Chapter 8
Nanoparticle Synthesis by Biogenic Approach

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Abstract Biological synthesis of nanoparticles has been present in living organisms over the course of evolution to serve a variety of purposes. In this chapter, we discuss the latest trends and application for nanoparticle synthesis via plants, algae, yeast, bacteria, fungi, etc. There exists several review articles among others documenting studies about various biogenic sources and associated nanoparticle synthesis; we have rather emphasized on recent research works which probed into novel applications of these bio-nanoparticles along with some important historical findings. Also, we have discussed the challenges faced by biogenic methods along with possible areas to tweak in order to standardize this synthesis technique. Biogenic synthesis of nanoparticles has the potential to provide cost-effective, eco-friendly alternative to work as "biological nanofactories"/functionalization method once the attention has been shifted to understand the underlying mechanism, its in vitro replication and obtaining shape/size control over the nanoparticles being synthesized.

Keywords Biosynthesis • Bioinspired materials • Biogenic synthesis • Green chemistry • Nanoparticles • Nanotechnology

8.1   Introduction

In recent years, nanoscience and nanotechnology has made considerable progress towards synthesis and characterization of new materials due to their widespread application in everyday life. Nanoparticles in particular have revolutionized almost all the spheres of our life: catalysis, drug delivery, sensors, paints, surface coatings, energy systems, electronics, cosmetics/clothing/accessories, aerospace/defence, etc. During the last decade, exhaustive research has been carried out in understanding more about these nanoparticles and their possible applications.

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Today, nanoparticles are not only responsible for miniaturization of devices but also for the development of several key-enabled technologies which could not have been possible without them. As per the National Nanotechnology Initiative, nanotechnology can be defined as the manipulation of matter with at least one dimension in the size range from 1 to 100 nm or 10^{-9} of a metre. This miniaturization allows them to exhibit novel and significantly improved physical, chemical, and biological properties, phenomena and processes owing to their size. When characteristic structural features are intermediate between isolated atoms and bulk materials in the range of about 1–100 nm, the objects often display physical attributes substantially different from those displayed by either atoms or bulk materials. The properties of material changes as their size approaches the nanoscale and as the percentage of atoms at the surface of a material becomes significant at the nanoscale size-dependent properties are observed. These interesting and sometimes unexpected properties of nanoparticles (NPs) are therefore largely due to the large surface area of the material which governs the contribution made by the small bulk of material [1].

Important behavioural changes are caused not only by continuous modification of characteristics with diminishing size but also by the emergence of totally new phenomena such as quantum confinement [2], a typical example of which is that the colour of light emitting from semiconductor nanoparticles depends on their sizes.

Generally speaking, the first way is to start with a bulk material and then break it into smaller pieces using mechanical, chemical or other form of energy (top-down). An opposite approach is to synthesize the material from atomic or molecular species via chemical reactions, allowing for the precursor particles to grow in size (bottom-up). Then there are functional approaches like Biogenic techniques, which seek to develop components of desired functionality without less control on how they might be assembled. Last two decades have witnessed rapid increase in environmentally sustainable processes in material development and chemical engineering as a result of worldwide problems associated with environmental contamination. Nature has been the oldest and largest producer of several nano-structures which are not only organized at multiple scales but, in many ways, adapted to the environment [3]. These materials are generally formed in mild conditions like neutral pH, minimal temperature control and low reactant concentrations. Furthermore, these processes are highly efficient with the continuous recycling of materials and minimal toxicity to surrounding environment. Keeping our discussion limited for nanoparticles only, there exists several "natural systems" around us which produce nanoparticles of different size and functions: silica shells of diatoms, heavy metal remediation by microbes, uptake of mineral and elements by plants, etc. In fact, ever since inception of life on planet Earth, biological entities have been in constant touch with organic/inorganic materials present in the atmosphere (volcanoes, oceans, mineral deposits, etc.) resulting in life as we see today. The rise in alchemy resulted in the intentional addition of different metals and their salts (e.g. Au, Pb, Cu, Ag, As and Hg) to food and plant extracts, which were then "formulated" into medicinal potions, potentially yielding complex mixtures of nano-biocomposites [4]. Some of these can still be seen today in form of Roman Chalice, Chichen Itza statue

(Mayan blue dye) and several ancient medicinal formulations (like bhasma in Ayurveda) [5]. It is evident that biogenic nanomaterials and its application has always been a part of human history albeit not scientifically well understood/analyzed as we can do today and will be righteous to understand the face that despite our great advances in synthetic materials, nature still has plenty to teach us [6].

Biogenic synthesis of nanomaterials revolves around the philosophy of utilizing active compounds present in our nature for synthesizing/imparting novel properties which in turn can provide a breakthrough in its application [7, 8]. With the help of nature's molecules, chemical engineers have found ways to create new materials that can do everything ranging from bone/tissue regeneration, cancer treatment, efficient chemical catalysis and clean energy production [9]. This requires identification and extraction of active biomolecules which may originate from any living system or part of living system with the possibility of creating bio-nano hybrid systems [10]. Also, due to its biological origin, these nanomaterials are generally observed to be eco-friendly and non-toxic thereby proving to be excellent material for drug delivery [11] and clean energy [12]. This subset of bio-nanotechnology can be defined as a field representing all facets of research at the intersection of biology and material science generally following the principles of green chemistry. These biogenic materials tend to inherit specific chemical/material properties either in form of functional activity or passively incorporated as an inert coating/layer or scaffolding material. It is important to note that although there exists several physical and chemical methods to produce monodisperse nanoparticles, they require extensive process control including surfactants (for stability) and use of toxic chemicals (reductants). Also, the traces of toxic chemicals over the nanoparticle surface and non-polar solvents in their synthesis medium limit their application in the clinical field.

