

Gold Nanoparticles Strategies: Comparing Modern with Ancient Techniques

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ABSTRACT

Gold nanoparticles (AuNPs), due to their excellent optical, catalytic, physicochemical, and biological properties, have emerged as one of the most promising nanomaterials. This review summarizes recent advances in the synthesis strategies of AuNPs, focusing on green, chemical, and physical synthesis methods. It emphasizes critical discussions on the applications of AuNPs in cancer therapy, drug delivery, catalysis, antimicrobial activity, imaging, and environmental remediation. Special emphasis is placed on eco-friendly green synthesis approaches using plant extracts and biopolymers, as well as recent developments in photothermal therapy, radio sensitization, immunotherapy, and clinical translation. Key challenges, which include toxicity, long-term bio distribution, scalability, and regulatory barriers, are also analyzed.

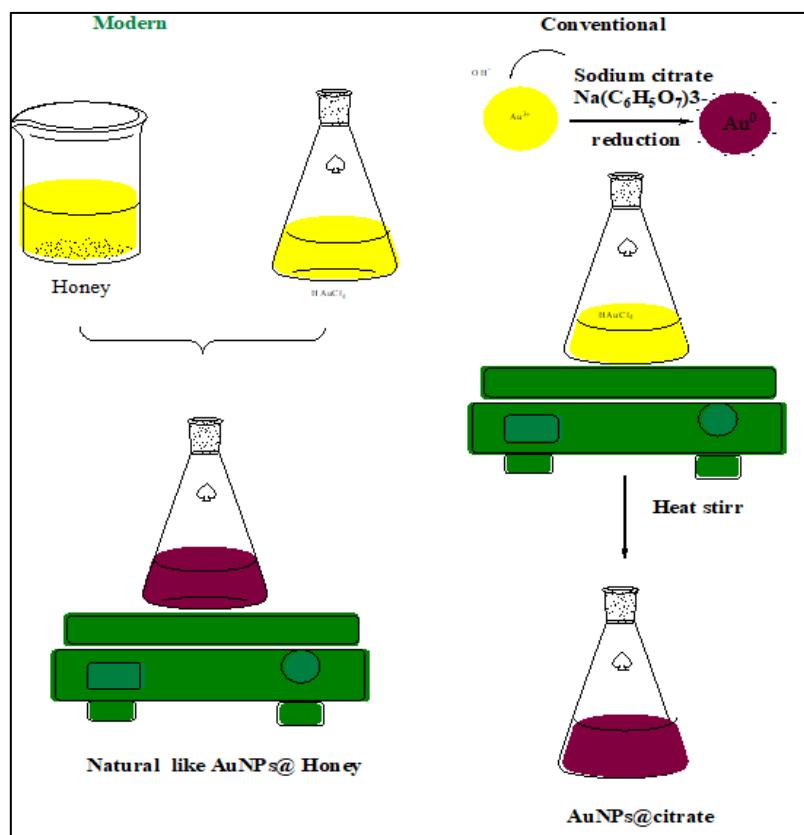


Figure 1: Modern and conventional synthesis of AuNPs

Keywords: Gold Nanoparticles, Modern Synthesis, Green Synthesis, Green Technology, Conventional approaches.



1. INTRODUCTION

Gold nanoparticles (AuNPs) have emerged as a cornerstone of nanomedicine and materials science owing to their unique optical, electronic, catalytic, and biological properties. Their exceptional versatility arises from their nanoscale dimensions and tunable surface chemistry, enabling applications across fields as disparate as diagnostics, targeted drug delivery, catalysis, sensing, and environmental remediation. Over recent decades, an increasing focus on sustainable, precise, and application-driven nanotechnology has profoundly influenced the development of AuNP synthesis methodologies, particularly for biomedical applications such as cancer therapy, including breast cancer. This systematic review aims to provide a comprehensive overview of AuNP synthesis methods, tracing their evolution from ancient and traditional practices through to cutting-edge modern techniques. The review also examines recent advancements in AuNP preparation, explores the impact of synthesis methods on nanoparticle properties, and critically evaluates the relevance of these developments for cancer therapy, with particular attention to breast cancer applications. The review further discusses the environmental, reproducibility, scalability, and regulatory challenges associated with AuNP synthesis, before offering perspectives on future research directions. [1-8]

