Green Synthesis:Natural Way for Gold Nanoparticles Synthesis and Application.

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ABSTRACT

Recently a lot of research on nanoparticles (NPS) has been conducted in terms of therapeutics and diagnosis. The basic behind this concept (nanotechnology) is to use specific molecules and atoms to build structures that work. This technology has a wide area of application in medical fields nanoparticles are unique in their properties. The concept of nanotechnology changes medical treatment with enhanced quality. Based on a number of factors, the creation of nanoparticles using green technology is preferable. Green techniques eliminate the demerits and generate environment-friendly products. This involves the use of plant or plant parts for the bio-reduction of metal ions. This process eliminates all demerits with conventional synthetic processes i.e., they are eco-friendly. Now a days bio-waste materials to produce highly efficient, biocompatible, economic, and eco-friendly metallic nanoparticles could support waste valorization and lead to environmental sustainability**.**The goal of the current review is to highlight the processes used to create metallic nanoparticles, with a focus on the use of diverse natural antioxidants in their production.

KEYWORDS- Green synthesis, gold nanoparticles, natural reducing agent, nanoparticles, chemical nanoparticle

I. INTRODUCTION

Intensive research on nanoparticles(NPS) hasbeen conducted in the field of therapeutics and diagnosis, Nanoparticles areunique in theirproperties that change the scenario ofdisease treatment with more potent, less toxic, and smart outcomes. This chapter highlightsthe major categories of NPS used for drug delivery and diagnosis. fabrication techniques, characterization methods, and the utilities of NPs in drug/gene delivery [1] The creation and advancement of nanoparticles are the focus of the rapidly expanding study field known as nanotechnology. Nanoparticles are tiny objects with sizes between 1 and 100 nm that are smaller than the bulk substance. Nanoparticles of different types are currently being produced using differenttechniques. Numerous fields of other businesses, including medicine and a number of cosmetic and apparel companies, utilize nanoparticles for a variety of purposes. [2]

II. GOLD NANOPARTICLES

For millennia, gold has been regarded as a mysterious and valuable commodity,[3] Gold nanoparticles are attracting a lot of interest in biomedical applications right now. nanoparticles of Gold can be of different colors or various hues according to their physical properties and surrounding conditions.[4]. After being irradiated with light of appropriate wavelengths, these visible hues represent the underlying coherent oscillations of conduction-band electrons ("plasmons").These plasmons are responsible for light's strong absorption and elastic scattering, which makes gold nanoparticles ideal for biological sensing and imaging.In a visible light microscope, it's enough to identify individual nanoparticles but researchers must aware of the potential toxicity before any in vivo applications of gold nanoparticles. [5]

A. Fabrication of gold nanoparticles

There are several methods for making nanoparticles, the most basic of which is to reduce gold salts in the presence of a reducing agent. This causes the gold ions to nucleate, resulting in nanoparticles. A stabilizing agent is frequently added throughout the synthesis process to help prevent aggregation. [6]) was the first to report on this strategy, which was later improved upon by Frens. Sodium citrate serves a dual purpose in this technique: it acts as a reducing agent and then as a stabilizer once it is absorbed onto the surface. Recent improvements in nanoparticle production have made it possible to create stable particles with smaller (2–6 nm) and more monodisperse size and form.

The Brust-Schiffrin system, which produces huge numbers of higher quality monolayer shielded gold clusters, is the most advanced of these methods. A phase-transfer agent is used to transport gold ions from an aqueous solution of gold salt into toluene (tetrabutylammonium bromide, TOAB). After adding a non-polar organic thiol (typically a thiol-terminated long-chain alkane), a reducing agent is quickly added. The thiol-mediated capping of the gold cluster eventually prevents the reduced gold atoms from agglomerating. Because of the strong gold-sulfur interaction, the thiol ligands create an extremely stable organic monolayer. The gold:ligand stoichiometry can be changed to control the size of the gold clusters.