Nanoparticles can be classified into two major categories namely organic and inorganic nanoparticles. Carbon nanoparticles/carbonaceous substrates comprises for organic nanoparticles. Metal nanoparticles which for the majority of nanoparticle applications as stated above falls under the category of inorganic nanoparticles. This chapter is focused on inorganic nanoparticle synthesis by biogenic agents including both eukaryotic and prokaryotic sources. With abundant biological resources available in the nature in form of plants/phytochemicals, algae, fungi, yeast, bacteria, etc., we have emphasized on developing industrially feasible, cost-efficient and environmentally benign processes for nanoparticles synthesis with the inherent potential to be developed into biomimetic systems.

Although, each biogenic agent has a specific reaction mechanism, they essentially work in the same manner where we a "complex broth" results in formation of desired nanostructures. Apart from characterization of such nanostructures, emphasis should be laid on extraction and analysis of the involved biological (macro)-molecules in order to use them as templates for the nanomaterial synthesis, better described as "biomimetic materials". Although still in its infancy, some biogenic methods have evolved into biomimetic approach giving rise to complex bionanohybrid materials, self-assembled functional materials, advanced biomedical applications, etc. In this chapter, we provide an overview on different classes of biogenic

agents that can be used to synthesize a vast array of nanoparticles. It should be noted that there have been tremendous developments in the field of biogenic production of nanoparticles and their applications over the last decade. Therefore, we have focused our discussion on the groundbreaking approaches/applications of these nanoparticles. At the end of this chapter, we have discussed in brief about recent studies showing successful transformation of biogenic approach into biomimetic model for nanoparticle synthesis and application. This paradigm shift from using a "broth mixture" to pinning the active molecules for a stand-alone assembly is the need and challenge for biogenic nanomaterials.

8.2 Biogenic Synthesis of Nanoparticles

8.2.1 Bacteria and Yeast

As discussed above, the use of biological systems has emerged as a radical technology for synthesizing nanoparticles with an aim to control nanoparticle morphology and imparting value-added properties. Bacteria have an innate ability to reduce metallic ions to their respective metallic nanoparticles functioning as "green" nanofactories. This reduction mechanism in bacteria is due to their chemical detoxification acting as a defence [13] mechanism as well as due to energy-dependent ion efflux from the cell by membrane proteins that function either as ATPase or iontransporters [14]. In fact, interactions between metals and microbes have been used for such biological applications [15] as biomineralization, bioremediation, bioleaching and biocorrosion leading to microbial synthesis of nanoparticles.

Examples include the formation of magnetic nanoparticles by magnetotactic bacteria, synthesis of gold nanoparticles with varying shape and sizes by several fungal species, the production of silver nanoparticles within the periplasmic space of *Pseudomonas stutzeri*, synthesis of nanoscale, semi-conducting CdS crystals in the yeast *Schizosaccharomyces pombe,* the formation of palladium nanoparticles using sulphate reducing bacteria in the presence of an exogenous electron donor, etc. The interest also extends to the synthesis of other nanostructures like nanowires and the assembly of nanoparticles using biological templates such as DNA, proteins, S-layers and viruses [15–17].

Bacteria can produce inorganic nanoparticles either intracellularly or extracellularly with a well-defined shape and monodispersity. Nanoparticle production by microorganisms can be broadly divided into three categories: chemolithotrophy for energy production, use of such particles for specialized functions and detoxification for survival in toxic environments [18]. Detoxification of its immediate environment is vital for bacteria's survival and to overcome the same, it either reduces the ions or form water insoluble complexes by incorporating hydrophobic moieties as a defence mechanism [19]. The exact mechanism of bioreduction however will largely depend on the bacterial strain and growth conditions of the reaction mixture. Also, bacterial structural diversity in its morphology such as bacillus, coccus,

spirillum, fusiform bacilli, star-shaped bacteria [20] can be utilized for template based synthesis as discussed later. It is interesting to note that starting from the earlier reporting of silver nanoparticle (35–45 nm) produced by a silver-resistant strain isolated from a silver mine, we have witnessed biomimetic synthesis of silver nanoparticles [21] using silver-binding peptides identified from a combinatorial phage display peptide library. Extracellular reductases (NADH-dependent, nitrate-dependent, etc.) produced by the microorganisms tends to reduce the silver ions. The reductase enzyme gets its electrons from NADH, which is then oxidized to NAD+. Also, certain genes have been identified which suggests molecular evidence of silver resistance in bacteria [22]. Silver nanoparticles of the size range of 10–15 nm [23] were produced with the dried cells of *Corynebacterium* sp. were treated with diamine silver complex. The ionized carboxyl group of amino acid residues and the amide of peptide chains and some reducing groups, such as aldehyde and ketone were the main groups found responsible for trapping $[Ag(NH_3)_2]^+$ onto the cell wall. They were associated with the subsequent bioreduction of the ions to nanoparticles. Similarly, gold nanoparticles have been synthesized extensively from various biogenic agents. Klaus et al. observed that variation in incubation conditions may lead to different particle sizes [24]. In another bacteria (*R. capsulate*) mediated synthesis of Au NPs, the shape of the gold nanoparticles was found to be pH dependent. Gold nanoparticles of size range 10–20 nm were formed at pH 7 while nanoplates/spherical gold nanoparticles were observed at pH 4 [25]. In another study, Ahmad et al. showed extracellular synthesis of gold nanoparticle by an extremophile (*Thermomonospora* sp.) [26], while Lahr et al. demonstrated Surface-Enhanced Raman Spectroscopy (SERS) cellular imaging of intracellularly biosynthesized (*Pseudokirchneriella subcapitata*) gold nanoparticles [27]. Sloick et al. presented cowpea chlorotic mottle viral templates for gold nanoparticle synthesis where the viral capsid actively carried out the reduction of $AuCl_4^-$ by electron transfer from surface tyrosine residue [28]. In another "biogenic to biomimetic" transition, Kim et al. published peptide-mediated shape- and size-tunable synthesis of gold nanostructures which linked single amino acid change greatly influencing the size of nanoparticle (~100 nm) being synthesized [29]. We also demonstrated an array of monometallic nanoparticles (Ag, Pd, Fe, Rh, Ni, Ru, Pt, Co and Li) synthesized from *Pseudomonas aeruginosa* SM1 as shown in Fig. 8.1.

