



Review on Green Synthesis of Gold Nanoparticles

Shabnam¹, Jagdeep Kumar^{2,*}

Department Of Chemistry, University Institute of Sciences,

Chandigarh University, Gharuan-140413, Mohali, Punjab, India

Corresponding Author, e-mail-shabnamchoudharybalol@gmail.com

Abstract

Because of the impact of their greater surface area and smaller quantum sizes compared to bulk metal or other metal atoms, metal nanoparticles, such as those formed of gold, exhibit a number of unusual chemical and physical properties. The qualities that depend on size and shape of gold nanoparticles (GNPs) are particularly notable. Metal nanoparticles have received a lot of notice because of their distinct qualities and exciting prospective uses in biological sensing, electronics, photonics, and imaging. The latest developments in GNP synthesis are discussed in this review. Green chemistry measures were used to assess the production of gold nanoparticles, with a focus on Process Mass Intensity (PMI). Based on these measurements, opportunities for improving synthetic approaches were found. With PMIs that were often in the thousands, solvent usage was found to be the main obstacle for nanoparticle synthesis, even ones that were otherwise considered to be environmentally friendly. Since ligated metal nanoparticles are the most industrially relevant, but least environmentally friendly, their synthesis by arrested precipitation was chosen as the best chance for significant advances. Gold nanoparticles of small sizes and bio-stability are produced biochemically, and they are used in many biological applications.

Keywords: Gold, Nanoparticles, Green Synthesis, Gold Nanoparticles.

Introduction

Due of their unique physical, chemical, and potential properties use as metallic nanostructures, building blocks for nanodevices have received a lot of attention in the rapidly developing fields of nanoscience and nanotechnology. Therefore, it is crucial to synthesise nanoparticles with precise dimensions, high yields, high purity, and under gentle, environmentally friendly circumstances. The production of AuNP has generated significant interest due to its great stability, wide range of uses, and distinctive characteristic plasmon band among other metallic nanostructures[1]. Physical, chemical, and biological processes can all be used to make nanoparticles, however, the first two frequently require large energy inputs, as well as high temperatures and pressures, toxic substances are frequently used as well. Contrarily, biological methods that mimic nature by creating nanoparticles using microbes, algae, or plant extracts are far more hygienic and environment friendly. This feature has given the production of biomimetic nanoparticles tremendous relevance[2]. It implies that a researcher can alter proper behaviour in order to achieve a specific goal. For instance, it is possible to recognise diseases by altering the fluorescence colour of a particle. A more recent technique is the extra-cellular Using plant extracts, metallic nanoparticles are synthesys. Only roughly 41 papers have been published in this topic as of now, the first report in this field, which was released in 2003[3]. The word 'nanotechnology' is generally used to describe a field of engineering and research that concentrates on materials with dimensions between 1 and 100 nm. The adjective 'dwarf,' which in Greek means 'extremely small,' is where the word 'nano' originates. Its meaning 10⁻⁹ or 0.000000001 when used as a prefix. One billionth of a meter is a nanometer(nm)[4]. Numerous varieties of nanoparticles are covered in the literature, such as manganese nanoparticles, gold nanoparticles, silver nanoparticles, and so forth. The most popular nanoparticles among these are those made of gold and silver[5]. There are numerous ways to create these nanoparticles. These techniques include Synthesis by physical, chemical, and biological means. Because of its cost-effectiveness and environmental friendliness, green synthesis of nanoparticles is greatly preferred over chemical synthesis [6]. For synthesis of nanoparticles two types of approaches are seen. These are "Bottom-up" and "Top-down" approaches.

Top-down Approach: A top-down tactic is used to break down the material in bulk into nanometre scale structures or particles. Top-down synthesis methods are an improvement on those that have been utilized to create particles with a diameter less than a micron. In order to produce the appropriate structure with the proper qualities, top-down procedures either rely on the partition of bulk materials, their elimination, or bulk production methods' shrinkage. They are fundamentally easier to obtain. The semiconductor sector is a good

illustration of how the top-down strategy is being employed in industry to fabricate numerous man-made materials[7,8] where characteristics of metal oxide semiconductor field effect by using a lithography-based technique called photolithography, transistors (MOSFETs) are imprinted into a silica wafer. The process is centered on a forecast printing technology that's carried out in an instrument known as a 'stepper'. A silicon wafer that has been UV-light pre-spun with a light-sensitive substance is used as the substrate for the projection printing system, which projects transistor features through a photomask.