2. Historical Perspective: From Ancient Gold Nanoparticles to Early Modern Synthesis

2.1 Early Uses of Gold Nanoparticles

The use of gold for medicinal and decorative purposes dates back millennia, with colloidal gold suspensions being utilized in ancient China and India for therapeutic applications. However, it was not until the Middle Ages in Europe that the preparation of colloidal gold for health elixirs known as “aurum potabile” gained popularity, albeit with limited scientific control over the process or understanding of particle size and composition. Early recipes for colloidal gold often involved the reduction of gold salts using plant extracts, honey, or other organic substances, reflecting rudimentary green synthesis concepts. These methods produced suspensions containing a wide range of particle sizes and shapes, with properties heavily dependent on the nature of the reducing and stabilizing agents, as well as reaction conditions.

While lacking the precision of modern techniques, these approaches laid the groundwork for subsequent scientific investigation into the synthesis and biomedical utility of AuNPs. [9-14]

2.2 Emergence of Controlled Chemical Methods

The 19th and 20th centuries witnessed significant advances in colloidal chemistry, culminating in the development of standardized chemical methods for AuNP preparation. The Turkevich-Frens method, introduced in 1951, remains the archetype of classical chemical synthesis. In this approach, gold (III) chloride is reduced to metallic gold by sodium citrate in aqueous solution, yielding relatively monodisperse, spherical nanoparticles. The Brust-Schiffirn method, developed in the 1990s, allowed for the synthesis of hydrophobic AuNPs in organic solvents using thiol ligands, greatly expanding the versatility and functionalization potential of AuNPs.

While these chemical methods represented a leap forward in control and reproducibility, they often relied on hazardous reducing agents and surfactants, limiting their biocompatibility and scalability for medical applications. Nonetheless, they provided the foundation for the modern science of nanoparticle synthesis and enabled systematic exploration of AuNP properties as a function of size, shape, and surface chemistry. [15-19]

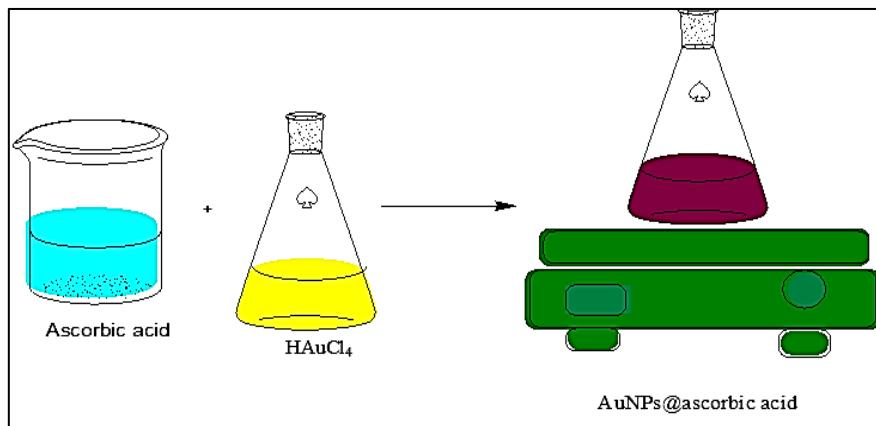
3. Classification of Synthesis Methods: Traditional Versus Modern Approaches

3.1 Traditional Synthesis Techniques

3.1.1 Chemical Reduction Methods

The classical chemical reduction of gold salts remains one of the most widely used and well-understood approaches to AuNP synthesis. The Turkevich-Frens and Brust-Schiffirn methods allow for precise control over particle size and morphology by modulating reactant concentrations, temperature, and reducing agent strength. Variations of these methods have enabled the generation of diverse nanostructures, including spheres, rods, cages, and core-shell architectures. [19-27]