This first of its kind study showed room-temperature synthesis of several important catalytically active nanoparticles produced in a very efficient and low-cost manner.

In another study, we successfully utilized the *E. coli* extracellular matrix in a fixed column reactor for continuous production of Au NPs. Similarly, semiconductor nanoparticles like that of CdS have been formed by *E. coli* (intracellularly) as well as extracellularly by *Rhodopseudomonas palustris* [31]. Shenton et al. demonstrated synthesis of cadmium sulphide superlattices (5 nm) using self-assembled bacterial S-layers [32]. Nucleation of the inorganic phase was confined to the pores between subunits in the S-layers. Platinum nanoparticles (5 nm) has been reportedly produced by *S. algae* (in the periplasm) when hexachloroplatinate ions were introduced in presence of lactate as electron donor [33]. In another study, Riddin et al.
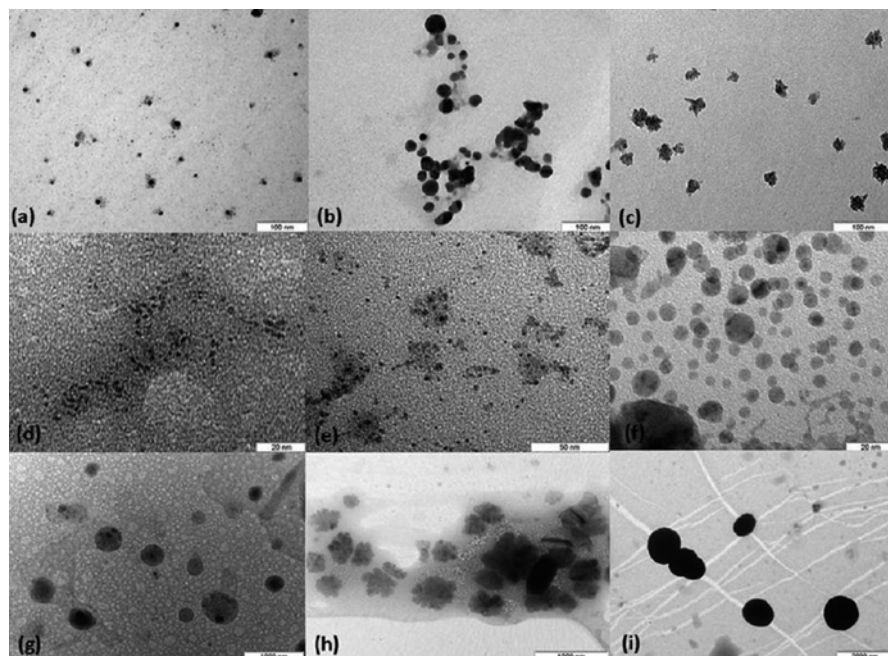
Fig. 8.1 Room temperature synthesis of (**a**) Ag, (**b**) Pd, (**c**) Fe, (**d**) Rh, (**e**) Ni, (**f**) Ru, (**g**) Pt, (**h**) Co, (**i**) Li. Reprinted from ref. [30] with permission by Springer Science + Business Media B.V.

demonstrated cell-free, cell-soluble protein extract from a consortium of sulphate-reducing bacteria in the biosynthesis of geometric Pt(0) nanoparticles [34]. Similarly, Bharde et al. demonstrated magnetite nanoparticle synthesis by *Actinobacter*, a nonmagnetotactic bacterium, using iron precursors under aerobic conditions [35]. While earlier studies were very slow (about 1 week) and required strictly anaerobic conditions, this study tends to ease the required process control, one of the several benefits of biogenic synthesis.

Apart from monometallic nanoparticles, bacterial have shown unique properties for producing an altogether different and complex nanoparticles. Li et al. showed in-situ CdS nanoparticles (8 nm) synthesis and via bacterial cellulose (BC) nanofibers [36]. In another study, Bao et al. showed biosynthesis of CdTe quantum dots using *E. coli* [37] and yeast cells. In this process, yeast secreted proteins coordinated with Cd_2^+ and Te_2^+ ions forming caps on the surface of the QDs (~3 nm) thereby improving the biocompatibility as well as high fluorescent properties as shown in Fig. 8.2 [38].

This work provides a cost-effective green approach to synthesize highly fluorescent biocompatible CdTe QDs with high quantum yield ~33 % at a reaction temperature of 35 °C as compared to high quality CdTe nanocrystals obtained under hydrothermal conditions 180 °C [39], indicating that the biosynthesized CdTe QDs area good candidate for bio-imaging. It is worth noting that yeasts can accumulate
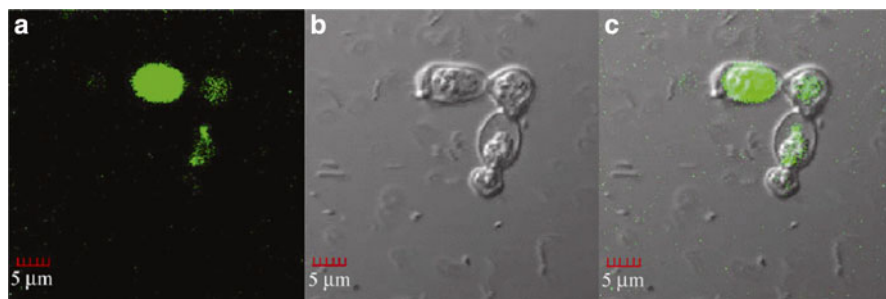
Fig. 8.2 Confocal image of CdTe QDs (**a**) excited by 488 nm laser (**b**) bright-field image (**c**) over-laid image. Reprinted from ref. [38] with permission by Springer Science + Business Media B.V.