Drawbacks of the top-down approach of Synthesis: With Intel's May 2011 release of Tri-Gate, a manufacturing 3D transistor technique for 22 nm, semiconductor development is starting to approach its physical limits. Although though 193 nm light is already utilized to pattern wafers, it is projected that when smaller aspects need to be created, technical and material limits would be met. When smaller features are created, quantum effects and patterning errors, for example, will become more prominent (see Nanoelectronics, Nanotechnology). New intense UV irradiation, a mapping method, makes use of innovative solvents, optic components, and resistive components with high indices, must be used to create smaller features [9].

Bottom-up Approach: -The bottom-up alternative idea is the most effective since it potentially produces lesser waste and is therefore more cost-efficient. A substance is constructed from the bottom up, atom by atom, molecule by molecule, or cluster by cluster. This is referred to as a bottom-up technique. Scientists' desire to comprehend and imitate the pre-programmed ability of biological architectures to gather and organize oneself organised, yet dynamic, and functional, the development of the bottom-up technique has been greatly influenced by the supramolecular structures found in nature. In fact, the creation of three-dimensional intelligent nanodevices is made possible by the intriguing tool that supramolecular chemistry offers, which combines the ideas of molecular recognition and self-assembly. Artificial systems behave similarly to natural ones in that they can either respond to outside factors like electrical, chemical/biochemical, thermal, and photonic stimuli, or they can interact with other isolated molecules to generate functional materials. Several two-dimensional and three-dimensional self-assemblies can be used as the building blocks for creating brand-new nanotechnological devices.

Discussion

Methods to synthesize Gold Nanoparticles

Gold nanoparticles can be created using a variety of techniques, such as chemical, thermal, electrochemical, and sonochemical processes. [10,11]. These are some of the various techniques for creating gold nanoparticles:

Turkevich Method

Among the most popular techniques for creating AuNPs was developed by Turkevich in 1951 and is focused on the degradation of HAuCl_4 by citrate in H_2O . This is followed by a rapid addition of the trisodium citrate dihydrate and vigorous stirring of the boiling HAuCl_4 solution. The solution's colour shifts from bright yellow to wine red after a short while. Using this technique, AuNPs with a 20 nm diameter are produced. Citrate ions serve as both stabilising and reducing agents in this method [13,14]. In order to create AuNPs with diameters ranging from 15 to 150 nm, Frens modified the Turkevich process in 1973 by adjusting the ratio of the reducing agent or stabilising agent (trisodium citrate/gold). Numerous research teams have further modified the Turkevich-Frens approach (Frens 1973). According to research by Kimling et al., smaller AuNPs are more immediately stabilised by high citrate concentrations, but large AuNPs tend to assemble into bulk materials at low citrate concentrations [15]. According to a theoretical model and experimental findings, sodium citrate has recently been shown to play a significant impact in influencing the pH of the solution and size of the nanoparticle[16]. The impact of heat, pH, citrate content, and gold chloride concentrations has been extensively studied in the literature [17-19] discusses the distinctive qualities of AuNPs produced using citrate as the reductant.

Burst-Schiffrin Method

Brust and Schiffrin developed the Brust-Schiffrin technique in 1994. This technique made it simple to create AuNPs with regulated size and low dispersion that are thermally and air-stable. As a phase-transfer agent, tetraoctylammonium bromide (TOAB) is used. AuCl_4^- was moved from a water-based solution to a toluene phase in this technique, where it was subsequently reduced by NaBH_4 to produce dodecanethiol. As TOAB does not have a very strong affinity for the gold nanoparticles, Over the course of about two weeks, the solution will progressively aggregate. To prevent this, one can substitute gold with a stronger binder, such as an alkanethiol, which will bond to the metal and produce a nearly permanent solution. It is possible to precipitate and then

dissolve gold nanoparticles protected by alkanethiol. Thiols work better as binders because they have a strong affinity for the sulfur-gold bonds that result from the interaction of the two components. The organic phase turns from orange to deep brown when the reducing agent is added. This conclusively proves that AuNPs are produced [20].

