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Possibilities of Using Bio-Based Nanomaterials in Sustainable Agriculture

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ABSTRACT

Emerging demand for food coupled with increasing agricultural use of hazardous chemicals is propelling development of environmentally sustainable nanotechnologies. Nanoscale materials derived from green sources like plants and microbes could transform agriculture via nanosensors detecting toxins, precise nutrient delivery systems, soil and water monitoring, plant growth promotion and reduced reliance on agrochemicals. Though no single nano-enabled solution offers complete sustainability currently, this analysis explores varied sustainable nanotechnology applications to bolster crop yield, protection and surveillance through innovative farming methods. However, progress commercializing and researching these technologies remains restricted. Elucidating complex nanomaterial behaviors in environments, thoroughly evaluating functionality and distribution plus instituting robust governmental oversight are essential prerequisites for fully harnessing green nanotechnology's potential to enable sustainable agriculture.

Keywords: sustainable agriculture; bio-based nanomaterials, fertilization, plant protection, plant tolerance to stress, plant yield.

INTRODUCTION

Sustainable management of natural resources is the most serious challenge facing agriculture globally [Hakim 2019]. While technological innovations and capital investments have effectively increased food production [Pingali 2012], dominant farming practices profoundly damage ecosystems by disrupting natural cycles [Reganold and Wachter 2016]. Issues like soil degradation [Wienhold et al. 2004], salinization [Rengasamy 2006], water and organic matter deficits [Lal 2004], biodiversity declines [Huang et al. 2012], pesticide-resistant pathogens [Gould 1998], and agricultural chemical contamination of groundwater [Schreinemachers and Tipraqsa 2012] pose barriers to sustainable development. Many countries have tried increasing production by switching to perennial crops and expanding land exploitation. Technologies that drive growth while meeting food challenges without environmental damage are becoming critical.

"Green nanotechnologies" refer to synthesizing nanomaterials while minimizing harmful chemicals and harsh reactions [Savithramma et al. 2011; Makarov et al. 2014]. Using plants and microbes to produce nanomaterials is gaining popularity due to the genetic and biochemical diversity of these organisms [Rajan et al. 2015], which can reduce metal ions to the nanoscale [Shekhawat and Arya 2009]. Applying nanomaterials in agriculture has revolutionized food production through eco-friendly natural resource management, unveiling new possibilities.

Interest has skyrocketed recently in utilizing plant extracts and microbes to synthesize metal nanoparticles via "green synthesis", an alternative to conventional chemical and physical approaches requiring toxic reagents and extreme temperatures and pressures [Ahmed et al. 2016]. The main advantages of green methods are simplicity, low cost, and potentially less environmental impact. Moreover, abundant biologically active compounds in plants and microbes like polyphenols, alkaloids and flavonoids promote reducing metal ions into nanoparticles [Rajan et al. 2015].

MICROORGANISM DIVERSITY AS A SOURCE OF NANOMATERIALS

Microbes like bacteria, fungi and yeast offer promising green nanoparticle synthesis alternatives to plants [Hulkoti and Taranath 2014]. Advantages include rapid growth, scalability and tremendous metabolic diversity from hundreds of millions of years of evolution [Singh et al. 2016]. For instance, soil Pseudomonas bacteria can reduce silver compounds into ~200 nm nanoparticles [Shahverdi et al. 2007]. Similar properties occur in dairy *Lactobacillus* spp. [Nair and Pradeep 2002]. Filamentous Fusarium fungi synthesize controllable silver nanowires over 100 µm long [Castro-Longoria et al. 2011]. Even greater nanoparticle shape/size diversity arises from yeast like Saccharomyces cerevisiae. Depending on conditions, they yield silver/gold nanospheres, nanotriangles or nanotubes [Kowshik et al. 2002]. Such morphology control directly tunes optical, electrical and biological nanomaterial properties. These examples show microbes can ideally produce diverse advanced nanomaterials due to metabolic flexibility and engineering potential.

