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INFLUENCE OF PLANT PHYTOCHEMICALS ON THE GREEN SYNTHESIS AND FUNCTIONAL PROPERTIES OF METAL OXIDE NANOPARTICLES: A REVIEW

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ABSTRACT
Plant-mediated (green) synthesis of metal oxide nanoparticles (MONPs) has attracted sustained interest as an environmentally compatible alternative to conventional chemical routes, with phytochemicals serving as reducing, chelating, and capping agents throughout nucleation, crystal growth, and stabilization. Existing reviews typically address this literature one metal oxide or one plant species at a time, making it difficult to judge whether the underlying phytochemical mechanisms actually generalize across systems. This review instead takes a comparative approach across eight widely studied MONPs, ZnO, TiO_2 , Fe_3O_4 , CuO, CeO_2 , MgO, NiO, and MnO_x, examining how a broadly shared synthesis pathway nonetheless produces materially different functional outcomes depending on each oxide's intrinsic physicochemical properties. Structure–property relationships, synthesis-condition effects, and application domains are considered alongside several unresolved debates, including the role of specific phytochemical classes, the reduction mechanism itself, and the balance between antioxidant surface coatings and reactive-oxygen-species-mediated activity. The analysis indicates that the nanoparticle property most sensitive to phytochemical control, particle size, phase composition, magnetic phase purity, or oxygen-vacancy concentration, among others, differs systematically by oxide family, offering a framework for application-specific extract and condition selection rather than a universal green-synthesis protocol.

KEYWORDS: Nanotechnology; Phytochemicals; Metal oxide nanoparticles; Biogenic nanoparticles; Green synthesis; Structure–property relationships.

1. INTRODUCTION
Metal oxide nanoparticles (MONPs) are valued across medicine, agriculture, environmental remediation, energy storage, and sensing for optical, electrical, magnetic, catalytic, antimicrobial, and biomedical properties that their bulk counterparts lack.[1-4] Conventional physical and chemical synthesis routes offer precise control over size and morphology, but they typically demand high energy input, elevated temperature and pressure, and hazardous reducing or stabilizing chemicals that generate toxic by-products.[1-5] Growing concern over these costs, together with pressure toward more sustainable manufacturing, has driven the rise of green nanotechnology, an approach that applies green-chemistry principles to nanomaterial synthesis without sacrificing efficiency.[1,2,4,5] Among green routes, plant-mediated synthesis has become the preferred alternative to microbial, algal, or fungal systems. Plants are inexpensive, renewable, need no sterile culture maintenance, and are rich in phytochemicals that act simultaneously as reducing, chelating, stabilizing, and capping agents.[1-7] Research attention has shifted accordingly, moving from simply producing nanoparticles toward understanding how phytochemical

composition governs metal-ion reduction, nucleation, crystal growth, stabilization, and surface functionalization.[1,3,4,6,8,9] This mechanistic view reframes plant extracts as active biochemical regulators of nanoparticle formation rather than passive "green" substitutes for chemical reducing agents.

Plant extracts contain a wide range of primary and secondary metabolites, polyphenols, flavonoids, tannins, terpenoids, alkaloids, saponins, proteins, amino acids, polysaccharides, and organic acids, whose hydroxyl, carbonyl, carboxyl, amino, and methoxy groups drive electron transfer, metal-ion chelation, and surface adsorption.[1-4, 8] Because this composition varies with species, plant part, extraction method, and growing conditions, it directly shapes nanoparticle size, morphology, crystallinity, surface chemistry, and colloidal stability.[3,6,8,10] Green-synthesized ZnO, iron oxide, TiO_2, CuO, CeO_2, MgO, NiO, and MnO_x nanoparticles have all shown enhanced antimicrobial, antioxidant, anticancer, photocatalytic, catalytic, sensing, agricultural, and environmental performance relative to conventionally synthesized counterparts, an improvement widely attributed to residual phytochemicals retained on the nanoparticle surface.[3,4,6,9,11,12] The field's central obstacle is variability. Differences in genotype, geography, season, extraction protocol, and storage produce inconsistent phytochemical profiles and, in turn, poor reproducibility, while the molecular mechanisms of phytochemical-mediated reduction and stabilization remain only partially understood.[1,4,6,8] This review examines how plant-derived phytochemicals govern the green synthesis of metal oxide nanoparticles: their classification and molecular functions, the synthesis of the major MONP systems, and the resulting relationships between phytochemical composition and nanoparticle performance across biomedical, environmental, catalytic, agricultural, and sensing applications, before closing with current limitations and future directions.[1,3,4,6-9,11-13]

Existing reviews of plant-mediated MONP synthesis are usually organized around a single oxide or a single plant species, which makes it difficult to see whether the phytochemical mechanisms involved actually generalize across systems. Comparatively few have asked, systematically, how phytochemical composition governs nucleation, crystal growth, surface chemistry, and downstream functional performance across a range of MONPs rather than within one material family at a time. This review takes that comparative question as its starting point, treating phytochemical-driven synthesis as a mechanistic thread common to all these systems, but one that produces materially different functional outcomes depending on the oxide involved.