Metal nanoparticle synthesis processes entail reducing metal ions into nanoparticles. Reducing agents can be found in both natural and synthetic forms.Chemical procedures require the use of synthetic substances that are not healthy or environmentally friendly, necessitating the development of green methods. Nowadays Plant-based extracts or phytoconstituents, as well as microorganisms, are used in the reductionof metal ions, processes [7] These techniques areless cost, nanoparticles are high in polyols and antioxidants, which, in addition to their reducing characteristics, help to stabilize the nanoparticles once they've been created. Furthermore, the size of nanoparticles can be modified based on the reducing agent's method of action.[8]. chemical, reducing agents are used to preparepure and stable nanoparticleswithout any accumulation.

III. GOLD NANOPARTICLES(AuNP)

According to new research, nanomaterials serve a critical role in the growth of nanoscience and nanotechnology. In comparison to other tiny or bulk materials, nanostructured materials exhibit a wide range of physical and chemical properties due to their larger surface area, nanoparticles have a unique inherent reactivity that makes them excellent for the production of medicines.[9] The type of surface functional groups on nanoparticles, influence how nanomaterials interact with biological systems

Due to their distinctive characteristics, gold nanoparticles (AuNPs) have caught the attention of researchers in a number of fields. Since the turn of the century, scientists have been researching the existence of anisotropic gold nanoparticles. They have found that these particles differ from spherical gold nanoparticles in terms of structure, optical properties, electronic properties, magnetic properties, and catalytic properties and that anisotropic gold nanoparticles are generally better than spherical gold nanoparticles[10] When analytes attach to AuNPs, their physicochemical properties, such as conductivity and redox behavior right alter, producing detectable signals in diagnostics.Due to their enormous surface area, which enables a dense presentation of multifunctional moieties, AuNPs can also be employed as therapeutic platforms (e.g., drugs and targeting agents).

IV. PHYSICAL PROPERTIES OF GOLD NANOPARTICLES

A. Diameter, surface area, and volume

As the size is unique Nanoparticles have unique properties. All nanoparticles regardless of their chemical constituents, have a surface area:extremely high-volume ratios. The physical properties associated with nanoparticles such as solubility and stability are dominated by thenature of the nanoparticle surface.Large surface-to-volume ratios are essential in applications like catalysis, but gold's true properties are different at the nanoscale. Because of their plasmon resonance, spherical gold nanoparticles, for instance, have a remarkable capacity to scatter visible light.

B. Shape and crystallinity

The shape and crystallinity of gold nanoparticles Depend on the process of manufacturing, The presence of a stabilizing polymer that binds to one crystal face more strongly than the others is what most frequently leads to the formation of anisotropic forms. They developed methods at nanocomposite for reducing the size of crystalline domains within our spherical nanoparticles so that their spectral properties are less variable.

C. Nanoparticles surface

In solution, molecules attach to the surface of nanoparticles to form a double layer of charge that inhibits particle aggregation. Citrate is frequently employed as a capping agent because it is weakly attached to the nanoparticle surface and easily displaced by other molecules Tannic acid is a multidentate capping ligand[11]

It's vital to note that most nanoparticles' surfaces are dynamic and heavily impacted by their surroundings. Varied conditions will have different effects on the particle. The double layer will collapse in high salt settings, causing nanoparticle aggregation. Proteins and other biomolecules frequently bind to particles and stabilize them. When working with nanoparticles, it's important to anticipate surface changes and plan accordingly. When functionalizing nanoparticles with biomolecules, for example, it is advisable to first expose the particles to the biomolecule in a low-salt solution before adding salt to bring the solution up to isotonic conditions.PVP (polyvinylpyrrolidone) is a polymer that adheres tightly to the surface of gold nanoparticles. it gives better stabilityand difficult to displace.