NANOFERTILIZERS

Agricultural intensification and agrochemical usage have depleted and acidified soils [Schroder et al. 2011]. Moreover, traditional fertilizers exhibit limited nutrient bioavailability [Davis et al. 2012]. Promising alternatives utilize nanotechnology-enabled fertilizers. Key advantages are precisely delivering nutrients at lower doses while maintaining efficacy [Liu and Lal 2015]. For instance, nanocrystalline calcium phosphate shows twofold greater lability versus standard phosphorus fertilizers [El-Ghany et al. 2021]. Similarly, nanoforms of micronutrients like zinc, copper and iron demonstrate enhanced bioactivity and can increase yields even at low concentrations [Raliya and Tarafdar 2013]. Also promising is stimulated release of growth regulators such as auxins and cytokinins from smart

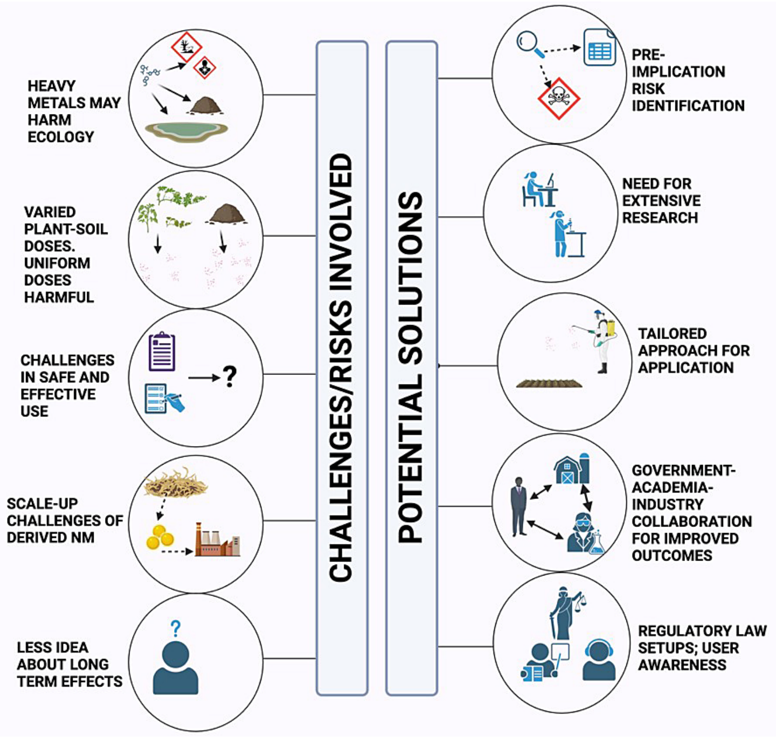

Figure 1. Challenges and potential solutions regarding the implications of green nanomaterials for sustainable agriculture

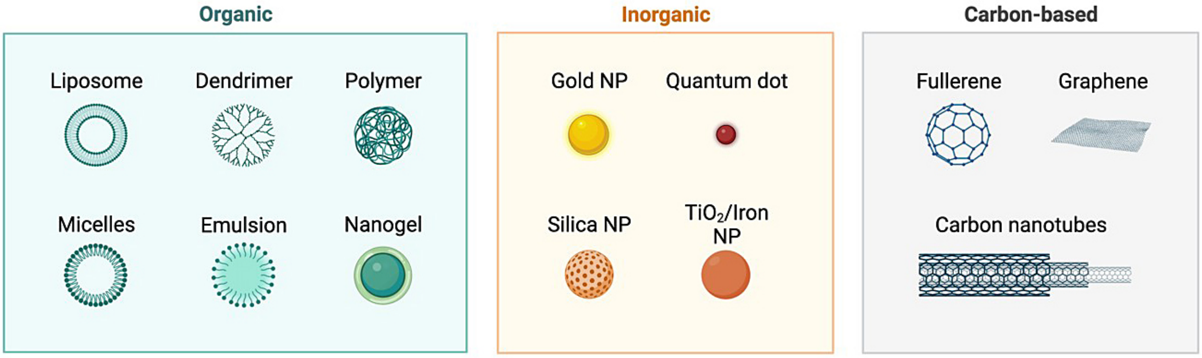

Figure 2. Different types of nanoparticles

nanoparticle carriers responding to rhizosphere stimuli [Bielach et al. 2012]. This facilitates precise belowground root system development control. Nanofertilizer usage could therefore significantly decrease application rates while improving nutrient delivery efficiency. This aligns with precision agriculture goals of minimizing environmental impacts while optimally leveraging inputs.