Biological Method or Green Synthesis

Despite the fact that chemical techniques are the most popular to make metallic nanoparticles, the application of these methods is constrained since they require expensive and dangerous chemicals to act as reducing and stabilising agents. These nanoparticles could also be hazardous in medical applications [21]. Seeing this growing demand for development of cost-effective and environmentally responsible procedures for producing nanoparticles without the use of dangerous chemicals. Recent years have seen increased interest in biological manufacturing of nanoparticles as a green and ecologically safe method. Nanoparticles are created biologically by microbes, enzymes, and plants or plant extracts [22]. Because they are readily available, inexpensive, environmentally friendly, and non-toxic, plants are increasingly being used in nanoparticle production. A number of plants, including, Aloe vera, camphor tree, Coriander, Indian-almond, and lemongrass, and many more plants and herbs have recently been utilised in the biosynthesis of AuNPs. According to [23], recent publications of multiple works describe the production of AuNPs from plant extracts, including Ironwood, Horse gram, Lemon, Orange, and many more, that serves both as a reducing and stabilising agent.

These were a few of the techniques used to create gold nanoparticles. After being familiar with the processes used to create gold nanoparticles, we will explore the synthesis process, which is the primary goal of this review article. We will now shift our focus to the 'Green' synthesis, which refers to synthesis utilising plants and plant extracts, flowers and flower extracts, etc., since this review paper focuses primarily on the Green synthesis of gold nanoparticles.

Techniques to Extract Plant Materials

Utilizing extraction technology is the separating plant metabolites from raw materials is the initial step. Some fundamental factors need be taken into account before beginning an extraction process because they affect the extract's quality [24]. Key elements in the extraction of the targeted components are the chosen section of the plant material and the solvents, which must demonstrate easy absorption and the inability to change the solutes chemically. The used solvent must have low toxicity because the finished product will have residues of it. Temperature, the solvent's pH, the duration of the extraction, and the solvent-to-sample ratio, and the raw material particle size must all be taken into consideration when choosing an extraction technique. These elements may cause changes in the extracts' metabolite makeup [25]. AuNPs are generally produced using three extraction methods: solvent-based extraction, microwave-assisted extraction, and maceration extraction. [26]. However, one essential alternative to increase process efficiency is ultrasound-assisted extraction. The optimum extraction technique should be affordable, easy to use, quick, and simple enough to be completed in any laboratory [27].

Now, let us first discuss the different methods to extract plant extracts.

Solvent-based Extraction

The approach with the highest usage rate for getting natural compounds is solvent-based extraction. Using a suitable solvent, this procedure separates plant soluble metabolites, discarding the insoluble components [28]. Prior to beginning, it is crucial to have knowledge of the plant's characteristics, such as the raw materials' particle sizes and individual components, in order to choose the right solvent for the extracting. The extraction temperature, solvent to solid ratio, and process length, must all be carefully calculated. Element that enhances solute solubilization and diffusion can increase experiment effectiveness [29]. Solvent must be absorbed further into the solid matrix in order to create contacts with the accessible surface during the early stages of the extraction process. Later, for the solute to be collected, it must diffuse out of the solid matrix. Later, for the solute to be collected, it must diffuse out of the solid matrix. [30].

Microwave-Assisted Extraction

Solvent extraction has been widely employed in a variety of sectors, including environmental analysis, food and agricultural analysis, pharmaceutical medications, and herbal medicine, for the isolation of significant chemicals

as well as for qualitative and quantitative analysis. Since synthetic pharmaceuticals can have unwanted side effects, the latter, in particular, has drawn the attention of many researchers who are interested in substituting alternative medicine for them. Microwave energy is used to separate the analytes from the sample and place them in the solution. This causes rapid heating as a result of interacting with polar and polarisable substances, like water and those present in the plant matrix sample. They allow materials to transfer process heat to obtain the necessary quantity of energy [31]. Since they are both moving in the same direction, heat and mass transfer also have a synergistic impact that speeds up and enhances analyte recovery. As a result, when compared to other procedures, its application shortens the process time and solution volume [32]. Investigations have also uncovered more benefits including raising extract yield and selectively heating plant matter [33].