2. PHYTOCHEMICALS: CLASSES AND ROLES IN GREEN SYNTHESIS

Phytochemicals are the functional core of plant-mediated MONP synthesis, simultaneously reducing metal ions, directing nucleation and crystal growth, and stabilizing and functionalizing the resulting nanoparticle surface.[1,2,13] Because plant extracts contain dozens of these compounds at once, they form a synergistic system that regularly outperforms single purified reagents, crude extracts frequently yield more stable, better-functionalized nanoparticles than isolated compounds do.[1,2,8,14-16] Composition varies with species, organ, developmental stage, and extraction method, which is why reduction kinetics, nucleation rate, and final morphology differ so much between studies using ostensibly similar plant material.[1,8,14,15] Polyphenols are usually treated as the principal reducing agents in plant-mediated synthesis, largely on account of their abundant hydroxyl groups and generally favorable redox chemistry. That said, a number of studies attribute comparable, or in some cases larger, contributions to proteins, reducing sugars, or organic acids, depending on the plant species and how the extract was prepared. Part of the difficulty here is that crude extracts are chemically messy: several phytochemical classes are typically active at once rather than acting in isolation, which makes it hard to assign nanoparticle formation to any single compound class without detailed fractionation and phytochemical profiling. Until that kind of profiling becomes more routine, claims about which metabolite class drives reduction in a given system are probably best read as provisional rather than settled.

Table 1: Phytochemical classes, their functional groups, and their primary synthetic roles, with representative molecules.

Phytochemical	Functional groups	Primary role	Representative molecules	Major MONPs
Polyphenols	–OH	Reduction	Gallic acid, tannic acid, chlorogenic acid	ZnO, CuO, CeO_2
Flavonoids	–OH, C=O	Reduction + Capping	Quercetin, kaempferol, catechin	ZnO, TiO_2
Tannins	Phenolic –OH	Chelation + Stabilization	Ellagitannins, condensed tannins	Fe_3O_4, ZnO
Proteins	$–NH_2$, –COOH	Capping	Enzymes and structural proteins (extract-dependent)	Fe_3O_4, NiO
Organic acids	–COOH	Chelation	Citric acid, ascorbic acid, malic acid	TiO_2, CeO_2

No single class typically acts alone: nucleation, growth, aggregation control, and surface functionalization all depend on the simultaneous presence of several of these compounds, which is the main reason crude extracts are hard to standardize but consistently effective.[1,2,8,14-16] Establishing quantitative structure–property relationships between phytochemical composition and nanoparticle characteristics remains the central open problem for reproducible, application-specific green synthesis.[1,2,8,14-21]

3. MECHANISMS OF PHYTOCHEMICAL-MEDIATED SYNTHESIS

Green MONP synthesis is a multistep process in which plant-derived phytochemicals simultaneously reduce metal ions, form coordination complexes, and regulate nucleation, crystal growth, stabilization, and surface functionalization, unlike conventional synthesis, where these roles are handled by separate reagents.[1,4,6,14] The sequence generally runs as follows: electron-rich functional groups (hydroxyl, carbonyl, carboxyl, amino) reduce dissolved metal ions while chelating them; supersaturation of the reduced species triggers nucleation; crystal growth proceeds through addition of new atoms or ions; and phytochemicals adsorbed on the growing surface regulate that growth and prevent aggregation.[4,14,19,22] For metal oxides specifically, subsequent hydrolysis, oxidation, and calcination convert these intermediates into stable crystalline oxide phases.[7,23,24]

Reduction. Polyphenols, flavonoids, tannins, terpenoids, reducing sugars, proteins, and organic acids all donate electrons to metal ions through redox reactions, with phenolic hydroxyls oxidizing to quinones as they reduce metal cations.[1,4,6,14,19] Reduction rate depends on phytochemical concentration and structure, precursor reduction potential, pH, and temperature; extracts richer in antioxidants reduce faster, nucleate more centers, and yield smaller particles.[4,14,16]

Chelation. Before reduction, functional groups bind metal ions into intermediate phytochemical–metal complexes. This localizes ions for efficient electron transfer, moderates reduction kinetics to prevent precipitation, and, because the complexes act as molecular templates, influences the nucleation behavior and crystal orientation that follows.[4,14,16,19,22,23]

Nucleation and crystal growth. Once reduced species become supersaturated, stable nuclei form once they exceed a critical size, consistent with classical nucleation theory.[7,22,23] Rapid reduction produces many nuclei and smaller particles; slow reduction produces fewer nuclei that keep growing into larger, more size-heterogeneous particles.[14,23,24] Growth then proceeds by atom-by-atom addition, aggregation, or oriented attachment, with phytochemicals adsorbing preferentially onto specific crystal faces to selectively inhibit growth along particular directions. This is why different phytochemical mixtures yield different morphologies, spheres, rods, flowers, plates, cubes.[4,14,16,19,23,24]

Stabilization. High-surface-energy fresh nanoparticles are protected from aggregation by two mechanisms that often operate together: electrostatic stabilization from adsorbed charged groups (carboxylate, phenolate), and steric stabilization from larger biomolecules (proteins, polysaccharides, tannins, saponins) forming physical barriers between particles.[1,4,14,16,19]

Surface functionalization. Residual phytochemicals remain bound to the finished nanoparticle surface via hydrogen bonding, electrostatic interaction, van der Waals forces, and coordination bonds, increasing hydrophilicity and biocompatibility and frequently boosting antimicrobial, antioxidant, catalytic, and photocatalytic performance, a signature confirmed by FTIR and XPS in most studies.[4,7,14,16,19,24]

