Review Paper: Living Plant-Mediated Synthesis of Nanoparticles

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ABSTRACT

Techniques to fabricate nanostructured materials are in constant development. These techniques initiated with physical and chemical approaches and now are developed to biosynthesis and green synthesis techniques. Nowadays, bioactive compounds from microbial cells and plant extracts are hugely tested and employed for the green synthesis of nanoparticles. Similar to microbial cells that can produce intracellular nanostructures, some plants can synthesize and maintain nanostructures in their tissue. The evidence of these finding is the phytomining technology. Now it is known that various parameters such as soil pH, geographical area, and ionic precursor can influence the process of in situ fabrication of nanoparticles. Plant metabolites such as terpenoids, polyphenols, reducing sugars, alkaloids, phenolic acids, and proteins play a major role in the reduction of metal ions as well as stabilization of the produced nanoparticles. These in situ synthesized nanoparticles can be extracted and purified via ashing techniques.

Highlights

- Green plants can synthesize and maintain nanoparticles in their tissues.
- The plants can be used for synthesis of Au, Ag, Cu, Co, Zn, and Ni nanoparticles.

Plain Language Summary

Nanoparticles are particles with extremely small size. Their diameters are about 1000 folds smaller than the diameter of human hair (less than 0.0001 mm). These particles are unique due to their novel physicochemical and biological properties. In Iran, nanoparticles have gained increasing applications in various technologies. Over the last decade, researchers attempted to find and develop new techniques for the fabrication of these ultra-small particles. Some of these techniques are energy consuming and in most cases employ organic solvents and toxic chemicals. However, plant-mediated synthesis of nanoparticles is a novel approach for the green synthesis of nanoparticles. Plants are abundant with biochemical compounds which are able to reduce metal ions to the nanoparticles and stabilize them. The current review aimed at discussing this issue in detail.

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1. Introduction

Nanotechnology is one of the most recent technologies with immense effects on human life. Nanoparticles are now employed in various fields of science and technology. Traditionally, nanoparticles were synthesized via physical and chemical techniques. These techniques are usually performed through harsh processes such as high temperatures and controlled atmosphere. Also, chemical techniques employ toxic materials and organic solvents to do the job [1].

Due to the increasing demand for the nanostructures and nanomaterials, novel approaches are developed to synthetize these compounds. These novel techniques are developed based on the reduction in the application of chemical toxic compounds and organic solvents. Green chemistry emerged as a worldwide trend to make the chemical reactions environmentally friendly and sustainable. Green chemistry is based on the substitution of organic solvents and chemical agents with aqueous matrices and biochemical compounds. Green synthesis and biosynthesis are now familiar terms in the nanostructure fabrication techniques. Now, it is known that biologic materials can be employed to fabricate various nanostructures. Among living creatures, microorganisms and plants are the most employed ones to fabricate nanoparticles in a green manner [2, 3].

Till now, various microbial cells such as bacteria, fungi, diatoms, and microalgae are used to fabricate nanoparticles. The particles can be synthesized extracellularly or intracellularly [2, 4-13]. The major disadvantage of employing microbial cells in the synthesis of nanoparticles is that most of the employed organisms are pathogenic or opportunistic. On the other hand, the media used for the microbial cell cultures are usually complex and expensive. Also, the process of the culture is labor and time consuming. Plants are the next source for cheap and ubiquitous bioactive compounds that can be employed in green synthesis. These bioactive compounds can be simply extracted from the plant into the plant extracts.

Plant extracts are now vastly studied and used for the green synthesis of various nanostructures. The potential of extracts from different parts of plants such as leaf, fruit, flower, and seed is examined for the green synthesis of nanoparticles [3, 14-19]. In addition to plant extract, living plants have also the potential to perform green synthesis of nanoparticles, which means that some living plants are able to synthesize and maintain nanoparticles in their tissue. The current mini review aimed at discussing this issue in details. In this regard, data were provided for the effective parameters that influence formation of nanoparticles in living plants. Also, mechanisms that might be responsible for the living plant mediated synthesis of nanoparticles were presented. Finally, the prospective and limitations of this approach were discussed.

2. History

History of the synthesis of nanoparticles in the living plants goes back to the discovery of the phytomining phenomenon. "Phytomining technology" is the employment of hyperaccumulator plants to extract valuable metals that are on a mineralized soil or low-grade ore bodies [20]. Phytomining process studies showed that metals are usually stored as nanoparticles in plants. In situ synthesis of metal nanoparticles comes from metal-tolerance ability in plants that helps them to survive in high concentrations of metals by rendering minerals to a nontoxic form (to be farfetched from active metabolic sites of plant) [21, 22].