Maceration Extraction

To complete this process, following three basic steps are to be followed: The plant must first be ground into small pieces, added to a suitable solvent in a closed container, allowed to soak at room temperature for three days, and then pressed or strained by filtration to distinguish the liquid phase [34]. Even though it would seem like the simplest and most straightforward method, the necessity for large quantities of organic solvents leads to an issue with organic wastes, making a proper chemical waste management system necessary [35]. Additionally, this traditional approach for extracting natural products is time-consuming and exhibits low extraction efficiency. In order to facilitate the discharge of soluble phytochemicals, the method aims to soften and break down the cell walls of the raw materials. However, it can be advantageous to utilize it to extract thermolabile components [36].

Now, as we have learnt enough about GNP's, their methods of preparation and the green approach synthesis, let us discuss the green synthesis of Gold Nano Particles (GNPs) by using different types of plants, flowers and fruits extracts. Despite the fact that there are numerous plants, flowers, etc., to synthesize Gold Nanoparticles, we are hereby reviewing a few of them.

Green Synthesis of Gold Nanoparticles (GNPs) Using Aqueous Extract of Elettaria cardamomum (ELAICHI)

Plants and other plant-based bioresources that include phytochemicals can act as long-lasting, ecologically friendly reservoirs for the creation of metallic nanoparticles. By combining an aqueous solution of hydroxy tetrachloroauric acid (HAuCl) with an aqueous extract of Elettaria Cardamomum seed pod, a highly straightforward and time-friendly technique of producing green AuNPs. According to the Indian Medical System [37], a family of spices called Zingiberaceae is also known as "Cardamon," Choti elaichi in Hindi, and Alleicha in Odia. The fruit have three chambers, each with two rows of seeds that can range in quantity from 5 to 10, make up the bulk of its use. Uses for cardamom include fragrant, carminative, and as stimulant. It is applied as a compound tincture. [38].

Green Synthesis of Gold Nanoparticles with Aqueous Extracts of Neem (Azadirachta indica)

Neem is particularly appealing as a bioagent since it is affordable, accessible, and has potent antibacterial qualities that could improve the nanoparticles' biological activity created using the stabilizing effects of its broth's ingredients. Shankar et al's [40] investigation of neem in the synthesis of bimetallic gold-core, silver-shell nanoparticles were their first and only attempt to date. The goal of the study was to create a simple, scalable method for synthesizing gold nanoparticles that could be used for mass production. Drying a known quantity of Azadirachta Indica (Neem) to a fixed weight at 105°C allowed researchers to calculate the total solids content of the plant. This technology used the affordable and widely accessible bioagent neem to quickly and environmentally create gold nanoparticles. The resulting nanoparticles are fairly uniform in size and shape. These characteristics make this process potentially scalable for the mass manufacture of gold nanoparticles.

CONCLUSION

Green chemistry is a cutting-edge and constantly growing resource in the ongoing search for more environmentally friendly processes. The use of plant extracts in the creation of metal nanoparticles has recently gained a lot of interest due to its benefits over traditional physicochemical methods. Agriculture and the agroindustry may benefit from the use of AuNPs produced through green synthesis, notably as pathogen-specific antibacterial agents for which their efficacy has been demonstrated. Further research is needed to determine the impacts that continuous exposure to these nanoparticles may have on the soil, plants, and the ecosystem at large, even though recent research suggests that environmental concentrations of AuNPs have no impact on the diversity of microbial biomass. Therefore, for better utilisation of these nanotechnological advancements, local and national regulatory organisations must set norms and monitoring techniques. This literature examined the literature on the bio-reduction of AuNPs utilizing diverse bioagents, including microbial

cells and plant tissue. The optimum approach for the synthesis of AuNPs resulted from the advancement of bio-reduction over conventional chemical methods for large-scale NP manufacturing. These NPs are devoid of harmful chemicals, environmentally safe, straightforward, one step, and provide a standard reducing agent for the best stability, which results in green techniques.

