone, 2.0 g/L of KH_2PO_4, 1.7 g/L of $MgSO_4$ at pH 5.5 (Five media factors) (Nehad and El-Shamy, 2010) was used for the inoculation of the cultures of the wild and mutant strains of L. *edodes*. Further, they incubated the cultures at 25 ± 2 °C (100 rpm for 7 days) and obtained laccase by sieving broth cultures of the respective strains using Whatman No 1 filter paper after seven days of the cultivation. Then, it was centrifuged at 4000 rpm at 10 °C for15 min and resultant was collected for the studies. They synthesized AgNPs by reacting crude laccase of UV10 which had the highest laccase activity with 1 mM solution of silver nitrate ($AgNO_3$) as described by Lateef et al., (2015). For the AgNPs green synthesis, about 12 ml of crude laccase was dispensed into reaction vessel containing 30 ml of 1 mM $AgNO_3$.They visually monitored the development of color due to the formation of AgNPs while measured the absorbance spectrum of the reaction mixture using UV–visible spectrophotometer. Due to the bio-reduction of silver ions by enzyme, AgNPs were characterized with typical yellowish brown color. Intensity of color increased with the progress of silver ion bio-reduction and became stable after completion of the reaction. They obtained a peak at 430 nm in the UV–Vis absorption spectrum of the biosynthesized AgNPs of UV_{10} **(Fig. 5a)**. SEM done for the biosynthesized AgNPs showed walnut shape and size was found in the range of 50–100 nm **(Fig. 5b)**. They studied antibacterial activities of biosynthesized AgNPs and found that the biosynthesized AgNPs showed the selective antimicrobial activities against the ten clinical bacterial isolates tested. Notable antimicrobial activity was found against clinical isolates of *E. coli, Pseudomonas aeruginosa,* and *Klebsiella pneumoniae* by the biosynthesized nanoparticles (Lateef and Adeeyo, 2015). A quick look on the characterization of biosynthesized silver nanoparticles has been shown in the form of **Fig. 5**(a) UV–Vis absorption spectrum of the laccase catalyzed biosynthesis of silver nanoparticles (b) SEM of the biosynthesized silver nanoparticles Lateef and Adeeyo, (2015).

Semi-purified laccase from *Trametes versicolor* has been used in the synthesis of AgNPs by Durán et al., (2014) along with detailed characterization of the synthesized AgNPs. Work of Cordi et al., (2007) was followed by them for the laccase purification process (Cordi et al., 2007). Laccase was obtained by the cultivation of *T. versicolor* (CCT 4521) for 4–20 days at 30 °C and shaking was done in a liquid medium at 240 rpm following Cordi et al., (2007). The culture filtrate in the presence of copper sulfate (0.1 mmol L^{-1}) was frozen, thawed, filtrated through a Millipore membrane (0.45 mm) and lyophilized. Ammonium sulfate (90%) was used for the precipitation of a solution having lyophilized crude extract (2.0 g) and citrate-phosphate buffer (30 ml, 75 mmol L^{-1}, pH 5.0). Using same buffer as the mobile phase, precipitate was eluted in a Sephacryl S-200 (Sigma) column. Fractions showing laccase activity were collected and lyophilized and then, re-suspension