D.Particle stability

For charge-stabilized particles, the zeta potential serves as an indicator of the particle's stability. Electrostatic repulsion is frequently sufficient for nanoparticles with zeta potentials between 20 and -20 mV to remain stable in the solution.[12].The zeta potential is very responsive to other molecules or pollutants in the solution, and gold nanoparticles are rapidly displaced. An unwashed pipet tip may add enough material to destabilize the particles by dislodging the ionically attached stabilizing molecules. Highly acidic or basic solutions can speed up the dissolution of nanoparticles into an ionic state, which can then be re-deposit onto existing nanoparticles, altering their average diameter and size distribution.[13]

E. Surface chemistry and Functionalization

A wide range of materials can be used to functionalize gold nanoparticles. Capping agents like polyvinylpyrrolidone (PVP) and tannic acid are commonly employed to stabilize gold nanoparticles. a variety of other proteins, peptides, and oligonucleotides are often employed to coat gold nanoparticles utilized in biological applications. Physisorption or making use of the exceptionally stable thiol-gold bonds can be used to bind molecules to a gold surface. Molecules that 'flip' the surface charge of negatively charged gold nanoparticles to a positively charged surface can be used to functionalize particles.[14]

Particles can also be functionalized to provide reactive groups (for example, amine- or carboxy-terminated surfaces) for subsequent conjugation by the customer. Dielectric shells (for example, silica, aluminum oxide, and titanium dioxide) with a precisely controlled thickness can be used to encapsulate the particles, change the optical properties, or incorporate fluorescent dyes. NanoComposix provides a wide range of custom modifications to nanoparticle surfaces.[15]

Table 1. DIFFERENT METHODS FOR SYNTHESIS OF GOLD NANOPARTICLES

Name of the Method	Method and output	References
Turkevich method	It's generally utilized to make somewhat monodisperse spherical gold nanoparticles. suspended in water (diameters of roughly 10 nm to 20 nm). Larger particles can be made, but only at the expense of the form and mono disparity of the nanoparticles. The reaction of a small amount of heated H[AuCl4] with an equal amount of trisodium citrate solution is used in this approach. citrate ions serve as both a capping and a reducing agent, this reaction results in the formation of gold nanoparticles. By using less trisodium citrate, as little as 0.05 percent, larger nanoparticles can be created.	[16]

Brust method	It's being utilized to make gold nanoparticles in organic solvents that aren't generally miscible with water like toluene. H[AuCl4] or chloroauric acid solution reacts with tetraoctylammonium bromide solution in this procedure. The reaction takes place in sodium borohydride (NaBH4) and toluene, which are both reducing agents and anticoagulants. 3. This method produces gold nanoparticles with a diameter of 5 nm to 6 nm.[16]	[17]
Perrault's method	This involves using hydroquinone to reduce H[AuCl4] or chloroauric acid inside an aqua solution containing gold nanoparticle seed (of 15 nm diameter). This seed-based gold nanoparticle synthesis approach is quite similar to the one employed in the production of photographic film. The latter involves the injection of reduced silver on the film's surface, which causes silver grains to grow inside the film. Similarly, gold nanoparticles can catalyze the reduction of ionic gold on their surface by combining it with hydroquinone. A stabilizer such as a citrate aids in the regulated deposition of gold atoms on nanoparticles. [17]	[18]
Martin's method	In 2010, Martin and Each created a reasonably easy method that produces practically monodisperse gold nanoparticles in water. This technique involves changing the ratio of NaBH4-NaOH ions to HAuCl4-HCl ions so that it remains well inside the sweet zone in order to fine-tune the reduction stoichiometry. It enables repeatable diameters in the 3–6 nm range when combined with heating. The aqueous particles retain their colloidal stability due to the high charge produced by the excess ions in the solution. They can be combined with hydrophobic molecules or coated with various hydrophilic functionalities to make them usable in non-polar liquids.	[19]

V. GREEN SYNTHESIS OF METAL NANOPARTICLES

The green synthesis of metallic nanoparticles has been an exciting new field of study in recent years. Due to a number of benefits, such as being affordable, producing nanoparticles with good stability, requiring less time, producing non-toxic by-products, being environmentally friendly, and is easily scaled up for large-scale synthesis.Green nanoparticle synthesis has gained popularity in recent years. [20] Since chemical synthesis techniques lead to the presence of toxic chemical species adsorbed on the surface of nanoparticles, green synthesis has attracted interest in the development of various metal and metal oxide nanoparticles. These metal nanoparticles may now be produced more reliably and affordably using green synthesis techniques. [21]