NANOPESTICIDES

Despite efficacy, traditional pesticides risk toxicity and environmental contamination [Damalas and Eleftherohorinos 2011]. Nanopesticides – nanoforms of active ingredients or carriers – could provide an alternative. Key nanopesticide advantages are precisely delivering bioactive compounds with controlled release rates and doses [Kah and Hofmann 2014], enabling plant protection with less environmental impact. Graphene carriers [Chen et al. 2022], chitosan [Xu et al. 2018; Mehta et al. 2021] and silver nanoparticles [Kathiravan et al. 2014] have successfully combated pathogens and pests already. A prominent nanopesticide achievement is pH-responsive ferrimagnetic nanoparticle carriers releasing agents [Xiang et al. 2017]. Highly porous materials like chitosan-coated diatomite/Fe3O4 store significant bioactive payloads. Afterwards, magnetic retrieval collects residual nanoparticle carriers, enabling reuse or removal without soil contamination. Such controlled release magnetic nanocarriers could revolutionize precise, sustainable crop protection delivery.

Cu-based nanoparticles

Cu ion antibacterial/antifungal properties are well-known, with Cu(OH)2NPs as the active ingredient in Kocide 3000 pesticide. Copper nanoparticles have shown efficacy against bacterial and fungal plant pathogens [Yoon et al. 2007]. Comparative research found better CuNP performance versus the fungicide bavistin (carbendazim) [Kanhed et al. 2014]. Recently, Borgatta et al. [2018] compared CuONP and $Cu_3(PO_4)_2 \cdot 3H_2O$ nanoplate abilities to combat Fusarium oxysporum f. sp. niveum fusarium wilt in watermelon. In a greenhouse study, 10 mg/L Cu nanoplates significantly reduced disease severity, outperforming 1000 mg/L CuONPs. Further studies have demonstrated CuNP efficacy in lowering Clavibacter michiganensis infection in tomatoes [Cumplido-Nájera et al. 2019] and increasing cotton insect resistance with CuONPs [Van et al. 2016].

Ag-based nanoparticles

Rising fungal pathogen and pest resistance to chemical pesticides has focused attention on new crop protection approaches. Due to broad antibacterial properties, silver nanoparticles (AgNPs) have attracted great interest as potential nanopesticides [Cromwell et al. 2017]. Ocsoy et al. (2013) synthesized DNA-wrapped graphene oxide-supported AgNPs (Ag@dsDNA@GO) and found 16 mg/L significantly inhibited cultivated Xanthomonas perforans, which causes 10-50% tomato yield losses to bacterial spot disease. Similar greenhouse results occurred with 100 mg/L Ag@dsDNA@GO. Additionally, AgNPs have exhibited nematicidal potential. Exposure to 30–150 mg/mL AgNPs killed 99% of Meloidogyne spp. nematodes within 6 days [Cromwell et al. 2014]. In a field study, 150 mg/mL AgNPs reduced nematodes by 82% and 92% on days 2 and 4. Compared to chemicals, green AgNPs synthesized with plant or bacterial extracts as reducing/stabilizing agents are more environmentally friendly [Mishra et al. 2014]. Mishra et al. [2014] used the plant growth-promoting bacterium Serratia sp. to biosynthesize AgNPs with potent antifungal activity against the wheat spot blotch pathogen Bipolaris sorokiniana. Narayanan and Park [2014] synthesized ~16 nm AgNPs with turnip leaf extract possessing broad spectrum wood-rotting fungal activity. Despite promising agriculture applications, potential AgNP phytotoxicity has raised concerns. Foliar 0.4 mg/plant AgNPs induced oxidative stress in cucumber leaves [Zhang et al. 2011]. Further research on dose responses and biological impacts is essential to determine safe usage.