significantly high amounts of toxic metals. This species has developed different mechanism to overcome the toxic effects of heavy metals including enzymatic oxidation or reduction, sorption at the cell wall, chelating with extracellular peptides or polysaccharides, controlled cell membrane transport of heavy metals towards or their active efflux from the cell. Ability of yeast to produce CdS and PbS has earned them the tag of green factories for semi-conductor crystals [40]. While discussing complex nanoparticles, it is worth noting that microbial systems have shown capability to produce bimetallic nanoparticles as well. Hosseinkhani et al. showed synthesis of bimetallic Pd-Au nanoparticles via *Cupriavidus necator* cells as support material [41]. The synthesis was carried out in two steps where monometallic Pd(0) and Au(0) layer was formed on *Cupriavidus necator* cell surface followed by formate assisted reduction of Au(III)/Pd(II) on to the pre-formed core. In another interesting study, Deplance et al. reported a novel biochemical method based on sacrificial hydrogen strategy to synthesize core/shell Pd@Au NPs as shown in Fig. 8.3 [42]. They utilized the ability of *E. coli* cells supplied with H2 as electron donor to precipitate Pd(II) ions from solution followed by the reduction of soluble Au(III) over its surface thereby generating characteristic core-shell morphology with high catalytic activity in oxidation of benzyl alcohol.

In another study by Carmona et al. magneto-optical bacteria were produced using probiotic *Lactobacillus fermentum* [43]. By exploiting metal-reduction properties (to produce gold nanoparticles) and their capacity to incorporate iron oxide nanoparticles at their external surface, they reported living magneto-optical bacteria behaving as a magnet at room temperature. Biogenic inorganic NP synthesis has several advantages due to their flexibility in terms of minimal process control, benign reaction conditions, minimal by-products and non-toxic nanomaterials. Bacteria and yeast in particular are an interesting class to function as green nanofactory mainly because while former has high multiplication rate the latter happens to be one of the most researched living system. Bacterial cultures can be easily scaled up depending upon the strain type and large amounts of required extracellular proteins/surfactants responsible for certain type of nanomaterial synthesis can be extracted at high purity. Similarly, yeast offers an additional advantage to act as a host for genetic modifications leading to highly specific bio-nano hybrids including

Fig. 8.3 *E.coli* mediated synthesis of bimetallic Au-Pd nanoparticles. (**a**) TEM image following sequential reduction of Pd (II) and (**b**) Au (III) (**c**) EDX mapping of two Pd–Au particles showing superimposed Au and Pd distributions. Reprinted from ref. [42] with permission by the Royal Society
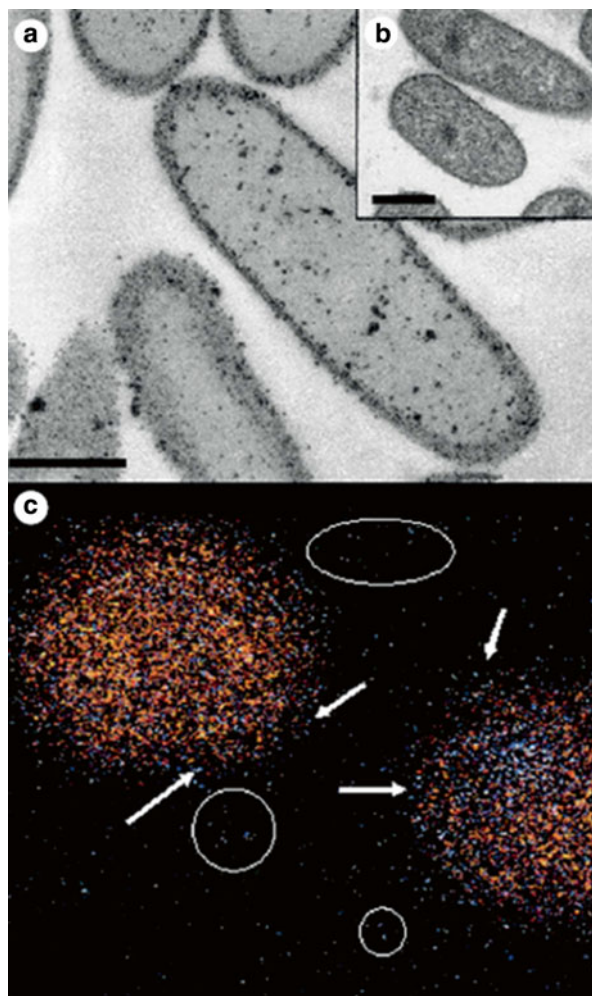
special function nanoparticles. However, there are several challenges which need to be addressed before microbial assisted nanoparticles synthesis can become an industrially viable alternative for nanomaterial production. The first and foremost, similar to other biogenic agents, nanomaterial synthesis happens by a complex mixture of broth where one or more chemical entities may be responsible for the synthesis/functioning of the desired nanomaterial. There exists a plethora of reports where "mix n match" approach of utilizing different strain with different metal ion solution results in certain type of precipitation/reduction leading to colloidal nanoparticle solution. However, not much is being been done in pinning the active biomolecules which are responsible for the nanoparticle/nanomaterial synthesis. The aim biogenic synthesis should remain the same as with almost all the domains