Oxide formation. Unlike noble-metal nanoparticles, MONPs require additional transformation after reduction: hydrolysis and oxidation produce metal hydroxide intermediates that calcination then converts into crystalline oxides. Calcination temperature is a key lever here. Moderate temperatures improve crystallinity while preserving nanoscale dimensions, but excessive heat causes sintering and particle growth, so temperature must be optimized against this crystallinity/surface-area trade-off.[7,23-25]

Together, these stages are sequential but overlapping, and the concentration and diversity of phytochemicals present set the kinetics of each. This is why mechanistic understanding at this level underpins any reproducible, scalable synthesis protocol.[1,4,6,14,16,19,22-25] The molecular mechanism behind phytochemical-mediated reduction is still not fully resolved. Most of what is known comes from FTIR spectral shifts or general redox-chemistry reasoning rather than from direct observation of reaction intermediates, the phenolic-hydroxyl-to-quinone pathway, for instance, is more often inferred than demonstrated outright. That leaves a fairly basic mechanistic question open: whether nanoparticle formation is dominated by direct electron transfer from phenolic compounds, by coordination-assisted reduction, by residual enzymatic activity in less-purified extracts, or by some synergistic combination of the three. Resolving this would likely require techniques capable of capturing transient species, such as time-resolved spectroscopy or DFT-based computational modeling, rather than relying on end-point characterization alone.

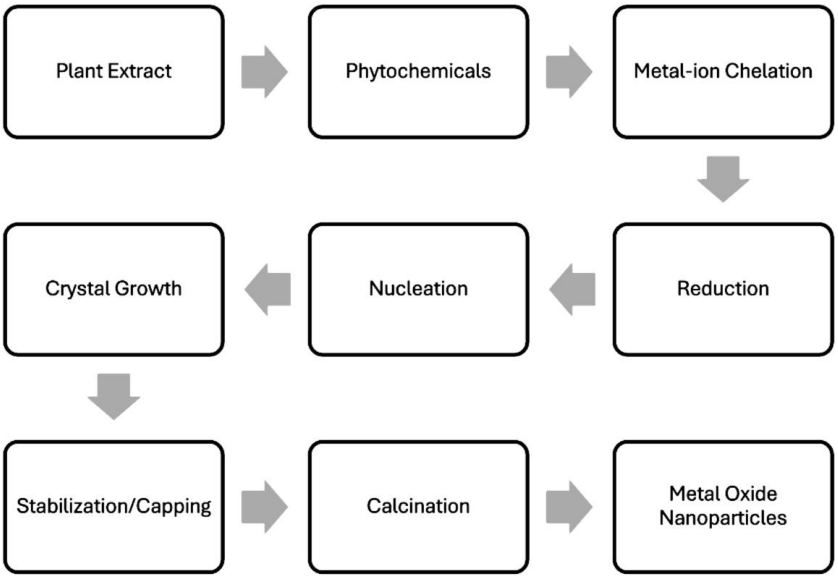

Figure 1: ***Mechanistic overview of phytochemical-mediated green synthesis, from plant extract through reduction, nucleation, and crystal growth to the calcined metal oxide product.***

Figure 1: Summarizes this pathway as a whole, from plant extract through to the calcined nanoparticle, before the sections below examine how each step plays out differently across individual metal oxides.

4. INDIVIDUAL METAL OXIDE NANOPARTICLES: A COMPARATIVE ANALYSIS

Sections organized one oxide at a time are easy to follow but tend to obscure a more useful question: given that essentially all plant-mediated MONPs pass through the same broad sequence of phytochemical-assisted reduction, chelation, nucleation, and stabilization, why do the resulting materials end up so functionally different? The short answer is that precursor chemistry, crystal structure, and the intrinsic physicochemical properties of each oxide determine which step in that shared pathway ends up mattering most. ZnO and TiO_2, for example, are investigated overwhelmingly for photocatalytic and antimicrobial behavior because of their semiconducting character; iron oxide nanoparticles are valued instead for their magnetic behavior, which underlies biomedical imaging and magnetic separation; CeO_2 derives its functionality mainly from reversible Ce^{3+}/Ce^{4+} redox cycling rather than from reactive-oxygen-species (ROS) generation alone; and NiO and MnO_x are pursued largely for electrochemical energy storage, owing to their high theoretical capacitance and multiple accessible oxidation states. Phytochemicals regulate a shared synthesis pathway, in other words, but the functional payoff depends on what each oxide is intrinsically capable of.

4.1 Photocatalytic systems: ZnO versus TiO_2

ZnO and TiO_2 remain the two most widely studied photocatalytic MONPs, and both are routinely described as highly efficient, a comparison that is harder to make than it sounds, since degradation efficiencies reported across studies depend heavily on experimental variables such as light source, pollutant concentration, catalyst loading, pH, and reaction time. Read at the mechanistic level rather than the efficiency-number level, the two systems are governed by fairly different factors. ZnO photocatalytic performance tracks closely with particle size and the extent of surface phytochemical coverage, both of which are set during the reduction and capping stages of synthesis. TiO_2 performance, by contrast, depends more on anatase–rutile phase composition and overall crystallinity, properties fixed largely during calcination rather than at the initial reduction step. This has a practical consequence: phytochemical-mediated control of calcination conditions matters considerably more for TiO_2 than for ZnO, where extract composition during the reduction phase plays the larger role. Claims that one oxide outperforms the other should therefore be read cautiously unless the comparison controls for testing conditions, which, in practice, relatively few studies do.