However, the chemical synthesis of nanoparticles has been reported to have several issues.

a. Thermal processing is required for the creation of some nanoparticles, according to research.
b. The physicochemical properties of nanoparticles may be altered as a result of this procedure. Comprising their density, crystal structure, and the presence of surface pollutants are synthesized.
c. There is a risk of toxicity from chemically manufactured nanoparticles, also known as engineered nanomaterials (ENM) if they are used for biological applications.
d. pollutants, are synthesized. The environment should likewise be treated with caution when these particles are released.Small changes in ambient temperature during synthesis and storage, might cause unanticipated and non-reproducible features in nanoparticles[22].

Because of the aforementioned facts, eco-friendly nanoparticle production technologies have received considerable attention. The goal was to use green synthesis and biotechnological technologies to create ecologically friendly and nontoxic nanoparticles [23]. The advantage of green nanoparticle synthesis over chemical nanoparticle synthesis is that the nanoparticles created have a more diversified nature, greater stability, and acceptable dimensions, and they are synthesized in a single process. During chemical synthesis, undesirable circumstances are avoided, and only physiological temperatures, pH, and pressure are employed in green synthesis, with biological components acting as reducing and capping agents, all at a low cost [24,25]

VI. ROLE OF REDUCING AGENTS ON NANOPARTICLES SYNTHESIS

Two important processes are involved in the chemical reduction of AuNPs:1. Borohydrides, citric and oxalic acids, polyols, hydrogen peroxide, and sulfites are only a few examples of reduction agents. They supply electrons to decrease gold ions, Au3 and Au, to Au0, the electric state of nanoparticles, and Stabilizers such as trisodium citrate dihydrate, sulfur ligands (mainly thiolates), phosphorus ligands, polymers, surfactants (especially cetyltrimethylammonium bromide, CTAB), and others They prevent nanoparticles from aggregating by imputing a repulsive force that regulates the velocity, final size, and geometric shape of the nanoparticles' growth. The stabilizing agent and the reducing agent are probably the same molecules. The synthesis of nanoparticles is very dependent on several variables. Increased dissolution rate to ionic form, which can re-deposit onto existing nanoparticles, can affect the average diameter and size distribution in acidic or basic fluids.

NATURAL REDUCING AGENTS

Techniques for creating metal nanoparticles mainly include reducing metal ions in order to form nanoparticles. Hanping and others, 2021) Reducing agents come from both natural and artificial sources. Green approaches are required since chemical methods use synthetic substances that are not safe or environmentally friendly. Using plant-based extracts or phytoconstituents and microorganisms like bacteria, yeast, and fungi, green synthesis processes reduce metal ions. (Mandal and others, 2021).Polyols and antioxidants, which have reducing characteristics as well as the ability to stabilize newly created nanoparticles, are abundant among the phytoconstituents used in the synthesis of metal nanoparticles. Additionally, the mechanism of the reducing agents involved in nanoparticle synthesis can be used to modulate nanoparticle size. (Mandal and others, 2021)

CHARACTERISTICS OF NATURAL REDUCING AGENTS:

- Reducing agents tend to give away electrons. top reducing agents are the metals present at s-block in the periodic table.

- The reducing agent after losing electrons gets oxidized and also causes the other reactant to get reduced via providing electrons.
- All of the correct reducing agents have atoms that have low electronegativity and a good capacity of an atom or a molecule to attract the bonding electrons and the species have very small ionization energies.
- All the oxidation and reduction reactions contain the transfer of electrons.
- While a few substances are oxidized, it is said to lose electrons and the substance which gets electrons is stated to be reduced.
- If the substance has a strong tendency to lose electrons, then it is said to be a strong reducing agent (because it will reduce the opposite substances through donating electrons).