Si-based nanoparticles

Numerous studies indicate silicon enhances plant resistance to abiotic and biotic stresses via undetermined mechanisms [Guntzer et al. 2010, Wang et al. 2022]. For example, SiO_2 nanoparticles improve tomato seed germination [Siddiqui and Al-Whaibi 2014]. Mesoporous silicon nanoparticles (MSNs) also benefit plants. MSNs accumulated in wheat and lupine chloroplasts during hydroponic growth, stimulating photosynthesis. MSNs increased seed germination, biomass, protein and chlorophyll without oxidative stress [Sun et al. 2016]. Comparing nanoparticles in maize showed SiO_2NPs least disturbed plant physiology [Sillen et al. 2015]. Moreover, nano-SiO_2 enhances strawberry growth and yield under salt stress [Avestan et al. 2019]. SiO_2NPs may also affect potassium homeostasis, representing a promising drought alleviation research direction.

Mg-based nanoparticles

Magnesium has essential roles in chlorophyll synthesis and photosynthesis [Li et al. 2001; Kashem and Kawai 2007]. Studies show magnesium nanoparticles (MgNPs) beneficially impact plant growth and development. For example, MgNPs significantly increased photosynthesis and biomass in black-eyed peas while altering cell membrane permeability [Delfani et al. 2014]. Similar biomass and root growth increases occurred with biosynthesized MgNPs in wheat [Dawas and Ali 2022]. Proposed mechanisms include improved light energy capture in leaves. MgONPs also increase antioxidant enzymes like SOD and POD in tobacco [Cai et al. 2018b]. Since magnesium is an essential micronutrient where MgNPs provide added antioxidant boosts, agricultural utilization holds promise – both correcting deficiencies and improving stress tolerance. For instance, MgONPs far more effectively inhibited tobacco growth of the phytopathogen Ralstonia solanacearum versus MgO [Cai et al. 2018a].

Mo-based nanoparticles

Molybdenum cofactors nitrogenase and nitrate reductase perform key roles in plant nitrogen fixation, reduction and transport [Alam et al. 2015]. Investigated for exceptional electronic, optical and catalytic semiconductor properties, MoS_2 nanoparticles impact remains little studied in plants [Parzinger et al. 2015]. One study showed 125 mg/L MoS_2 nanoparticles increased rice biomass and leaf chlorophyll without affecting seed germination, malondialdehyde or antioxidants. MoS2 also upregulated rice aquaporin genes, though the chlorophyll increase mechanism is undetermined [Li et al. 2018]. Recently, Chen et al. [2018] synthesized MoS2 nanoparticles that mimic antioxidant enzyme (SOD, CAT, POD) activity. Additionally, 1000 mg/L MoS_2 nanoparticles significantly inhibited E. coli growth and viability [Wu et al. 2016]. These findings suggest potential roles enhancing plant photosynthesis and stress resilience, meriting further research.

IMPROVING SOIL QUALITY AND WATER RETENTION USING NANOTECHNOLOGY

Declining arable soil fertility stems primarily from low organic matter and insufficient macro- and micronutrients [Canton 2021]. This affects both light and heavy soils, with the latter frequently containing excessive anthropogenic heavy metals [Yang and Jia 2024]. Nanomaterial application shows promise in this context. Due to extensive surface area, specialized morphology and tuned reactivity, nanomaterials can selectively bind contaminants, steadily discharge nutrients, and retain soil moisture [Du et al. 2011]. For example, carbon nanotubes and graphene increase soil water retention up to 10-fold, boosting drought tolerance [Mukhopadhyay 2014]. Iron nanoparticles immobilize problematic elements like arsenic and cadmium [Wang et al. 2018]. Chitosan, cellulose and starch nanocarriers provide controlled nitrogen fertilizer release, benefiting yields [Liu and Lal 2015]. Precision remediation effects at low doses indicate promise combining environmental and production objectives via