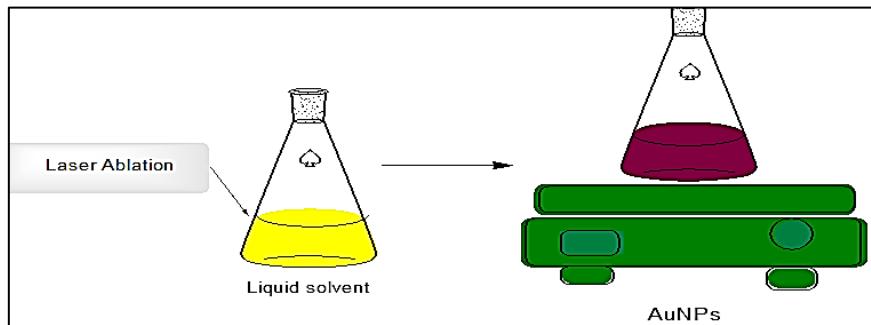
However, a major limitation of traditional chemical methods is the frequent use of toxic reducing and capping agents, such as sodium borohydride, hydrazine, and cetyltrimethylammonium ammonium bromide (CTAB), which pose environmental and biosafety risks. The need for extensive post-synthesis purification and surface modification further complicates their integration into biomedical workflows. [28-30]

**Figure 2: Chemical method of AuNPs synthesis**

3.1.2 Physical Techniques

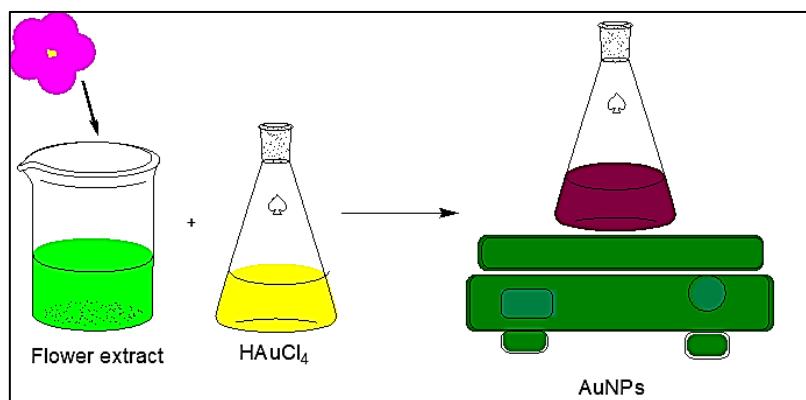
Physical methods for AuNPs synthesis, such as laser ablation in liquids, thermal evaporation, and sputtering, offer the advantage of producing high-purity nanoparticles without chemical contamination. Pulsed laser ablation, in particular, has been recognized as a rapid and “green” route to generate spherical, highly stable, and biocompatible AuNPs with strong photothermal properties. [31-39]

The principal drawbacks of physical methods include high energy consumption, expensive instrumentation, and challenges in scaling up for large-scale production. Furthermore, while particle purity is high, control over size distribution and shape is often inferior to chemical methods unless complex post-processing is employed. [40-43]

**Figure 3: Physical method of AuNPs synthesis**

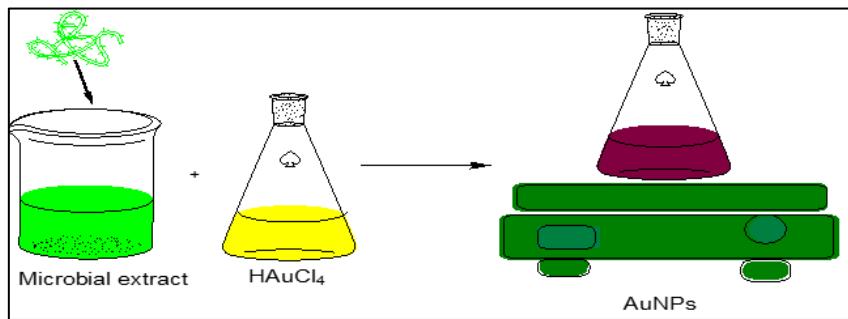
3.1.3 Early Biological (Green) Approaches