Table 8.1 Summary of nanoparticles synthesized by biogenic approach

Microbe	Nanoparticle type and morphology	Reference
Escherichia coli	Au (50 nm, circular)	Srivastava et al. [44]
Rhodopseudomonas capsulata	Au nanowires (10–20 nm)	He et al. [45]
Lactobacillus sp.	Au (20–50 nm, Hexagonal)	Nair et al. [46]
Clostridium thermoaceticum	CdS	Cunningham et al. [47]
Actinobacter sp.	Magnetite (10–40 nm)	Bharde et al. [35]
Shewanella oneidensis	Uranium (IV) extracellular	Marshall et al. [48]
Desulfovibrio desulfuricans	Pd (~50 nm)	Yong et al. [49]
Klebsiella pneumoniae	Ag (5–30 nm)	Shahverdi et al. [50]
Pseudomonas aeruginosa	Ag (13 nm, spherical)	Ganesh Kumar et al. [51]
Streptomyces sp.	$MnSO_4$ and $ZnSO_4$ (10–20 nm)	Waghmare et al. [52]
Candida glabrata	CdS (200 nm)	Dameron et al. [53]
Pichia jadinii	Au (~100 nm)	Gericke et al. [54]
Yarrowia lipolytica	Au	Agnihotri et al. [55]
Torulopsis sp.	PbS (2–5 nm)	Kowshik et al. [56]

of science, i.e. to evolve into a more concrete and standard practice. Further, bacterial synthesis of nanoparticles generally results in coating of extracellular biomolecules (resulting in stabilization) over the nanoparticle being synthesized. This may not be required for certain specific applications along with the probability of initiating step for purification of resulting nanoparticles. Therefore, biogenic chemists should focus on developing "standard operating procedures" which can create a benchmark for homogeneity of the process among similar strains and culture conditions. As of now, production of nanoparticle by microbial strain has been established. Therefore, microbial synthesis of nanoparticle needs a little more than just synthesis characterization and generic application to combat its existing challenges. Emphasis should be laid on understanding the biochemical mechanism of nanoparticle synthesis via proteomic, genetic or metabolomics analysis. With the advent of biomimetic materials and template assisted synthesis of nanomaterials, these well-studied and well-developed biogenic systems will play a key-role in the future of green processes for nanotechnology. Similarly, there exists a vast plethora of bacteria and yeast mediated nanoparticle synthesis as shown in Table 8.1.

8.2.2 Fungi and Algae

Fungi and algae are among the prominent key players for biogenic synthesis of nanoparticles. In fact, fungi offer some distinct advantages as compared to other biogenic agents in terms of high enzymatic production, ability to scale-up (e.g. thin substrate fermentation method) and high tolerance against metals. High

extracellular proteins/enzymes results in high yield of nanoparticles. Mukherjee et al. reported biosynthesis of silver nanoparticles (25 ± 12 nm) using *Verticillium* sp [57]. While exposure to fungal biomass in presence of aqueous Ag^+ ions solution resulted in the intracellular reduction of the metal ions, the cells continued to multiply after biosynthesis of the silver nanoparticles showing high metal resistance. This study was important as silver nanoparticles are generally regarded as the panache for antimicrobial agent. Similarly, Ahmad et al. reported extracellular synthesis of CdS nanoparticles by *Fusarium oxysporum* via extracellular sulphate reductase enzymes [58]. The enzyme mixture was responsible for the conversion of sulphate ions to sulphide ions that subsequently reacted with aqueous Cd_2^+ ions to yield highly stable CdS nanoparticles.

High extracellular protein yield from fungal systems were also utilized for the synthesis of gold nanocrystals with varied morphology including spherical, regular nanoplates, spiral nanoplates, nanowalls, lamellar nanoagglomerates, and spherical nanoagglomerates via mycelia-free spent medium (*Aspergillus niger*) which were found to be temperature and pH dependent [59]. Similarly, heat treatment of cell-free filtrate (*T. koningii*) indicated that the presence of aromatic and aliphatic amines (Cysteine, Tyrosine, etc.) is responsible for the nanoparticle production and stabilization [60, 61]. This extracellular yield of enzyme/proteins from fungal system with its ability to grow on mineral media (metal ions) is a key feature for biogenic synthesis of nanoparticles via fungal strains. A SDS-PAGE study on Au NP synthesized via *Rhizopus oryzae* confirmed that two proteins of 45 and 42 kDa participate in gold reduction, while an 80 kDa protein serves as a capping agent [62]. This "capping agent" property from fungus was also utilized in the synthesis of core-shell nanoparticle (silver-protein; 30.5 ± 4.0 nm) synthesis by spent mushroom substrate [63]. *Fusarium oxysporum* provided some interesting results by producing Pt NPs (5–30 nm) via "two-cycle two-electron mechanism" for Pt NP formation. H_2PtCl_6 with its octahedral structure was may fit into the hydrolase active site, and then subsequently getting reduced at the surface of the enzyme to form Pt^{+2}. Next, $PtCl_2$ moves to the hydrophobic channel of the hydrolase active site and is reduced at pH 7.5 and 38 °C. This study further reaffirms the importance of reaction parameters like pH and temperature as stated above since H_2PtCl_6 was unreactive at pH 7.5, 38 °C; $PtCl_2$ was unreactive at pH 9, 65 °C [64]. Also, a fungal strains of *Fusarium* sp. found to produce Au–Ag bimetallic nanoparticles and silica nanoparticles. In another study, magnetite nanoparticles were produced by *Verticillium* sp. and subsequent SDS-PAGE analysis suggested cationic 55 kDa protein may be responsible for the hydrolysis of the $[Fe(CN)_6]_3$ and $[Fe(CN)_6]_4$ precursors; The presence of the 13 kDa protein, which was suggested to be induced by the presence of the iron complexes. Therefore, as evident, despite a decade long research of utilizing fungal strains for nanoparticle production and being able to establish some key-findings regarding the "extracellular synthesis" route, biogenic synthesis is in dire need of identifying the underlying mechanism of such processes. Although a few studies reported preliminary SDS-PAGE analysis asserting extracellular proteins responsible for nanoparticle production, it is vital to establish the proteomic/genetic route of such biogenic studies. Since, biogenic synthesis is an established