REFERENCES

1. G. M. Whitesides, J. P. Mathias and C. T. Seto, *Science*, 1991, 254, 1312–1319.
2. Ankamwar B., Chaudhary M. and Sastry M., Gold nanotriangles biologically synthesized using tamarind leaf extract and potential application in vapor sensing, *Synth React Inorg Metal-Org NanoMetal Chem*, 35, 19–26 (2005).
3. Shankar S.S., Ahmad A. and Sastry M., Geranium Leaf Assisted Biosynthesis of Silver Nanoparticles, *Biotechnology Progress*, 19 (6), 1627-1631 (2003).
4. Th akkar KN ., Mhatre SS , and Parikh RY . 2010 . Biological synthesis of metallic nanoparticles . *Nanomedicine*. 6 : 257 – 262 .
5. Hainfeld JF, Slatkin DN, Focella TM, Smilowitz HM. *Br J Radiol* 2006;79:248–53.
6. Huang X, El-Sayed IH, Qian W, El-Sayed MA. *J Am Chem Soc* 2006;128:2115–20.
7. Y. Xia and G. M. Whitesides, *Angew. Chem. Int. Ed.*, 2006, 16, 3997.
8. H.-J. Kim, K.-J. Kim, and D.-S. Kwok, *Qual. Reliab. Eng. Int.*, 2010, 26, 765.
9. B. K. Teo and X. H. Sun, *J. Cluster Sci.*, 2006, 17, 529.
10. Mandal S . 2014 . Synthesis of radioactive gold nanoparticle in surfactant medium . *J Radioanal Nucl Chem*. 299 : 1209 – 1212.
11. Nakanishi M , Takatani H , Kobayashi Y , Hori F , Taniguchi R , Iwase A , and Oshima R . 2005 . Characterization of binary gold/platinum nanoparticles prepared by sonochemistry technique . *Appl Surf Sci*. 241 : 209 – 212.
12. Zhao P , Li N , Astruc D . 2013 . State of the art in gold nanoparticle synthesis . *Coord Chem Rev*. 257 : 638 – 665 .
13. Hu M , Chen J , Li ZY , Au L , Hartland GV , Li X , et al . 2006 . Gold nanostructures: engineering their plasmonic properties for biomedical applications . *Chem Soc Rev*. 35 : 1084 – 1094.
14. Turkevich J , Stevenson PC , Hillier J . 1951 . Nucleation and growth process in the synthesis of colloidal gold . *Discuss Faraday Soc*. 11 : 55 – 75.
15. Kimling J , Maier M , Okenve B , Kotaidis V , Ballot H , and Plech A . 2006 . Turkevich method for gold nanoparticle synthesis revisited . *J Phys Chem B*. 110 : 15700 – 15707.
16. Kumar A , Murugesan S , Pushparaj V , Xie J , Soldano C , John G , et al . 2007 . Conducting organic – metallic composite submicrometer rods based on Ionic liquids . *Small*. 3 : 429 – 433 .
17. Link S , El-Sayed MA . 1999 . Size and temperature dependence of the plasmon absorption of colloidal gold nanoparticles . *J Phys Chem B*. 103 : 4212 – 4217.
18. Patungwasa W , Hadak JH . 2008 . pH tunable morphology of the gold nanoparticles produced by citrate reduction . *Mater Chem Phys*. 108 : 45 – 54.
19. Zabetakis K , Ghann WE , Kumar S , Daniel M . 2012 . Effect of high gold salt concentrations on the size and polydispersity of gold nanoparticles prepared by an extended turkevich-frens method . *Gold Bull*. 45 : 203 – 211.
20. Brust M , Walker M , Bethell D , Schiffrin DJ , Whyman RJ . 1994 . Synthesis of thiol-derivatised gold nanoparticles in a two-phase liquid – liquid system . *Chem Soc Chem Commun*. 7 : 801 – 802.
21. Noruzi M , Zare D , Khoshnevisan K , Davoodi D . 2011 . Rapid green synthesis of gold nanoparticles using Rosa hybrida petal extract at room temperature . *Spectrochim Acta A Mol Biomol Spectrosc*. 79 : 1461 – 1465.
22. Singh M , Kalaivani R , Manikandan S , Sangeetha N , Kumaraguru AK . 2013 . Facile green synthesis of variable metallic gold nanoparticle using Padina gymnospora, a brown marine macroalga . *Appl Nanosci*. 3 : 145 – 151.
23. Vadlapudi V , D. S. V. G. K. Kaladhar . 2014 . Review: green synthesis of silver and gold nanoparticles . *Middle-East J Sci Res*. 19 : 834 – 842.
24. Pandey, A.; Tripathi, S. Concept of standardization, extraction and pre phytochemical screening strategies for herbal drug. *J. Pharmacogn. Phytochem*. 2014, 2, 115–119.
25. Belokurov, S.S.; Narkevich, I.A.; Flisyuk, E.V.; Kaukhova, I.E.; Aroyan, M.V. Modern Extraction Methods for Medicinal Plant Raw Material (Review). *Pharm. Chem. J*. 2019, 53, 559–563.
26. Azwanida, N.N. A Review on the Extraction Methods Use in Medicinal Plants, Principle, Strength and Limitation. *Med. Aromat. Plants* 2015, 4.
27. Yahya, N.A.; Attan, N.; Wahab, R.A. An overview of cosmeceutically relevant plant extracts and strategies for extraction of plant-based bioactive compounds. *Food Bioprod. Process*. 2018, 112, 69–85.
28. Dekebo, A. Introductory Chapter. *Plant Extr*. 2019.
29. Zhang, Q.-W.; Lin, L.-G.; Ye, W.-C. Techniques for extraction and isolation of natural products: A comprehensive review. *Chin. Med*. 2018, 13.