4.2 Biomedical systems: Fe_3O_4 versus CeO_2

Both Fe_3O_4 and CeO_2 nanoparticles have biomedical applications, but the underlying mechanisms have little in common. Iron oxide nanoparticles are used almost entirely because of their magnetic behavior: superparamagnetism at sufficiently small particle sizes enables MRI contrast enhancement and magnetic drug targeting, and phytochemical control here is mainly about preserving magnetite phase purity against oxidation to less useful phases such as hematite. CeO_2 nanoparticles work through an essentially different route, reversible Ce^{3+}/Ce^{4+} redox cycling at oxygen-vacancy sites allows them to scavenge reactive oxygen species, which is what makes them attractive for antioxidant and anti-inflammatory applications. Interestingly, this means the property phytochemicals need to control differs by system, phase purity for Fe_3O_4, oxygen-vacancy concentration for CeO_2, even though both syntheses start

from the same broad phytochemical-reduction framework.

4.3 Antimicrobial systems: ZnO, CuO, and MgO

ZnO, CuO, and MgO are all reported to show antimicrobial activity, though the dominant mechanism differs across the three. ZnO activity is generally attributed to a combination of ROS generation and Zn^{2+} ion release; CuO acts through a broadly similar ROS pathway but with Cu^{2+}-mediated membrane disruption playing a larger role; MgO, meanwhile, relies more on surface alkalinity together with oxidative stress than on metal-ion release as such. This suggests that phytochemical-mediated control of particle size and surface chemistry does not transfer cleanly from one oxide to another. A synthesis adjustment that improves ZnO's antimicrobial profile by shrinking particle size, for instance, will not necessarily have the same effect on MgO, where surface alkalinity is the more relevant lever.

4.4 Energy-storage systems: NiO and MnO_x

NiO and MnO_x are pursued for electrochemical energy storage rather than the photocatalytic or biomedical roles that dominate the systems above. Both benefit from high theoretical capacitance, but the property phytochemicals most usefully influence differs between them: NiO performance tracks closely with surface area, since a larger accessible surface supports more charge storage, while MnO_x performance depends instead on the range of accessible oxidation states, since manganese's multiple stable valences are what actually store charge. Phytochemical-assisted routes that emphasize high surface area are therefore more relevant to NiO, while routes that preserve or control mixed oxidation states matter more for MnO_x.

4.5 Limitations

The materials-specific challenges facing each oxide follow a similar logic. ZnO synthesis struggles most with particle-size reproducibility; TiO_2 with controlling phase during calcination; Fe_3O_4 with maintaining magnetite rather than hematite; CeO_2 with controlling oxygen-vacancy concentration; CuO with morphological consistency; and NiO and MnO_x with morphology optimization and oxidation-state control, respectively. MgO synthesis is, by comparison, simply understudied relative to the others, which limits how confidently its mechanistic picture can be drawn. All of these systems are additionally affected by the more general problem of plant-extract variability, but treating that as the only source of irreproducibility would miss the materials-specific bottleneck each oxide also carries.

Table 2: Metal oxide-specific sensitivity of nanoparticle properties to phytochemical control.

Metal oxide	Property most sensitive to phytochemical control	Why
ZnO	Particle size	Rate of reduction sets nucleation density
TiO_2	Crystallinity / phase composition	Calcination conditions govern anatase–rutile balance
Fe_3O_4	Phase purity	Fe^{2+}/Fe^{3+} balance determines magnetite vs. hematite formation
CeO_2	Oxygen-vacancy concentration	Ce^{3+}/Ce^{4+} ratio controls redox behavior
CuO	Morphology	Surface adsorption of phytochemicals affects catalytic activity
NiO	Surface area	Directly determines charge-storage capacity
MnO_x	Oxidation state	Multiple stable manganese phases coexist

Table 3: Comparative summary of key properties, major applications, and main synthesis challenges across the metal oxide systems discussed in this review.

MONP	Key property	Major applications	Main challenge
ZnO	Wide band gap semiconductor	Antimicrobial, photocatalysis	Particle-size reproducibility
TiO_2	Anatase-phase photocatalysis	Water treatment	Phase control during calcination
Fe_3O_4	Superparamagnetism	MRI, drug delivery	Magnetite/hematite phase purity
CuO	High conductivity	Sensors, antimicrobial	Morphological consistency
CeO_2	Ce^{3+}/Ce^{4+} redox cycling	Antioxidant	Oxygen-vacancy control
MgO	High surface area	Adsorption	Comparatively understudied
NiO	High capacitance	Supercapacitors	Morphology optimization
MnO_x	Multiple oxidation states	Energy storage	Oxidation-state control

Table 3 consolidates these comparisons into a single reference alongside each oxide's key property, major applications, and main synthesis challenge.

Taken together, these comparisons point to a fairly consistent pattern: phytochemicals participate in the same broad sequence, reduction, chelation, nucleation, crystal growth, stabilization, across essentially all MONP

systems, but the material property that actually governs downstream performance differs by oxide family. Particle size and morphology dominate for ZnO and CuO; phase composition matters most for TiO_2; magnetic phase purity is the critical variable for Fe_3O_4; oxygen-vacancy concentration governs CeO_2's redox activity; and electrochemical behavior in NiO and MnO_x depends largely on surface area and oxidation-state control, respectively. Recognizing which lever matters for which oxide is arguably more useful than a universal green-synthesis protocol, since it points toward selecting extract composition and reaction conditions based on the target application rather than applying the same approach indiscriminately across metal oxides.