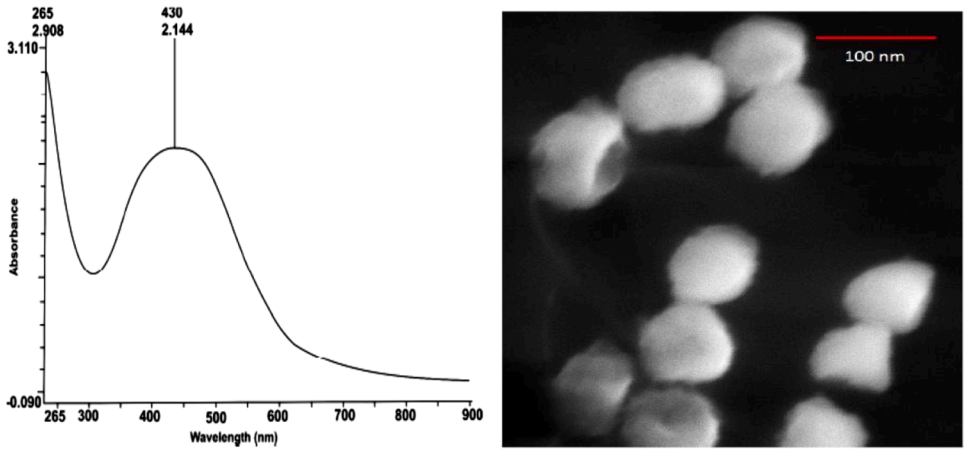

Fig. 5. (a) UV–Vis absorption spectrum obtained at 430 nm for the biosynthesized silver nanoparticles of UV_{10} strain of L. *edodes* **(b)** Scanning electron micrograph of synthesized silver nanoparticles showing walnut shaped and size between 50 and 100 nm (Lateef and Adeeyo, 2015).

of lyophilized sample was done in citrate-phosphate buffer (10 mmol L^{-1}, pH 5.0). After then, it was applied to DEAE cellulose column (Leonowicz and Grzywnowicz, 1981). Now, citrate-phosphate buffer (10 mmol L^{-1}) was used for the elution of laccase. Fractions were collected, lyophilized and stored in freeze (Cordi et al., 2007). In preparation of silver nanoparticles, they added an aqueous solution of 200 UL^{-1} semi-purified laccase to an aqueous solution of 1 mmol L^{-1} silver nitrate followed by incubation of the reaction mixture in the dark at different temperatures (30–50 °C). Brown color formation revealed the production of silver nanoparticles (Durán et al., 2007). UV–Vis spectroscopy, X-ray diffraction studies, particle size analysis, TEM, FTIR, and SEM techniques were used for the characterization of silver nanoparticles. Presence of the surface plasmon absorption of AgNPs between 420 and 440 nm in absorption spectra showed the formation of AgNPs. Different characterization studies were adopted for AgNPs. Effect of pH on the size distribution of AgNPs at 50 °C has also been nicely demonstrated. Zeta potential of the AgNPs obtained at pH 9 and 50 °C (72 h) of −30.0 mV displayed a negative charge distribution of the AgNP surface. XRD pattern was compatible with the cubic phase of Ag with diffractions points at 38°, 45°, 64.5°, 78° and 81.7° of 2θ, which can be indexed to the (111), (200), (220), (311) and (222) planes of the facet centered cubic structure (JCPDS file: 65–2871) that coexists with the cubic phase of AgCl at 27.9°, 32.3°, 46.3°, 55.0°, 57.6°, 67.6°, 74.6°, 76.9°, and 85.7° and that corresponds to the (111), (200), (220), (311), (222), (400), (331), (420), and (422) planes (JCPDS file: 31–1238). Spherical shape of Ag@AgCl nanoparticles and size of <100 nm were confirmed by the micrographic image (Durán et al., 2014).

Effect of temperature on the nanoparticles size was studied and a 90 to 370 nm distribution from 30 °C to 70 °C of silver nanoparticles after 72 h of incubation has been observed. Particle size distributions of approximately 200 nm at pH 9 were found for nanoparticles formed at 50 °C. A similar size of approximately 100 nm at pH 5 and pH 7 was observed. An agglomeration happened at pH 9 causing in a rise in the size distribution of up to 200 nm. Reduction from Ag^{+} to Ag^{o} takes place due to the incubation of semi-purified laccase in the presence of silver ions at different temperatures and interaction with silver ions generated Ag@AgCl nanoparticles (Durán et al., 2014). **Fig. 6** shows the hypothetical mechanism based on interaction between laccase and silver ions giving silver nanoparticles (Durán et al., 2014).