Table 02 :Research on Green synthesis by using natural substances and

	Work done	
Sinan et al., (2018)	Studied the oxidation of DA to create quinone units, which catalyze the creation of semiquinones, which are required for the synthesis of AuNPs. These semiquinone radicals (SMQs) reduce the Au(III) ions to generate the initial AuNPs, and the first AuNPs then accelerate continued growth, with nucleation taking place where the SMQs, phenols, and phenolates can act as reductive species. DA also oxidizes and polymerizes on the AuNPs, forming a polydopamine capping layer. As a result, we anticipate that the innovative process reported here will encourage us to look into producing noble metal NPs using additional polyphenols.	[26]

Singh et al., (1990)	Synthesized by changing the ratio of AuCl4 and AgNO3 to clove extract, where eugenol is the major component, gold and silver nanoparticles of various shapes and sizes were created. The evolution of Au and Ag nanoparticles resulting from the reduction of different ratios of AuCl4 and AgNO3 with an optimized concentration of clove extract was studied using surface plasmon behavior as a function of time. The inductive effect of methoxy and allyl groups situated at ortho and para positions of the proton releasing –OH group, as two electrons are released from one molecule of eugenol, is responsible for the reduction of AuCl4 and AgNO3 by eugenol. After then, the anionic form of eugenol develops a resonant structure	[27]
.3	Pomegranate peel extracts have been used as reducing and stabilizing agents in the biosynthesis of AuNPs. Appropriate concentrations of both pomegranate peel extract and chloroauric acid solution (HAuCl4) were mixed. The reaction mixture was held at room temperature for 24 h with periodic shaking and the colour change from gold to pink confirmed the formation of pomegranate extracted-Au NPs.	[28]
04Seo et al., (2015)	Caffeic acid was used as a green reducing agent in the sustainable production of gold nanoparticles from gold ions. Spectroscopic and microscopic measurements confirmed the creation of gold nanoparticles. High-resolution transmission electron microscopy and atomic force microscopy images revealed spherical nanoparticles with an average diameter of 29.99 7.43 nm. In the presence of sodium borohydride, the newly produced gold nanoparticles showed catalytic activity in the reduction of 4-nitrophenol to 4-aminophenol. This technique permits the production of green catalysts using plant natural products as reducing agents, meeting a growing demand for environmental efforts.	[29]

Osonga et al., (2016)	Osongareported using water-soluble naturally occurring flavonoids, a novel technique for the manufacture of gold nanoparticles (AuNPs) has been developed. The shape of the AuNPs that resulted was spherical, triangular, cubicle, hexagonal, and rectangular.	30
V.P. Aswathi, et. Al, 2022	Tea waste constitutes components such as polysaccharides, caffeine and tannic acid which has the potential to stabilize metal and metal oxide nanoparticles as it can act as a reducing and capping agent. Silver nanoparticles can be synthesized using an aqueous extract of tea waste. It has potential catalytic activity in degrading cationic organic dyes [16].	31

Conclusion

Biomedical sciences have used gold nanoparticles for a variety of purposes. These metal nanoparticles have special qualities like surface plasmon resonance and size-dependent color shift. Numerous compounds have been functionalized on the surface of gold nanoparticles, but because of their characteristics and significance in living systems, On the whole, this brief review explores the recent advances of the last decade in the utilization of natural products for the sustainable fabrication of NPs with numerous applications in the medical industry, drug delivery, cancer treatments, food industry, and water treatment. However, several obstacles make it challenging to obtain and sustain gold nanoparticle associations. Cumulatively, study on the last two decades shows an exponential increase in the pace of biowaste-assisted nanomaterials synthesis owing to its easy availability, better stability, and dispersion in aqueous solutions. In the final analysis, the use of biowaste is found to be more advantageous over other raw materials in terms of zero contamination, simple procedures, low toxicity, high stability, and cost-effectiveness in the NPs synthesis.

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