Gardea-torresdey et al. were among the first groups to evidence the synthesis of gold and silver nanoparticles inside living plants, and opened up a new horizon to fabricate nanoparticles [23, 24]. They used Medicago sativa (alfalfa) on agar medium enriched with AuCl4, and analyzed it through XANES (X-ray absorption near edge structure), EXAFS (extended X-ray absorption fine structure), X-ray, and confirmed the ability of up-taking zero valent gold from solid metal and formation of Au nanoparticles in different sizes. Further investigations showed the absorption of silver (as Ag^0) and transforming it to the shoot of plant. TEM and STEM analysis approved the arrangement and accumulation of silver atoms inside alfalfa plant to start nucleation and synthesis of Ag nanoparticles. It is interesting that alfalfa can store silver nanoparticles up to 13.6% of its weight. In addition to gold and silver, synthesis of other noble metal nanoparticles such as Cu, Co, Zn, and Ni nanoparticles via exposing living plants to the aqueous metal salt precursors were reported in the following studies reported in the next studies [25, 26].

3. Effective Parameters

Formation of nanoparticles in living plants is influenced by some environmental parameters [27-29]. Armendariz et al. observed that the size of gold nanoparticles greatly varied by altering pH value of the medium from biomass of Avena sativa [30]. The source of metals is also a critical factor in biosynthesis of nanoparticles in living plants. For instance, when Brassica junea was supplied with $AgNO_3$, the size of biosynthesized silver nanoparticles was around 10-35 nm, whereas plants supplied with $Ag(NH_3)^{2+}$ complex, synthesized the nanoparticles of about 2 nm in size [31].

Authors` recent study showed that geographical area is a significant factor in the process of in situ nanoparticles production. In the current study, the ability of three strains of Iranian alfalfa plants, harvested from different geographical areas, was examined for in situ synthesis of AuNPs. Results indicated that the type of alfalfa plant, concentrations of HAuCl4, pH of the culture media, and duration of exposure to HAuCl4 were the main factors in the synthesis of AuNPs [32].

4. Mechanism

Recent investigations hypothesized that big-reducing sugars and fructose in chloroplasts were responsible to convert metal salts into nanoparticles. Furthermore, plant metabolites such as terpenoids, polyphenols, sugars, alkaloids, phenolic acids, and proteins play a major role in the reduction of metal ions as well as stabilization of the produced nanoparticles. Further analyses confirmed that the synthesis of nanoparticles started some ultrastructural changes in different cell compartments. In response to the presence of high concentrations of nanoparticles, cells change their subcellular organization. One of these important changes occurs in cell membranes. High concentrations of silver nanoparticles can lead to the inhibition of sulfhydryl enzymes in cell membranes (e.g. membrane of plasmalemma, tonoplast, and chloroplast thylakoids), which modify membrane permeability and, as a result, cell damage [33-35].

In general, the synthesis mechanism of metal nanoparticles in a living plant consists of three main steps; the first step is activation phase, in which ions are reduced and the nuclei of the nanoparticles are formed; in the second step, growth phase, small nanoparticles are interconnected to make up larger particles, this phase is accompanied by an increase in the nanoparticles thermodynamic stability; eventually, in the termination phase, the final shape of the nanoparticles is determined, in this phase, nanoparticles have the most stable thermodynamic properties [36].

5. Prospective

Although living plants can be used to synthesize metal nanoparticles, this technology has limitations that challenge the entry of produced nanoparticles into the realm of industry. The size and shape of the synthesized nanoparticles are highly dependent on their storage position in the plant, which can be due to the difference in the permeability of metal ions in different parts of the plant and/or the presence of different biomolecules in different parts of the plant [37-40].

The heterogeneity of the size and shape of nanoparticles produced in a living plant that has high sensitivity to the shape and size of nanoparticles are the main drawbacks to their application in industries. Extraction and purification of in situ synthesized nanoparticles is another drawback of in situ synthesis. The metal nanoparticles accumulated in the plant tissue can be extracted by ashing and purification. But, this method has some major disadvantages such as complexity, high cost, and low efficiency. In addition to all these problems, environmental issues are the most controversial and challenging topic in this realm.

6. Conclusion

In situ synthesis of nanoparticles is one of the green techniques to fabricate nanoparticles. In contrast to the other green approaches such as using microbial synthesis or plant extract mediated synthesis, this technique does not seems to be efficient enough. But, by developing the phytomining technologies and introducing plants or even recombinant plants with increased efficiency for in situ syntheses of nanoparticles, this technique can be employed as nanoagriculture. It means that in the future it is possible to have farms that produce nanoparticles from the soil.

Ethical Considerations

Compliance with ethical guidelines

There was no ethical considerations to be considered in this research.

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Authors contributions

Writing: Saeed Taghizadeh and Seyedeh-Masoumeh Taghizadeh; Resources: Younes Ghasemi; Writing review & editing: Alireza Ebrahiminezhad.

Conflict of interest

The authors declared no conflict of interest.

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