On the basis of the study, there are the possibilities of two type's mechanism in case of *T. versicolor* laccase as shown in **Fig. 6** (Durán et al., 2014). First mechanism involves cysteine associated to Cu type I (T1 site) (sulfhydryl group of cysteine- Cys^{-}) in the laccase structure reacting with the silver ion, reducing it to silver nanoparticles while the

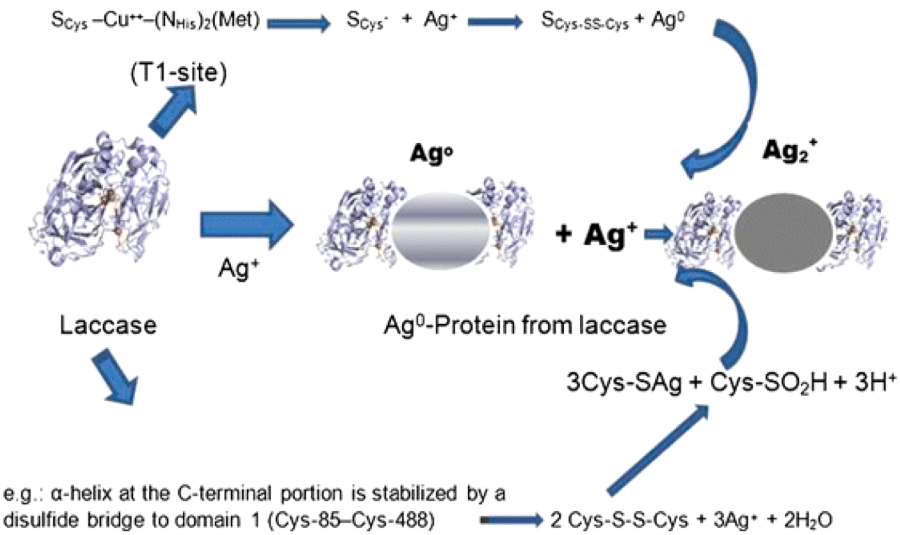

Fig. 6. Hypothetical mechanism showing the interaction between laccase and silver ions and producing silver nanoparticles (Durán et al., 2014).

cysteine anion is oxidized to Cys-Cys-in the laccase. Light blue color to the enzyme solution is imparted by T1 site of laccase and a characteristic pronounced band is found at 600 nm (Morozova et al., 2007). This type's mechanism may have possibility to happen because after the addition of silver ions, rapid disappearance of the absorption band at approximately 600 nm occurred with complete inactivation of enzymes. In the second possible mechanism, there is direct interaction of silver ions with the Cys-Cys-moiety, producing AgNPs, and the sulfhydryl moiety bound to AgNPs as capped proteins **(Fig. 6)** (Cecil and McPhee, 1957; Durán et al., 2014). Sulfhydryl group is the reducing agent demonstrated by the actual data on the biogenic synthesis of Ag@AgCl nanoparticles with laccase. After adding the silver ions, the typical absorption band of this blue protein of approximately 600 nm vanished instantly with the concomitant loss of laccase activity (Durán et al., 2014).

Role of laccases as reductive biocatalyst in the synthesis of silver nanoparticles from the respective metal salts is being evidenced on the basis of researches done, also, indicating its possible effective roles in the field of other metal nanoparticle synthesis. Crude laccase from L. *edodes* used by Lateef and Adeeyo (2015) and semi-purified laccase from *T. versicolor* (CCT 4521) used by Durán et al., (2014) revealed the effectiveness of this enzyme in the synthesis of AgNPs which were validated from various characterization techniques like UV–Vis spectroscopy, XRD, FT-IR, DLS, SEM, and TEM.

Conclusion and future perspectives

A subject centric discussion on the role of microbial enzymes showed the bright scopes of such enzymes in the field of nano-biotechnology. In this perspective, a thorough look has been given on the microbial laccase assisted synthesis of gold and silver nanoparticles based on the reported literatures. Various characterization techniques viz. UV–Vis spectrophotometry, Zeta potential, FT-IR, XRD, DLS, SEM, and TEM applied for characterizing the gold and silver nanoparticles validate the operative formation of these metal nanoparticles by the well discussed purified, semi-purified or crude microbial laccases and give it an operative attention for its future applicability in the field of nano-synthesis and nano-biotechnology. Based on above discussions, without any doubt, worth of the laccase as potential reductive biocatalyst is well established but due to lesser works on laccase assisted nanoparticle synthesis of metals, its recognition as efficient biocatalysts for metal nanoparticles' synthesis remained far behind. There is strong need of more research in the field of laccase assisted synthesis of metal nanoparticles in order to better justify its position as efficient biocatalyst.

Declaration of Competing Interest

Authors declare that there is no conflict of interest.

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