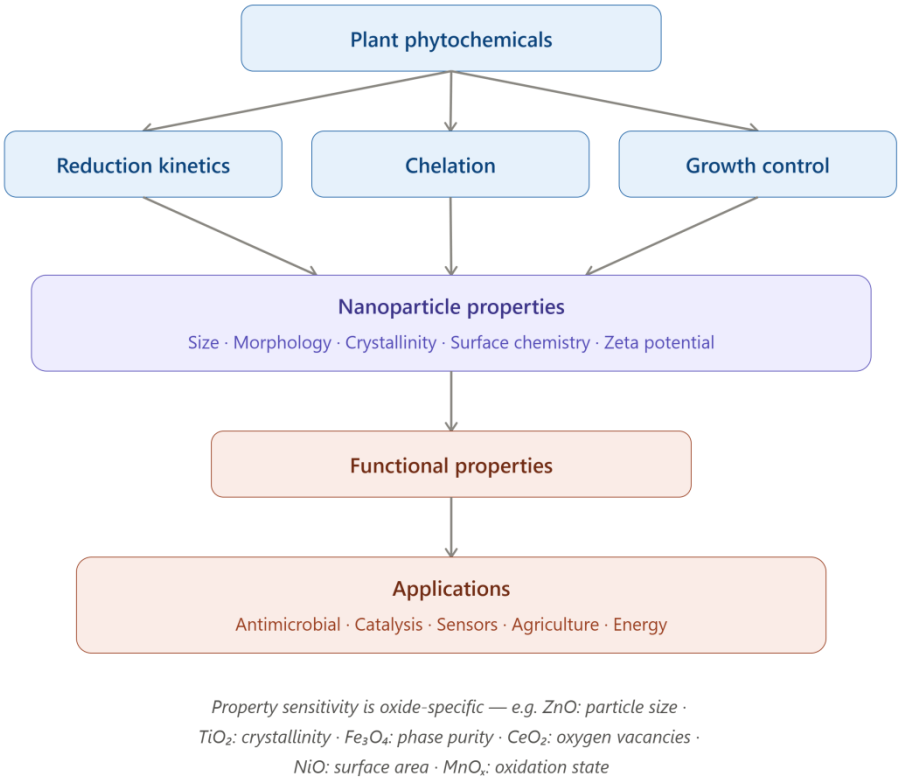

Figure 2: ***Structure–function relationship linking phytochemical-driven synthesis mechanisms to nanoparticle properties, functional performance, and application space, the review's central conceptual figure.***

5. STRUCTURE–PROPERTY RELATIONSHIPS

Because plant extracts deliver reduction, nucleation control, and stabilization simultaneously rather than through separately dosed reagents, phytochemical composition and concentration end up governing essentially every measurable nanoparticle characteristic.[14,15,19,26-28]

Particle size. Extracts rich in polyphenols and flavonoids drive fast electron transfer, generating many nuclei simultaneously and distributing available precursor across them, producing smaller, more narrowly distributed particles. Lower-reducing-capacity extracts do the opposite: fewer nuclei that keep growing, yielding larger and more heterogeneous particles.[14,15,19,24,26,28]

Morphology. Different phytochemical classes adsorb preferentially onto different crystallographic planes, directing anisotropic growth. Polyphenols and flavonoids tend to favor isotropic, spherical growth, while larger molecules, proteins, polysaccharides, tannins, impose steric constraints that favor more complex shapes such as rods, flowers, and plates.[14,15,19,24,27,29]

Crystallinity. Controlled nucleation followed by gradual growth produces more crystalline, defect-free particles; overly rapid reduction does the opposite. Calcination improves crystallinity by removing residual organics, but excessive temperature causes sintering that grows particles and shrinks surface area, a trade-off optimized alongside phytochemical concentration, not independently of it.[24-27,29]

Surface chemistry. Polyphenols, proteins, carbohydrates, tannins, and organic acids remain bound to the finished surface via hydrogen bonding, electrostatic interaction, and coordination, confirmed routinely by FTIR and XPS. This means surface chemistry is directly inherited from whatever extract was used.[14,15,19,20]

Colloidal stability. Electrostatic stabilization (charged groups like carboxylate/phenolate) and steric stabilization (larger biomolecules) typically operate together. Stronger phytochemical surface coverage correlates with higher zeta potential, less aggregation, and longer shelf life.[14,15,19,20]

Optical and magnetic properties. Particle size and crystallinity set band-gap energy through quantum confinement, so phytochemical control over those two properties indirectly controls UV–Vis absorption and photoluminescence, which matters particularly for photocatalytic performance.[24,26,27,29] In magnetic systems, chiefly iron oxide, smaller and more crystalline particles favor the superparamagnetic behavior needed for biomedical use, again set upstream by phytochemical-controlled nucleation and growth.[24,26-28]

Catalytic and biological activity. Smaller particles with more surface area and reactive sites generally show stronger catalytic, photocatalytic, antimicrobial, and antioxidant activity; residual surface phytochemicals frequently add their own synergistic contribution, for instance through additional ROS generation or intrinsic antioxidant capacity.[14,15,19,20,25,26,29]