The use of biological systems for AuNPs synthesis predates modern green nanotechnology. Plant extracts, bacteria, fungi, and algae have long been known to reduce gold ions and stabilize nascent nanoparticles. Plant-mediated synthesis is particularly attractive due to its simplicity, use of aqueous solvents, and operation at ambient conditions. The wide variety of phytochemicals flavonoids, phenolics, terpenoids, alkaloids in plant extracts serves as both reducing and capping agents, enabling the formation of biocompatible AuNPs with diverse morphologies. [44-45]

**Figure 4: Plant extract-mediated synthesis for AuNPs**

3.1.4 Microbial Synthesis

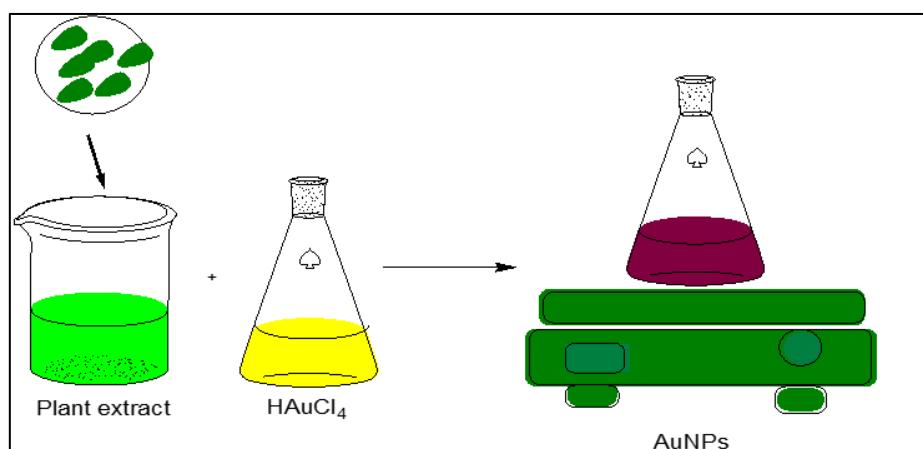
Microbial synthesis of AuNPs occurs via intra- or extracellular reduction of gold ions, mediated by enzymes and other biomolecules. While offering excellent biocompatibility, traditional biological methods often suffer from limited reproducibility due to variability in biological materials and challenges in controlling nanoparticle characteristics. [46]

**Figure 5: Microbial synthesis for AuNPs**

3.2 Modern and Advanced Synthesis Approaches

3.2.1 Green Nanotechnology and Sustainable Methods

Modern green synthesis methodologies seek to minimize environmental impact, reduce toxicity, and enhance biocompatibility by employing natural, biodegradable substances as reducing and stabilizing agents. These include plant-derived polyphenols, sugars, proteins, amino acids, polysaccharides (e.g., chitosan, alginate, starch), and vitamins (e.g., ascorbic acid). Such methods enable one-pot, low-temperature synthesis of AuNPs with inherent biomolecular coatings, improving colloidal stability and biological activity. Biomolecule-mediated synthesis leverages the specific functional groups of proteins, nucleic acids, and polysaccharides to direct particle nucleation, growth, and stabilization. The result is a high degree of control over size and shape, as well as improved compatibility with downstream biomedical applications. Waste-to-nanomaterial approaches further enhance sustainability by converting agricultural or food waste into valuable nanomaterials, aligning with circular economy principles. [47-48]