30. Schlosser, Š.; Kertész, R.; Marták, J. Recovery and separation of organic acids by membrane-based solvent extraction and pertraction: An overview with a case study on recovery of MPCA. *Sep. Purif. Technol.* 2005, 41, 237–266.
31. Bhat, A.R.; Najjar, M.H.; Dongre, R.S.; Akhter, M.S. Microwave assisted synthesis of Knoevenagel Derivatives using water as green solvent. *Curr. Res. Green Sustain. Chem.* 2020.
32. Lux, C.; Lubio, A.; Ruediger, A.; Robert, S.; Muehlethaler, C. Optimizing the analysis of dyes by Surface Enhanced Raman Spectroscopy (SERS) using a conventional-microwave silver nanoparticles synthesis. *Forensic Chem.* 2019, 16, 100186.
33. Ahmed, S.; Ahmad, M.; Swami, B.L.; Ikram, S. A review on plants extract mediated synthesis of silver nanoparticles for antimicrobial applications: A green expertise. *J. Adv. Res.* 2016, 7, 17–28.
34. Trusheva, B.; Trunkova, D.; Bankova, V. Different extraction methods of biologically active components from propolis: A preliminary study. *Chem. Cent. J.* 2007, 1, 13.
35. Ferioli, F.; Giambanelli, E.; D'Alessandro, V.; D'Antuono, L.F. Comparison of two extraction methods (high pressure extraction vs. maceration) for the total and relative amount of hydrophilic and lipophilic organosulfur compounds in garlic cloves and stems. An application to the Italian ecotype "Aglia Rosso di Sulmona" (Sulmona Red Garlic). *Food Chem.* 2020, 312, 126086.
36. Altemimi, A.; Lakhssassi, N.; Baharlouei, A.; Watson, D.G.; Lightfoot, D.A. Phytochemicals: Extraction, Isolation, and Identification of Bioactive Compounds from Plant Extracts. *Plants* 2017, 6, 42.
37. Shaban, M.A.E., K.M. Kandeel, G.A. Yacout and S.E. Mehaseb, The chemical composition of the volatile oil of *Elettaria cardamomum* seeds. *Pharmazie* 42: 207-208.
38. Trease and Evans, *Pharmacognosy*. W.B Saunders, 15 Edition, pp: 353-354.
39. Monalisa Pattanayak and P.L. Nayak, *World Journal of Nano Science & Technology* 2(1): 01-05, 2013.
40. Shankar S.S., Rai A., Ahmad A. and Sastry M., Rapid synthesis of Au, Ag, and bimetallic Au core–Ag shell nanoparticles using neem (*Azadirachta indica*) leaf broth, *J Colloid Interf Sci.*, 275, 496– 502 (2004).