In short, every characteristic above traces back to the same upstream variable: the phytochemical profile of the extract used. This is why building *quantitative* structure–property relationships, rather than the qualitative ones most current studies offer, is the field's most consequential open task.[14,15,19,20,24-29] Smaller-is-better is a common refrain in this literature, smaller nanoparticles are reported repeatedly to show stronger antimicrobial and catalytic activity, generally attributed to their larger specific surface area. That relationship is not universal, though. Several studies report comparable or even reduced biological activity at the smallest particle sizes, particularly when heavy phytochemical capping limits access to otherwise reactive surface sites. This points to a more complicated picture than size alone would suggest: surface chemistry, crystallinity, and defect density all appear to shape biological performance alongside particle size, and the residual phytochemical coating, itself a direct product of the synthesis method, may matter just as much as how small the particles actually are.

6. EFFECT OF SYNTHESIS CONDITIONS

Beyond phytochemical composition itself, five practical variables determine whether a given synthesis protocol is reproducible.[3,7,10,24,31]:

Plant species. Each species has a distinct phytochemical profile, so identical protocols applied to different species can yield markedly different particle size, morphology, and activity. Geography, climate, and season add further batch-to-batch variation within a single species, which is why phytochemical characterization *before* synthesis, not just after, improves reproducibility.[3,10,32]

Plant part. Leaves are used most often because they carry the highest phenolic/flavonoid/ antioxidant load and therefore the most reliable reduction and stabilization. Flowers, fruit, bark, roots, and seeds carry different specialized metabolites and can shift morphology and surface chemistry even within the same species.[3,7,10,31]

Extraction method. Solvent, temperature, time, and technique jointly determine which phytochemicals end up in the extract. Water is the default solvent for its low cost and ability to extract most polar compounds involved; ethanol and methanol pull in additional bioactive compounds and shift kinetics accordingly. Ultrasound- and microwave-assisted extraction can improve recovery and cut extraction time, but any method still needs careful optimization for consistent output.[7,10,30,31]

Reaction conditions. pH affects both phytochemical ionization and precursor solubility: alkaline conditions generally accelerate nucleation and improve crystallinity, while acidic conditions slow reduction and favor larger particles. Higher temperature speeds reduction and growth but risks degrading thermolabile compounds; extract and precursor concentration both need to be balanced against each other, since excess precursor relative to reducing capacity causes uncontrolled growth and aggregation.[3,10,24,30,31]

Calcination. Temperature, heating rate, duration, and atmosphere govern the final phase, crystal structure, and surface area. Moderate calcination improves crystallinity without much particle growth; excessive calcination sinters particles and shrinks the surface area that most applications depend on.[7,24,30]

These five variables interact with phytochemical composition rather than operating independently of it, which is the practical reason no single protocol transfers cleanly from one plant species or lab to another, and why standardized, phytochemically-profiled protocols remain the field's biggest reproducibility gap.[3,7,10,24,30,31] Calcination is generally described as improving crystallinity and phase purity, largely by removing residual organic matter left over from the phytochemical-reduction step. That description is accurate but incomplete: raising the calcination temperature also tends to promote particle growth, aggregation, and loss of surface area, which works against several of the same applications crystallinity is supposed to improve. The literature here reflects a genuine trade-off rather than a single optimum, and the appropriate calcination regime probably depends on whether crystallinity or surface area matters more for the intended application.

It is well established that nanoparticle characteristics vary considerably even when the nominal plant species is identical across studies. Much of this variability likely traces back to factors that are inconsistently reported, cultivar, geographic origin, harvest season, extraction solvent, and storage conditions among them. That raises a somewhat uncomfortable possibility: discrepancies between published studies on "same" plant-mediated synthesis may reflect differences in extract composition rather than any real difference in how metal oxide itself

behaves, which complicates cross-study comparison more than is often acknowledged.

Table 4: General directional trends linking synthesis conditions to nanoparticle characteristics. Directions only, drawn from classical nucleation/growth theory and colloid chemistry, confirm magnitudes and exceptions against your own cited literature before relying on this table.

Condition	Particle size	Morphology	Crystallinity	Zeta potential
Higher pH	Generally decreases	Trends toward more uniform, spherical particles	Variable; can improve up to a point	Often more negative
Higher temperature	Generally increases	Can promote irregular or aggregated morphology	Generally improves	Modest effect
Higher precursor concentration	Generally increases	Can promote aggregation at high loading	Minor effect	Minor effect
Extraction solvent polarity	Indirect, governs which phytochemicals are extracted	Indirect, via phytochemical profile	Indirect	Indirect, via capping-agent identity
Higher calcination temperature	Increases (grain growth)	Can promote aggregation, surface-area loss	Improves, up to onset of overgrowth	N/A post-calcination

7. APPLICATIONS

Across applications, performance consistently traces back to the same source: the inorganic metal-oxide core's intrinsic properties combined with the phytochemical coating retained from synthesis.[4–7,11,21,31,33,34]

Antimicrobial activity. The most-studied application. ZnO, CuO, TiO_2, MgO, iron oxide, and CeO_2 all show broad-spectrum activity against Gram-positive and Gram-negative bacteria and fungal pathogens, via membrane disruption, ROS generation, intracellular component leakage, protein denaturation, and metal-ion release. Surface phytochemicals frequently add a synergistic antimicrobial contribution beyond the metal oxide alone.[5,17,21,33,35-42]