**Figure 6: Sustainable method for the synthesis of AuNPs**

3.2.2 Microfluidic and Continuous-Flow Synthesis

Microfluidic and continuous-flow reactors represent a significant technological advancement in nanoparticle synthesis. By maintaining uniform reaction environments and precise control over mixing, temperature, and reactant delivery, these systems achieve superior reproducibility, monodispersity, and scalability compared to traditional batch processes. Microfluidic platforms also facilitate high-throughput screening and rapid optimization of synthesis parameters, supporting integration with automation and machine learning. [49]

3.2.3 Plasma-Assisted and Mechanochemical Methods

Plasma-assisted and mechanochemical synthesis techniques offer solvent-free, energy-efficient alternatives for preparing AuNPs with high purity and tunable shapes. Plasma-based nucleation enables the generation of reactive species that reduce gold ions without chemical additives, while mechanochemical milling exploits mechanical energy to drive nanoparticle formation. These approaches minimize solvent use and waste generation, positioning them as attractive options for sustainable, large-scale production.[49]

3.2.4 Machine Learning-Assisted Optimization

The application of artificial intelligence and machine learning to AuNP synthesis has begun to revolutionize the field by enabling data-driven optimization of reaction conditions, prediction of particle properties, and rapid identification of optimal formulations for specific applications. Such tools are particularly valuable for tailoring AuNPs to demanding biomedical tasks, including targeted drug delivery and photothermal therapy.[49]

4. Comparative Evaluation of Synthesis Methods

Comparison between the conventional method and modern methods is given below for better understanding:

Table 1: Comparison of Key features among AuNPs synthesis methods

Feature	Conventional Methods	Modern Methods
Reducing Agents	Synthetic chemicals	Plant extracts, biopolymers, enzymes
Reaction Environment	Batch-based, variable	Controlled, continuous-flow/green
Toxicity	Moderate to high	Low (eco-friendly)
Purity	Possible chemical residues	Very high in plasma/laser methods
Shape Control	Moderate	High precision
Scalability	Requires optimization	Excellent in microfluidics
Suitability for Biomedical Use	Requires surface modification	Often inherently biocompatible



4.1 Mechanistic Control and Nanostructure Precision

Traditional chemical synthesis typically relies on rapid nucleation induced by strong reducing agents, producing spherical AuNPs with moderate control over size. Achieving anisotropic shapes or high monodispersity often necessitates multistep protocols or specialized reagents. In contrast, modern green and microfluidic methods provide enhanced control over growth kinetics, leveraging the mild, biomolecular reducing and capping agents present in plant extracts or biopolymers. Continuous-flow reactors maintain consistent reaction conditions, enabling fine-tuning of particle morphology and size distribution. Plasma and laser-based approaches offer the additional benefit of producing clean, residue-free surfaces, facilitating post-synthesis functionalization with targeting ligands, drugs, or polymers.

4.2 Environmental Sustainability and Safety

Conventional chemical methods typically generate hazardous waste streams and require careful disposal of toxic reagents, limiting their scalability and suitability for biomedical production. Physical techniques, while avoiding chemical waste, are energy-intensive. Modern green synthesis, microfluidic, and mechanochemical methods dramatically reduce environmental burden by employing natural, biodegradable agents, operating under mild conditions, and minimizing solvent usage.

4.3 Reproducibility and Scale-Up Potential

Batch-based traditional syntheses are straightforward to implement and replicate on a laboratory scale but often display irreproducibility upon scale-up due to sensitivity to mixing, temperature, and concentration gradients. Microfluidic and continuous-flow systems, by virtue of their fixed and tightly controlled reaction environments, are inherently scalable and offer excellent reproducibility and throughput. However, green synthesis methods can still suffer from batch-to-batch variability due to differences in biological extract composition, highlighting the need for standardized protocols and quality control.