route of nanomaterial synthesis (as is the case now), a collective effort is needed to mimic the underlying molecular machinery so that the same advantages can be achieved more "controlled" manner. Also, it should be noted that a majority of filamentous fungi that have been reported for nanoparticle synthesis are plant and/or human pathogen. This makes handling and disposal of the biomass a major inconvenience toward commercialization of the process. Further, lack of proper control studies to ascertain the mechanism behind nanoparticle production is a major challenge which microbial biogenic synthesis needs to assess [60, 61]. Diatoms have been long regarded as a perfect "natural design" with highly efficient metabolism to remove large amounts of carbon dioxide, a major greenhouse gas. The very interesting design trait includes their cell wall which is made up entirely of glass, i.e. silica or silicon dioxide. The shell of these unicellular organisms are ornately patterned with features just tens of nanometers in size. With thousands of different species of diatoms, we have virtually a large library of extracellular design patterns waiting to be explored and utilized for nano-motors, nano-scale reactors, etc. Kröger et al. provided the first of its kind study to utilize polycationic peptides from diatom biosilica to direct silica nanosphere formation [65]. This set of polycationic peptides better known as silaffins were isolated from diatom cell walls and were responsible to form a network of silica nanospheres when added to a solution of silicic acid within a few seconds. Since, silaffins contain covalently modified lysine-lysine elements; this not only suggested the role of primary/secondary amines for catalytic structure formation but was able to confirm the underlying mechanism within a few years. The study done by Kröger et al. is all the more important since it addressed the major issue of biogenic synthesis, i.e. not only to synthesize/characterize the material but to provide in-depth analysis of the underlying mechanism in subsequent studies. Among early studies, Torres et al. also reported biosynthesis of gold nanoparticles by a single-step room temperature method of aqueous chloroaurate ions by brown seaweed (*Fucus spiralis*) [66]. Similarly, several algal strains have been found to produce Au, Ag and Pt NPs. Also, a batch reactor study of *Chlorella vulgaris* for silver nanoparticle synthesis in a continuously stirred non-aerated culture assembly was carried out to produce polydispersed (8–20 nm) Ag NPs [67]. On a slightly different perspective, alginate which is an algal polysaccharide has found application in the synthesis of ferromagnetic nanoparticles as well as an efficient catalyst matrix for oxidation reactions [24]. In another study, Govindaraju et al. investigated interaction of single-cell protein of *Spirulina platensis* for the synthesis of Ag, Au and Au core—Ag shell nanoparticles [68].

8.2.3 Plant Derived Materials

Plants have the tendency (often required as micronutrients and macronutrients) to uptake very low levels of metals and accumulate in tissues compared to the chemical methods, which is less effective in low levels of metals. It is interesting to note that although the biological reduction of metals by plant extracts has been known since

the early 1900s, the synthesis of nanoparticles using plant materials has only recently been studied within the decade [69]. The synthesis of metal nanoparticles using biological materials has been shown to produce nanoparticles of the same shapes and sizes as those produced through chemical or physical methods. An added advantage with using plants as biogenic agent is often their compatibility with living systems. A recent study by Zhang et al. reported that exosome-like nanoparticles from inexpensive, edible plants might be used to make nanovectors to bypass toxicity and cost related challenges. The nanoparticles from the juice of grapefruits, grapes and tomatoes were undertaken for this study [11]. However, the current chapter discusses important plant mediated nanoparticle synthesis strategies and reaction parameters required for obtaining desired nanoparticle morphology. In fact, the accumulation of metal ions in plants has been largely used in phytoremediation for about three decades or so, which has been a low-cost eco-friendly and efficient environmental clean-up technique [70]. This also resulted in phytomining technique where plants were used to extract mineral traces from below the Earth's surface [71]. In 2002, Gardea-Torresday et al. reported formation and growth of Au NP inside live alfalfa plant where they presented the possibility of using live plants for fabrication of nanoparticles. As claimed in this report, this indeed opened up a new and exciting method to fabricate nanoparticles with successive contribution for the now emerging field of nanobiotechnology. With nanoanalytical instruments and imaging coming into focus, subsequent years reported several reports of nanocrystalline metal in plants suggesting plant phytochemicals has not only the potential to reduce but also to stabilize the resulting nanoparticles [72]. Marshall et al. utilized *B. juncea* to report accumulation of metallic gold as nanoparticles (5–50 nm) [73]. Similarly, among earlier studies, Gardea-Torresdey et al. reported silver nanoparticles synthesis in alfalfa seedlings [74]. They reported that when seedlings were grown under aseptic conditions in a basal medium containing silver nitrate, silver(I) ions were reduced and accumulated as Ag(0) nanoparticles at physiological pH (5.8) both in roots and shoots. However, as expected from other biogenic agents, extracellular nanoparticle synthesis is what we are looking for. One major advantage of using plant extracts as biogenic agent for nanoparticle synthesis is that in comparison to microorganisms, the phytosynthesis method does not require complex processes like microbial isolation, culturing, maintenance, etc., thereby making it an ideal choice for cost-effective bulk production of nanoparticles. Also, there have been studies claiming that that the rate of nanoparticle synthesis is faster and more stable using plants as compared to microbes [75]. Shankar et al. reported formation of gold nanotriangles by lemongrass leaf extract [76]. They reported that the nanotriangles seem to grow by a process involving rapid reduction, assembly and room-temperature sintering of "liquid-like" spherical gold nanoparticles. In addition, leaf extracts of several plants including lemongrass, neem, tamarind, geranium, *Aloe vera*, and *Capsicum annuum* have been reported to demonstrated their potential in formation of Au and Ag nanoparticles [77] In another study, Gangula et al. reported synthesis of Gold (Au) and Silver (Ag) nanoparticles (NPs) from the stem extract of *Breynia rhamnoides* [78]. The phenolic glycosides and reducing sugars present in the extract were reported to be responsible for the rapid reduction rates of Au^{3+} ions to AuNPs.