Antioxidant activity. CeO_2 is the standout here, owing to its reversible Ce^{3+}/Ce^{4+} redox cycling, which continuously scavenges ROS in a manner similar to superoxide dismutase and catalase. Residual polyphenols, flavonoids, and tannins on any MONP surface add further radical-scavenging capacity, relevant to inflammation, aging, and neurodegeneration research.[21,33,34,43,44]

Anticancer applications. ZnO, iron oxide, TiO_2, CuO, and CeO_2 have shown selective cytotoxicity against cancer cell lines via ROS generation, mitochondrial dysfunction, DNA fragmentation, and apoptotic pathway activation. Phytochemical surface functionalization improves biocompatibility and cellular uptake, and offers an anchor point for further functionalization with therapeutic agents or targeting ligands.[33,35,37,38,44,45]

Environmental remediation. High surface area and catalytic activity make TiO_2, ZnO, CuO, MgO, and MnO_x effective at removing dyes, heavy metals, and pharmaceutical residues from water via photocatalytic degradation. Iron oxide adds magnetic recoverability, making post-treatment separation and reuse straightforward in a way the other oxides can't easily match.[4,31,37,40,41,45-48]

Photocatalysis. TiO_2, ZnO, CuO, and CeO_2 generate electron–hole pairs under UV or visible light that produce hydroxyl radicals and superoxide ions capable of degrading organic pollutants and disinfecting water. Efficiency tracks phytochemical-controlled particle size and defect density directly, smaller, less defective particles with reduced charge-carrier recombination perform best.[35,38,40,41,45]

Sensors. NiO, ZnO, TiO_2, CuO, and iron oxide have all been developed into gas sensors, biosensors, and electrochemical sensing platforms, where nanoscale surface area and phytochemical-enhanced molecular recognition improve sensitivity and response time for gases, glucose, heavy metals, and pathogens.[11,37,39,49]

Agricultural applications. ZnO, MgO, CuO, and iron oxide nanoparticles function as nanofertilizers and antimicrobial plant-protection agents, improving nutrient delivery and germination while reducing reliance on conventional pesticides, though dosage, persistence, and ecological impact still need more evaluation before wide field use.[31,36,40,50]

Energy applications. NiO and MnO_x perform well as supercapacitor and battery electrode materials due to high theoretical capacitance and multiple oxidation states; TiO_2 and CeO_2 show promise in photocatalytic hydrogen production and fuel cells. Phytochemical-controlled morphology and surface area contribute directly to electrode stability in both cases.[40,41,46,49,51]

Because these eight application areas draw on the same underlying set of phytochemical-controlled properties covered in Section 5, the practical takeaway is consistent

throughout: application-specific performance is tunable primarily through extract and reaction-condition choices made at the synthesis stage, not through post-synthesis processing.[4–7,11,35,36,37,43,46,49,51] There is an underappreciated tension in how phytochemical coatings are discussed across this literature. On one hand, residual phytochemicals are credited with enhancing antioxidant activity through radical-scavenging behavior. On the other, antimicrobial efficacy in the same particles is frequently attributed to ROS generation, in a sense, the opposite process. How an antioxidant surface coating coexists with ROS-mediated antimicrobial action is not well explained in the current literature, and the balance probably depends on the relative chemistry and thickness of the phytochemical layer versus the intrinsic reactivity of the underlying oxide, though this has not been systematically tested.

Surface-bound phytochemicals are usually framed as beneficial, since they improve colloidal stability and biocompatibility. Excessive surface coverage, though, can just as easily mask catalytically active sites, interfere with charge transfer, or block adsorption of reactant molecules at the surface. What counts as optimal surface functionalization is still not well defined, and different applications likely call for different answers, a coating that helps colloidal stability for a biomedical application might be exactly the wrong amount for a catalytic one. Read across all eight oxide systems, a fairly clear application-to-oxide mapping falls out of the mechanistic discussion in Section 4: ZnO and CuO are generally preferred for antimicrobial use because of their combined ROS-generation and metal-ion-release behavior; CeO_2 stands out for antioxidant applications on account of its Ce^{3+}/Ce^{4+} redox cycling; Fe_3O_4 is the default choice for MRI and magnetic applications because of its superparamagnetism; TiO_2 and ZnO dominate water-treatment photocatalysis; and NiO and MnO_x are the go-to systems for energy storage, given their capacitance and multiple oxidation states. Framed this way, the applications discussed above read less like a list of unrelated use cases and more like a direct consequence of the property-driven comparisons already established in Section 4.