4.4 Surface Chemistry and Functional Utility

Chemical reduction methods generally yield AuNPs capped with simple ligands (e.g., citrate, thiols), necessitating subsequent functionalization for biomedical use. In contrast, green synthesis produces nanoparticles with natural biomolecular coatings that enhance colloidal stability and biological activity. Plasma and laser methods result in highly reactive, clean surfaces amenable to direct conjugation with drugs or targeting moieties.

4.5 Performance in Application

The choice of synthesis method has a direct bearing on the suitability of AuNPs for specific applications. Traditional methods suffice for catalysis, simple sensing, and basic biomedical assays, but advanced therapeutic applications—such as photothermal therapy, radio sensitization, and targeted drug delivery demand rigorous control over particle geometry, surface chemistry, and purity. High-purity AuNPs from plasma or laser synthesis and naturally stabilized particles from green synthesis demonstrate superior performance in these contexts, particularly in cancer therapies.

5. Comparison of Key features among AuNPs synthesis methods Physicochemical Properties of Gold Nanoparticles: Implications for Biomedical Function

The unique properties of AuNPs are intrinsically linked to their size, shape, and surface chemistry. Size-dependent surface plasmon resonance (SPR) enables strong absorption and scattering in the visible to near-infrared (NIR) regions, a feature exploited for photothermal and imaging applications. Anisotropic shapes (e.g., nanorods, bipyramids) exhibit high photothermal conversion efficiency, ideal for deep-tissue cancer therapy.

Surface modification with polyethylene glycol (PEG), proteins, polymers, or phytochemicals extends circulation time, enhances tumor accumulation via the enhanced permeability and retention (EPR) effect, and enables active targeting. Controlled synthesis is therefore essential not only for optimizing the physicochemical attributes of AuNPs but also for ensuring their safety, biodistribution, and efficacy in complex biological environments. [51-52]

Table 2: Comparison of traditional and modern methods for the synthesis of AuNPs

Aspect	Conventional Methods	Modern Methods
Main Approaches	Chemical reduction, early physical methods	Green synthesis, microfluidics, plasma/laser, mechanochemistry
Reducing Sources	Synthetic chemicals (e.g., citrate, NaBH_4)	Plant extracts, biopolymers, enzymes, microbes
Environmental Impact	Chemical waste, moderate–high toxicity	Eco-friendly, minimal waste, biocompatible
Shape/Size Control	Moderate; dependent on reagent strength	High; tunable via flow control or biomolecules
Energy Requirement	Low–moderate (chemical); high (physical)	Low (green), moderate (flow), variable (plasma)
Reproducibility	Consistent in small batches; variable at scale	High in microfluidics; moderate in green synthesis
Scalability	Requires optimization; batch variability	Excellent for continuous-flow systems
Surface Chemistry	Basic ligands needing post-modification	Natural bio-coatings or clean reactive surfaces
Purity	Chemical residues may remain	Very high in plasma/laser methods
Typical Applications	Sensing, basic biomedical use, catalysis	Targeted therapy, imaging, radio sensitization, and advanced catalysis