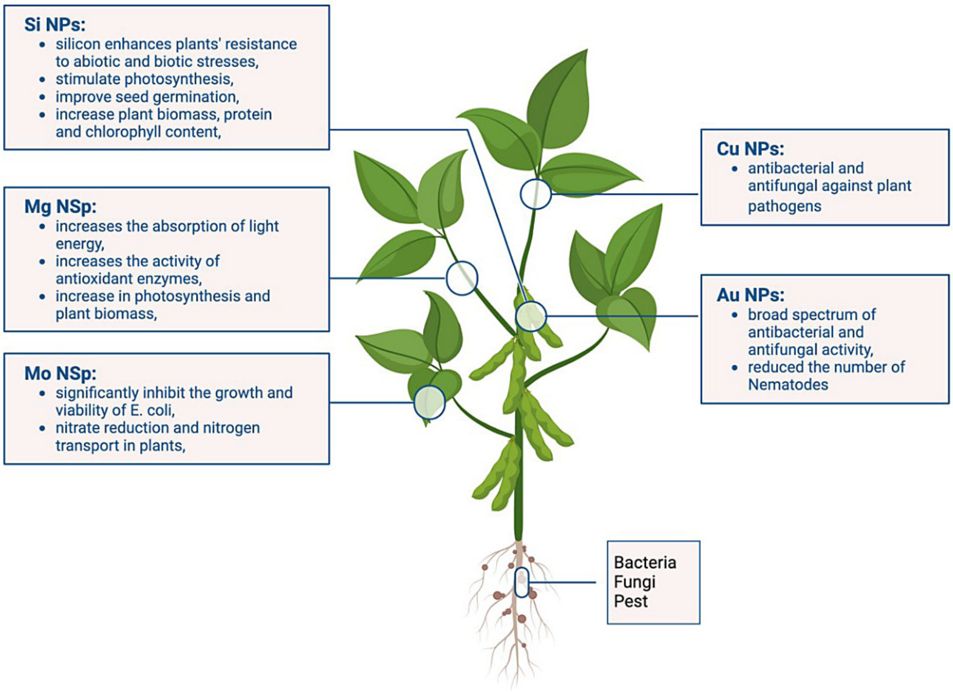

Figure 3. NPs are used to protect plants from stress and modulate plant growth

nanomaterials. However, safely implementing such large-scale soil applications requires extensive further research [Schwab et al. 2016].

ENHANCING PLANT GROWTH AND ABIOTIC STRESS TOLERANCE WITH NANOPARTICLES

Abiotic stresses like drought, extreme temperatures, salinity or heavy metals constitute the primary cause of over 50% average crop loss worldwide [Atkinson and Urwin 2012]. Cereals, roots and legumes may suffer 70–80% yield decreases [Wang et al. 2004]. Adverse effects manifest across levels, from germination inhibition through impeded growth/development to ultrastructural and genetic expression changes [Prasad et al. 2021]. For example, drought disrupts plant water relations, closing stomata, limiting photosynthesis/transpiration and inhibiting cell division/differentiation. High temperatures damage membranes, proteins and nucleic acids. Salinity interferes with nutrient and hormone homeostasis. Heavy metals induce oxidative stress by binding proteins and disrupting signaling [Tang et al. 2023].

Key plant oxidative stress defense mechanisms involve superoxide dismutase (SOD), catalase (CAT) and peroxidases (POD) neutralizing reactive oxygen species (ROS) [Mukhopadhyay 2014]. Under abiotic stress, excessive ROS accumulate in organelles, damaging DNA, lipids and proteins [Gill and Tuteja 2010]. Nanoparticles like CeO_2, TiO_2, ZnO, C60 and Fe_2O_3 exhibit ROS scavenging antioxidant properties [Nel et al. 2006]. As nanoscale redox switches, they accelerate superoxide dismutation and protect photosynthesis [Zuverza-Mena et al. 2017]. Consequently,

Table 1. Nanomaterials and their application for the removal of selected soil contaminants

Nanomaterial	Contaminant in soil	Reference
Nano-Fe/Cu	Nitrate ions	[Shubair et al., 2018]
Nano-Fe_3O_4@C-COOH	Pb	[Ma et al., 2020]
Single-walled carbon nanotubes	DDT	[Zhang et al., 2017]
	Polycyclic aromatic hydrocarbons	[Yang et al., 2006]
Multiwalled carbon nanotubes	Pb	[Konczyk et al., 2019]
Modified carbon black nanoparticle	Cd, Ni	[Cheng et al., 2019]
Magnetite nanoparticles	Cd, Pb	[Yang et al., 2018]

engineering plants with these nanoparticles enhances drought, salinity and heavy metal tolerance, reducing yield losses [Faizan et al. 2021; Faizan et al. 2023]. Stress-mitigating nanoparticle plant engineering shows promise to alleviate unfavorable environment-driven crop losses.