8. CURRENT CHALLENGES

Plant-mediated MONP synthesis still faces several interlocking obstacles to reproducibility, scalability, and commercial translation.[10,23,26,31,52,53]

Extract variability. Phytochemical concentration varies with species, cultivar, geography, climate, season, developmental stage, and storage, so extracts from the "same" species can still produce nanoparticles with different size, morphology, and activity, complicating comparison across published studies.[10,26,31,53]

Limited standardization. Most studies use crude extracts without quantifying the specific compounds responsible for synthesis, making it hard to establish direct links between phytochemical class and nanoparticle outcome. Standardized extraction, solvent selection, and phytochemical profiling would make outcomes more predictable.[10,26,53]

Incomplete mechanistic understanding. Most proposed mechanisms rest on indirect spectroscopic evidence rather than direct molecular observation, so the individual contribution of each phytochemical class is still mostly inferred rather than demonstrated. Closing this gap needs combined experimental and computational work.[23,52,53]

Reproducibility and process control. Because so many interdependent variables (species, part, extraction, precursor concentration, pH, temperature, time, calcination) affect the outcome, small protocol variations produce large differences in result, and the field still lacks universally accepted synthesis protocols to control for this.[10,31]

Scale-up. Laboratory-scale success doesn't automatically translate to industrial production, which needs consistent phytochemical input, controlled kinetics, efficient purification, and economically viable processing, all while preserving the environmental advantages that motivated green synthesis in the first place.[26,31,52]

Regulatory and safety gaps. Plant-mediated nanoparticles are generally assumed to be more biocompatible than chemically synthesized ones, but systematic toxicological data and harmonized regulatory guidelines remain limited.[31,53]

Characterization limitations. Many studies rely on a narrow set of analytical techniques, insufficient to fully resolve nanoparticle composition, structure, and, critically, the specific phytochemical-binding mechanisms at the surface.[23,53]

9. FUTURE PERSPECTIVES

Phytochemical fingerprinting. Routine use of LC–MS, GC–MS, NMR, and metabolomics to identify and quantify the specific compounds responsible for synthesis would let researchers correlate extract composition directly with nanoparticle outcome, rather than relying on generic class-level descriptions.[24,53]

Mechanistic modeling. Combining spectroscopy with DFT and molecular dynamics simulations could replace empirical optimization with rational nanoparticle design.[24,25]

AI and data-driven optimization. Machine learning models trained on phytochemical composition, synthesis parameters, and resulting nanoparticle characteristics could predict optimal reaction conditions and cut experimental workload substantially.[24,25,53]

Omics-guided selection. Genomics, transcriptomics,

proteomics, and metabolomics could help identify plant species with favorable phytochemical profiles before synthesis even begins, rather than through trial and error.[12,53]

Continuous-flow manufacturing. Moving from batch lab synthesis to continuous-flow reactors with real-time quality control is likeliest path to industrial-scale reproducibility.[24,25]

Hybrid systems. Combining plant extracts with purified biomolecules, biopolymers, enzymes, or microbial metabolites could tighten control over nanoparticle formation while keeping most of green synthesis's environmental advantages.[12, 53]

International standardization. Internationally accepted protocols, covering plant selection, extraction, characterization, reaction conditions, and biological evaluation, remain the single highest-leverage step toward regulatory approval and commercial translation[24,25]

Beyond the practical recommendations above, several more fundamental questions remain genuinely unresolved. Which phytochemical classes actually dominate reduction under a given set of reaction conditions, and does this shift predictably with extract composition? Are synergistic interactions among multiple metabolites more important than any single compound's activity? Could nanoparticle characteristics eventually be predicted directly from a phytochemical fingerprint, rather than determined empirically after the fact? What level of surface phytochemical coverage actually optimizes the trade-off between colloidal stability and catalytic or biological performance? And, perhaps most practically, how does laboratory-scale synthesis, typically optimized on a gram scale with carefully controlled extracts, translate into reproducible industrial manufacturing without losing the green-chemistry advantages that motivated the approach in the first place? Addressing these will likely require combining phytochemistry, nanomaterials characterization, computational modeling, and more systematic reporting standards than the field currently applies.

Table 5: Current research gaps in phytochemical-mediated green synthesis and corresponding future priorities.

Current issue	Why it matters	Future direction
Variable plant extracts	Poor reproducibility across studies	Phytochemical fingerprinting
Unresolved reduction mechanisms	Difficult to optimize rationally	DFT modeling combined with time-resolved spectroscopy
Lack of standardized protocols	Poor comparability between studies	International reporting standards
Limited scale-up data	Industrial translation remains a barrier	Continuous-flow synthesis
Sparse quantitative structure–property correlations	Weak predictive capability	AI/ML-assisted modeling

10. CONCLUSION

Plant-mediated green synthesis integrates green-chemistry principles with the biochemical diversity of plant phytochemicals, which function throughout the process as reducing, chelating, stabilizing, and surface-functionalizing agents rather than as simple substitutes for chemical reagents. The composition of the extract used therefore directly determines nanoparticle size, morphology, crystallinity, surface chemistry, and ultimately functional performance.[1,6,7,10,24,25,53] This review has covered eight metal oxide systems, ZnO, Fe_3O_4/Fe_2O_3, TiO_2, CuO, CeO_2, MgO, NiO, and MnO_x, synthesized via plant extracts and applied across antimicrobial, antioxidant, anticancer, photocatalytic, catalytic, sensing, agricultural, and energy-related domains, with performance in every case arising from the combined contribution of the inorganic core and the phytochemical-derived surface.[4–7,11,35-37,43,46,49,51] The field's remaining obstacles are consistent across every system covered here: phytochemical variability, incomplete mechanistic understanding, limited reproducibility and standardization, and unresolved scale-up and regulatory questions.[10,24,25,53] Closing these gaps will likely come from integrating metabolomics, computational chemistry, artificial intelligence, and continuous-flow manufacturing into the field, building toward a predictive framework in which phytochemical composition reliably forecasts synthesis outcome and nanoparticle performance, rather than one where each new plant-precursor combination has to be characterized from scratch.[1,6,7,10,11,24,25,53]

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