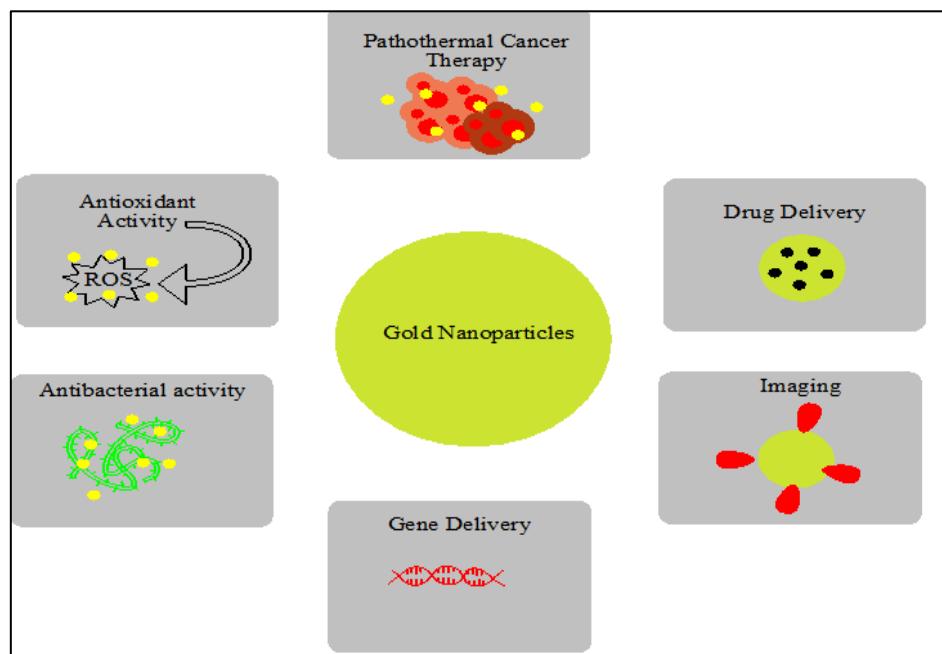
6. Applications of Gold Nanoparticles in Cancer Therapy: Emphasis on Breast Cancer

6.1 Drug Delivery

AuNPs serve as highly effective drug carriers due to their large surface area, ease of functionalization, and biocompatibility. Drugs can be attached via covalent, electrostatic, or hydrophobic interactions, and encapsulation of chemotherapeutics, antibiotics, or hydrophobic agents (e.g., dexamethasone, 6-gingerol) significantly improves bioavailability, stability, and targeted delivery while reducing off-target toxicity. Recent advances in ligand engineering and surface modification have enabled the development of AuNP-based platforms for active targeting of breast cancer cells, exploiting overexpressed receptors such as HER2.

6.2 Photothermal and Photodynamic Therapy

One of the most promising applications of AuNPs in breast cancer treatment is in photothermal therapy (PTT) and photodynamic therapy (PDT). AuNPs, particularly nanorods and bipyramids, exhibit strong NIR absorption, enabling efficient conversion of light to heat for localized tumor ablation with minimal damage to surrounding healthy tissue. NIR-driven AuNP systems have demonstrated remarkable efficacy in destroying breast tumor tissues *in vitro* and *in vivo*.

**Figure 7: Applications of AuNPs**



6.3 Radio Sensitization

AuNPs are established radiosensitizers, enhancing the efficacy of radiation therapy by increasing local dose deposition and promoting DNA damage in tumor cells. Size-dependent studies have shown that PEG-coated AuNPs of 12.1 and 27.3 nm diameter exhibit optimal tumor accumulation, potent radio sensitization, and significant reduction in tumor volume and weight *in vivo*, with minimal toxicity to non-target organs. The ability to fine-tune particle size and surface chemistry through advanced synthesis methods is critical to maximizing therapeutic benefit and minimizing side effects in breast cancer radiotherapy.

6.4 Modalities and Immunotherapy

Alginate-dopamine stabilized AuNPs have demonstrated dual functionality as radiosensitizers and photothermal agents, achieving synergistic tumor inhibition in animal models under combined X-ray and NIR irradiation. AuNPs also serve as carriers for immune checkpoint inhibitors and nucleic acids, enhancing tumor penetration, stabilizing therapeutics, and stimulating T-cell activation. While promising, these approaches necessitate further research into immune interactions and long-term safety.

6.5 Imaging and Diagnostics

The strong SPR and surface-enhanced Raman scattering (SERS) properties of AuNPs facilitate their use as imaging agents for tumor detection, margin delineation during surgery, and real-time monitoring of therapeutic response. Integration with machine learning and artificial intelligence is poised to further enhance the diagnostic capabilities of AuNP-based platforms.

6.6 Antimicrobial, Antioxidant, and Environmental Applications

Green-synthesized AuNPs exhibit pronounced antimicrobial and antioxidant activity, enabling their use in wound healing, infection control in cancer patients, and environmental remediation. Their ability to degrade pollutants and function as biosensors further broadens their application spectrum.