Similarly, Huang et al. reported Au NP formation from the sun-dried leaves of *Cinnamomum camphora* [79]. Song et al. claimed first report of Pt nanoparticles using the leaf extract of *Diospyros kaki* from aqueous $H_2PtCl_6 \cdot 6H_2O$ solution [80]. This study also highlighted the fact that biogenic nanoparticle synthesis may not necessarily be an enzyme dependent process. Likewise, syntheses of platinum and palladium nanoparticles have been reported using extracts of several different plant species [81, 82]. Jia et al. reported formation of Pd nanocatalyst for p-Nitrotoluene hydrogenation with *Gardenia jasminoides* stating 100 % conversion efficiency under specified reaction conditions [83]. This study highlighted that geniposide, chlorogenic acid, crocins and crocetin played an important part in reduction and stabilization of Pd nanoparticles (temperature dependent). Coccia et al. also reported one-pot synthesis of platinum and palladium nanoparticles using lignin isolated from red pine (*Pinus resinosa*) [84]. Likewise, bimetallic nanoparticles have also been synthesized using plant extracts. Lu et al. reported Ag−Pd alloy nanoparticles (NPs) using the aqueous extract of *Cacumen platycladi* leaves and its application as a catalyst for hydrogenation of 1,3-butadiene [85]. The results reported that biomolecules including saccharides, polyphenols, or carbonyl compounds were involved in the reduction process with (NH)C=O groups were responsible for the stabilization of the NPs. Similarly, Zhang et al. reported synthesis of bimetallic Au-Pd nanoparticles (~7 nm) with *Cacumen platycladi* leaf extract in aqueous environment [86]. Preliminary investigation suggested C=O and C-O groups in the plant extract responsible for capping the nanoparticles. Similarly, bimetallic nanoparticle synthesis of Au-Ag nanoparticles have been reported using dried leaf extract of *Anacardium occidentale* where water soluble biomolecules like polyols and proteins were suggested to be responsible for the bio-reduction [87]. In another study, Patel et al. demonstrated high-performance nanothermite composites derived from super-reactive CuO nanorods oxidizers fabricated by simple biogenic routes using *Aloe vera* plant extracts [88].

Recently, Nolasco-Arizmendi et al. reported silk–gold nanocomposite fabric by reduction of gold ions using aqueous extract of grapefruit pulp (*Citrus paradisi*) suggesting potential in development of functional fibres/fabrics using plant mediated biogenic method [89]. Carbohydrates and organic acids, present in *C. paradisi* were believed to be responsible for the formation of nanoparticles [89]. Also, Hang et al. reported bimetallic Au–Pd/TiO2 catalysts for solvent-free oxidation of benzyl alcohol (BzOH) to benzaldehyde (BzH) with *Cacumen platycladi* (*CP*) extract [90]. With high BzOH conversion (~78 %) and selectivity (~96 %), recycling tests showed that even after seven recycles, the catalyst still remained suggesting excellent durability and reusability leading towards industrial application [90].

Although with tremendous development shown towards plant mediated synthesis of inorganic nanoparticles, among prime challenges, it is important to understand the underlying mechanism and functional biomolecules involved for its subsequent developmental stage of biomimetic nanomaterial synthesis. Several researchers have reported that larger nanoparticles are formed at lower pH (2–4) while smaller nanoparticles are formed as the pH level increases [82, 83]. This was presumed as at low pH (pH 2 in case of Au NPs) they tend to aggregate to form

larger nanoparticles rather than to nucleate and form new nanoparticles. In contrast, at pH 3 and 4, a greater number of functional groups (carbonyl and hydroxyl) are available to act as nucleation sites, thereby producing nanoparticles of relatively small size. Similarly, it was reported that nanoparticles are formed at a higher rate with increase in temperatures. Grecke and Pinches observed that Au nanorods and platelets were synthesized at higher temperatures, while spherical-shaped nanoparticles were formed at lower temperatures [91]. This is understandable as with increase in temperature, the rate of reaction also increases, thereby enhancing the synthesis of nanoparticles [92, 93].

However, as evident from plant being used as biogenic agents, there exists no core proof underlining the reaction mechanism with purified active compound and the assessment of its catalytic binding site. This is detrimental for the growth of plants as biogenic agents since numerous plant extracts were randomly used to make metallic nanoparticles (Au and Ag due to their ease in synthesis and SPR related preliminary observation). Chemical groups including flavonoids, terpenoids, primary/secondary amines, polysaccharides, carbonyl and sulfhydryl groups, etc. have all been reported for NP synthesis. In absence of any process control, plant biogenic synthesis needs standardized protocols where the focus should shift from mere chemical groups (as provided from FTIR study) to actual extraction, purification and assessment of phytoactive chemicals. Very recently, a number of reports have been published on the synthesis of noble metal nanoparticles from plants with possible mechanism studies [94–96].