IMPACT OF ENZYMATIC NANOPARTICLES ON PLANT STRESS TOLERANCE

Recently, nanomaterials exhibiting antioxidant enzyme activity like superoxide dismutase (SOD), catalase (CAT) and peroxidases (POD) have emerged, including CeO_2, C60 fullerene, gold and platinum nanoparticles and transition metal oxides [Debnath et al. 2015, Ding et al. 2023]. For example, catalytic MoS2 nanosheets effectively neutralize superoxide, hydrogen peroxide and lipid peroxides [Chen et al. 2018]. Similar properties occur with biocompatible, functionalizable gold (AuNPs) and platinum nanoparticles (PtNPs) [He et al. 2012; Bai et al. 2017]. Moreover, enzyme-mimicking nanozymes (CeO_2, C60) stimulate plant growth and stress tolerance not only via reactive oxygen species elimination. C60 fullerene nanoparticles mitigated oxidative stress in drought-stressed sugar beet by intracellular water provision [Borišev et al. 2016]. CeO_2 nanoparticles increased biomass, chlorophyll and photosynthesis in salinized winter oilseed rape without completely alleviating effects. Nano-CeO_2 also shortened root apoplastic barriers, enabling shoot sodium ion transport to decrease root accumulation [Rossi et al. 2016]. Iron oxide nanoparticles (γ-Fe_2O_3) reduced drought-induced hydrogen peroxide and lipid peroxidation in oilseed rape [Palmqvist et al. 2017]. With similar properties, the micronutrient manganese oxide Mn3O4 also shows agricultural promise [Yao et al. 2018].

IMPACTS OF NON-ENZYMATIC NANOPARTICLES ON PLANTS STRESS TOLERANCE

Certain non-enzymatic nanoparticles also enhance plant stress resilience. For example, zero-valent iron nanoparticles (nZVIs) stimulate proton pump activity, increasing stomatal conductance and leaf surface area [Younas et al. 2023], though without affecting drought sensitivity. Further research should explore iron nanoparticle impacts on plants. Another mechanism involves upregulating antioxidant system gene expression, increasing natural plant stress tolerance, as shown for TiO_2 [Latef et al. 2018], SiO_2 [Behboudi et al. 2018] and ZnO [Siddiqui et al. 2014]. These regulate enzymes like superoxide dismutase (SOD) and peroxidases (POD), benefiting growth and yield. Additionally, ZnO and iron nanoparticles decrease heavy metal uptake and toxicity - including cadmium and arsenic [Tripathi et al. 2013; Manzoor et al. 2021] – highlighting prospective phytoremediation applications. These findings show nanostructures without enzymatic activity also protect plants from environmental stresses, though underlying mechanisms need further elucidation.

CONCLUSIONS

Rising food demand and agricultural chemical hazards are driving green nanotechnology development. Sustainably synthesized plant and microbe nanomaterials could revolutionize agriculture via nanosensors detecting toxins, micronutrient delivery, soil/water regulation, growth enhancement and agrochemical minimization. However, as no single nanotechnology enables complete sustainability, this review discusses varied sustainable nanomaterial applications to improve yield, protection and monitoring through innovative practices. Key conclusions include: (i) microbes efficiently and scalably synthesize nanomaterials with unique agricultural properties, (ii) nanoparticles precisely deliver nutrients/regulators as nanofertilizers and target pathogens as nanopesticides, minimizing environmental contamination, (iii) certain nanoparticles enhance plant stress tolerance to drought, salinity and metals through antioxidant effects or genetic regulation, (iv) nanomaterials help alleviate agricultural problems like nutrient deficiencies, low water retention and contamination by controlled nutrient/water release and pollutant binding, (v) significant knowledge gaps remain regarding nanoparticle environmental fate and safety requiring addressment prior to large-scale agricultural implementation. Nevertheless, research and commercial progress in this field is still limited. Elucidating complex nanoparticle environmental behaviors, thoroughly evaluating functionality and distributions plus establishing robust governmental oversight are essential to fully harness green nanotechnology's potential for enabling sustainable agriculture.

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