6.7 Catalysis

AuNPs display remarkable size-dependent catalytic activity, with smaller particles offering higher surface-to-volume ratios and superior efficiency. Embedding AuNPs in temperature-responsive microgels enables smart, reversible ON-OFF catalysis, with potential utility in bioprocessing and environmental cleanup. [50-52]

Table 3: Synthesis method-based application relevance

Application	Ideal Synthesis Methods	Reason
Photothermal Therapy	Microfluidic, plasma, seed-mediated	High control of shape and optical properties
Drug Delivery	Green synthesis, ligand-assisted chemical	Biocompatible coatings improve safety
Imaging	Laser-based, microfluidic	High purity and monodispersity
Catalysis	Plasma, mechanochemical	Clean surfaces and defect-rich structures
Antimicrobial Activity	Green synthesis	Natural organic coatings enhance bioactivity.
Environmental Remediation	Green, mechanochemical	Low toxicity and high stability



7. Critical Appraisal: Challenges and Future Perspectives

7.1 Toxicity, Biodistribution, and Regulatory Hurdles

Despite their promise, AuNPs face significant translational challenges. Toxicity is dependent on size, shape, coating, dose, and administration route. While PEGylated AuNPs generally exhibit favorable safety profiles, accumulation in the liver and potential for long-term retention necessitate careful evaluation. The establishment of standardized protocols for toxicity assessment, biodistribution, and clearance is essential for regulatory approval and clinical translation.

Green synthesis methods, though eco-friendly, suffer from variability in extract composition and inconsistent batch quality, impeding reproducibility and scalability. Addressing these issues will require rigorous standardization, mechanistic elucidation of biomolecular interactions, and development of robust quality control frameworks.

7.2 Advances in Manufacturing and Automation

The future of AuNP synthesis lies in the integration of advanced manufacturing technologies—microfluidic, plasma, mechanochemical and data driven optimization via artificial intelligence and machine learning. These platforms enable high-throughput, reproducible, and scalable production of designer AuNPs tailored for specific biomedical tasks. Widespread adoption will depend on lowering technical barriers and ensuring affordability and accessibility.

7.3 Environmental Sustainability

Sustainable and circular nanomanufacturing remains a top priority. Waste-to-nanomaterial approaches, solvent-free mechanochemical synthesis, and energy-efficient plasma methods are at the forefront of efforts to minimize environmental footprint. Life cycle assessment and green chemistry metrics should be incorporated into the design and evaluation of new synthesis protocols.

7.4 Personalized and Precision Nanomedicine

As understanding of the interaction between AuNPs and biological systems deepens, personalized nanoparticle design will become increasingly feasible. Data driven approaches to predicting optimal particle characteristics for individual patients and tumor types, coupled with responsive or hybrid nanostructures, will enhance therapeutic efficacy and safety in breast cancer and beyond.

8. Conclusion

The synthesis of gold nanoparticles has evolved from ancient, empirically guided practices to a highly sophisticated science that integrates chemistry, biology, engineering, and informatics. While traditional methods retain importance for their simplicity and foundational role, modern synthesis approaches particularly green, microfluidic, plasma-assisted, and machine learning-assisted methods offer superior control, reproducibility, scalability, and environmental compatibility.

These advances have been instrumental in unlocking the full potential of AuNPs as multifunctional agents for cancer therapy, especially in breast cancer, where they enable targeted drug delivery, photothermal ablation, radio sensitization, imaging, and immunomodulation. However, challenges remain in achieving standardized, reproducible, and clinically viable production of AuNPs, ensuring patient safety, and minimizing environmental impact.

Continued innovation at the intersection of synthetic methodology, automation, and data science will be paramount in bridging the gap between laboratory-scale advances and real-world clinical implementation. Ultimately, the future of AuNPs in medicine and technology depends on our ability to harmonize precision, sustainability, and translational efficacy.

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