8.3   Challenges for Biogenic Synthesis of Nanoparticles

Similar to any other nascent technology, biogenic synthesis of nanomaterials (or nanoparticles in particular) has several challenges which it needs to address before being considered as a viable alternative for industrial production of nanomaterials/nanoparticles. In this concluding section, our aim is highlight some key-challenges which need to be addressed for biogenic synthesis being evolved into biomimetic synthesis. It is interesting to note that although a plethora of scientific articles have been published in field of biogenic synthesis of nanoparticles within a decade, the challenges being highlighted here remains as important as they were before and for the future.

8.3.1   Protocol Designing: Stringent Control Setup

The first and foremost caution for biogenic synthesis is the designing of synthesis experiment. In a very recent article, Liu et al. showed synthesis of nanoparticles (Au) and reduced graphene oxide by using chemically defined microbe culture media alone, without the involvement of microbes [97]. These studies in one go highlighted

what many studies may have claimed in the past to be achieved microbiologically, could have been a mere control error. As this paper correctly points out that "using this article to alert researchers in the microbial nanosynthesis field to carefully design control experiments to avoid the misunderstanding of the microbial synthesis mechanisms and realize the implementation of complete green methods to fabricate technologically important nanomaterials." This is indeed an important issue which needs to be addressed systematically and providing video evidence (with time-lapsed study) to prove only the sought biogenic agent is being active is very important.

8.3.2 Putting Emphasis on Reaction Kinetics and Process Control: Understanding Reaction Mechanism

As of now, it is an established fact that biogenic agents can be used to produce metallic nanoparticles. As highlighted throughout this chapter, several eukaryotic and prokaryotic organisms have been utilized to synthesize an array of nanoparticles. Therefore, upcoming studies must focus on standardizing the protocol, understanding of reaction mechanism and controlling the morphology of nanoparticles in liquid media. The overexploitation of biogenic agents merely to report the synthesis aspect should be accompanied by the factors controlling the study. This can be better understood by the fact that as of now several plants/bacteria has been identified to produce nanoparticles while exact mechanism still largely remains elusive or rather process dependent. Although, utilizing a dozen different species to catalogue the nanoparticles being produced makes sense provided each of it undergoes to establish the rigorous process parameters for a more comprehensive and new set of information. Too often reports have been published where nanoparticle synthesis has been reported by a biogenic agent with the change of strain, part of the plant, culture condition, etc. This can be the initial foundation of the study but then needs greater information to be built upon before scientific community can transform such studies into more accurate biomimetic platforms. This can be better understood by the fact that recently Bhaduri et al. claimed Ag NP synthesis by sunlight [98]. Similarly, Kim et al. showed sunlight based synthesis of gold nanoparticles [99].

Therefore, what we see here is some studies which claim to achieve the nanoparticle synthesis just like biogenic agents with no requirement of laborious microorganism screening, plant culturing/Soxhlet extraction, cultivating and complex downstream separation processing can be eliminated. Our intention here is to highlight the importance that merely changing the biogenic substrate (knowing well that they are indeed capable of producing nanoparticles) and subsequent characterization of nanoparticles may not be sufficient considering the sheer amount of publications within the last decade. We need to address the underlying mechanism by carrying out proteomic and metabolomics studies as and when required. In place of multiple publications by utilizing different biogenic agents to produce Au/Ag or any nanoparticles, emphasis should be laid on advancing the already established bio-

genic agents with greater process control so that they can be mimicked into the lab for real applications. Although we have cited several biomimetic studies in this chapter, a good example at this point will be liposomes which are composed of lipid membranes just like cell-membrane with the ability to control the reaction kinetics at nano/micro scale [100]. While the first part of the issue is scientific where there is need to study the underlying mechanism, the latter is more ethical where the "quality and impact" of a study is considered into account.

8.3.3   Importance of the "Choice of Characterization" Studies

"There is no doubt that SPR from Au NPs can serve as the preliminary indicator for Au NP synthesis. However, as of now, where ample of studies has been done indicating the same, there is need to dwell deeper and extract more meaningful information like reaction kinetics or time-dependent stability of nanoparticles etc." The above statement highlights another important challenge for biogenic nanoparticle synthesis, i.e. the need to set a higher benchmark when it comes to characterization of nanomaterials. Another example of it can be TEM images where several biogenic synthesis studies claimed the nanoparticles to be "highly monodispersed" but did not provided a bell-graph study confirming the same. Obtaining highly monodisperse nanoparticles is a challenge for biogenic systems since there are several parameters acting upon. Studies done by Bastús et al. [101] and Perrault et al. [102] can be used as a benchmark while reporting reaction process dependent nanoparticle morphology and associated kinetics. Another key-feature as we have seen across most of the biogenic studies is the inclusion of FT-IR data generally confirming some active chemical groups (primary amines, secondary amines, thiols, etc.) which may be responsible for the chemical reaction. This needs to be further confirmed and complemented by more conclusive analytical studies including SDS-PAGE followed by 2D-PAGE and if possible, protein sequencing. This is important because as of now, it is already established that almost all sorts of active proteins in aqueous condition have the capacity to produce nanoparticles (especially Au NPs because of its low reduction potential). Therefore, there is an urgent need to raise the necessary scientific evidence from mere detection to its "extraction-purification and subsequent characterization" so that biogenic synthesis can match pace with the ever-growing need of biomimetic materials. Another important point is utilization of EDX data while confirming reduction taking place. It should be noted that EDX can detect the element even if it is present in its compound (salt) form and may not necessarily means reduction taking place or associated quantitative changes. Therefore, it is important to utilize XPS among others which given an edge over (EDX and FT-IR) by providing information about the chemical state of all the elements involved in the reaction.

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