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Green synthesis of metal-based nanoparticles for sustainable agriculture

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23 **Abstract:**

24 The large-scale use of conventional pesticides and fertilizers has put tremendous pressure on
25 agriculture and the environment. In recent years, nanoparticles (NPs) have become the focus of
26 many fields due to their cost-effectiveness, environmental friendliness and high performance,
27 especially in sustainable agriculture. Traditional NPs manufacturing methods are energy-intensive
28 and harmful to environment. In contrast, synthesizing metal-based NPs using plants is similar to
29 chemical synthesis, except the biological extracts replace the chemical reducing agent. This not only
30 greatly reduces the used of traditional chemicals, but also produces NPs that are more economical,
31 efficient, less toxic, and less polluting. Therefore, green synthesized metal nanoparticles (GS-MNPs)
32 are widely used in agriculture to improve yields and quality. This review provides a comprehensive
33 and detailed discussion of GS-MNPs for agriculture, highlights the importance of green synthesis,
34 compares the performance of conventional NPs with GS-MNPs, and highlights the advantages of
35 GS-MNPs in agriculture. The wide applications of these GS-MNPs in agriculture, including plant
36 growth promotion, plant disease control, and heavy metal stress mitigation under various exposure
37 pathways, are summarized. Finally, the shortcomings and prospects of GS-MNPs in agricultural
38 applications are highlighted to provide guidance to nanotechnology for sustainable agriculture.

39 **Keywords:** Green synthesized nanoparticles, Agriculture, Plant growth, Antimicrobial, Heavy-
40 metal stress

1. Introduction

Feeding the global population safely and sustainably will be one of the most significant challenges of the present era. According to the United Nations report, the population of the world will reach about 8.5 billion by 2030, then 50% more food will be required to meet the population demand (Singh et al., 2019). Therefore, improving agricultural productivity and agronomic measures are vital to global food security. For decades, farmers and scientists have been trying to increase agricultural output in the traditional way (Singh et al., 2019). However, agricultural development is hindered by various aspects. Inefficient fertilizer application leads to a vicious cycle of increased fertilizer application and environmental pollution (Broberg et al., 2017). Diseases caused by bacteria, fungi, pests and viruses reduces the grain quality and yield (Figuerola et al., 2018). Various abiotic stress environments produced by anthropogenic and natural conditions inhibit the growth of plants (Zhou et al., 2020). Agriculture urgently needs a new technology with high efficiency and low pollution to change this dilemma.

Nanotechnology manipulates and monitors substances at the nanoscale by using scientific expertise in physics, chemistry and biology (Rai et al., 2008). Nanotechnology has achieved tremendous development in the past few decades, and it is expected that the world will become a "NPs world" (Adeel et al., 2021a; Adeel et al., 2021b; Singaravelan and Alwar, 2015). NPs have unique optical, electrical, magnetic, chemical and mechanical properties due to their small size (<100 nm) and large specific surface area (Dinesh et al., 2012; Puay et al., 2015; Saif et al., 2016). In light of the various challenges facing agriculture, especially extreme environmental stress, climate changes and food security, nanotechnology can effectively improve the yield and quality of agricultural products and minimizing the negative environmental impact of fertilizers and pesticides. In addition, nanotechnology can alleviate various abiotic stresses through stimulating physiological processes during plant growth and improving the quality of soil and agricultural products (Santo Pereira et al., 2021). Thus, the distinct properties of NPs present an excellent candidate for entirely new weapons for agriculture and related fields (Adeel et al., 2020).

Compare to the traditional ways, the sustainable and green production of NPs using innovative technologies has attracted the attention of the scientific community worldwide (Singh et al., 2016).

Green synthesis is a bottom-up method that synthesizes NPs from smaller atoms. The reduction process of green synthesis is approximately the same as chemical reduction, except that the chemical reagents are replaced by plant extracts (leaves, fruits, roots or flowers) (Hussain et al., 2016a). Metal ions can be reduced faster to form stable metal NPs by the green synthesis method with less pollution, simple operation and low energy consumption (Iravani, 2011). In addition, the waste produced during the synthesis of plants based NPs, are non-toxic and more accessible to treat than chemical and physical methods (Hussain et al., 2016b). It is worth noting that the method of green synthesis of metal nanoparticles (GS-MNPs) can be used to recover some noble metal ions, such as gold (Au) and silver (Ag), which greatly improves the economic benefits (Wang et al., 2009). Therefore, GS-MNPs have more advantages over traditionally synthesized NPs (**Table 1**). First, GS-MNPs exhibit less toxicity due to the low toxic raw materials, and no sustained toxic effects in subsequent processes. In addition, GS-MNPs exhibit high stability, mainly because plant derived biomolecules, including proteins, enzymes, sugars and even whole cells, can effectively stabilize NPs (Yadi et al., 2018). Furthermore, compared with chemically produced NPs, Ag NPs synthesized by the green method showed 20-folds higher antibacterial activity to *E. coli* (Sintubin et al., 2011). GS-MNPs also show stronger antioxidant properties. For example, Santhoshkumar et al. reported that TiO₂ NPs synthesized from plant aqueous extracts had the most excellent antioxidant activity compared with ascorbic acid. The leaf extract contained large amount of phenolic compounds, which led to significantly higher yield of TiO₂ NPs than that was synthesized using ascorbic acid (Santhoshkumar et al., 2014).

In recent years, many reviews have summarized the applications of GS-MNPs in the fields of heavy metal contaminated soils remediation (Madhavi et al., 2013; Mystrioti et al., 2015), anti-microbial (Ali et al., 2021; Arciniegas-Grijalba et al., 2019), and biomedicine (Kumari et al., 2015). However, few studies systematically summarize the application of GS-MNPs in agriculture. This review for the first time conducts a screening and analysis of the relevant literature in the past ten years. Then, various synthetic methods of NPs and the various factors that affect the size and shape of the synthesized NPs, including temperature, pH, reaction time, and concentration of extraction solvent are highlighted (Makarov et al., 2014; Rahisuddin and Akrema, 2016; Sathishkumar et al., 2009a). Moreover, the advantages of GS-MNPs compared with traditional NPs in terms of toxicity,

antibacterial and antioxidant properties are emphasized. Then, the application status of GS-MNPs in agriculture is introduced. Finally, the positive effects of GS-MNPs in promoting plant growth, antibacterial activity, and alleviating heavy metal stress are elaborated. This review also provides an opportunity to summarize the effects of GS-MNPs on soil and plant health and nutrient transfer of heavy metals. However, the interaction mechanism between GS-MNPs and plants, such as plant uptake and transport, is not well established. Therefore, the application of GS-MNPs in agriculture still has great development space and prospects.

2. Synthesis of NPs

2.1. Data extraction and analysis

In this review, 126 articles were collected from Web of Science using the Keywords "nanoparticles", "green synthesis", "agriculture" and "plant". CiteSpace 5.8 was used for analysis. The number of publications is a valuable indicator to measure the trend of a research field. As shown in **Figure 1** that the number of publications related to GS-MNPs and their citations increases exponentially from 2019, with 2021 being the highest. The keywords can be broken down into specific research directions. **Figure 2** shows the analysis results obtained based on the keywords. It can be seen that Ag, Au and CeO₂ NPs are the most studied in the field of GS-MNPs research, and most of the current articles are on the antibacterial effect of GS-MNPs.

2.2. Methods of NPs synthesis

Methods of synthesizing NPs usually include "top-down" and "bottom-up" synthesis (Sepeur, 2008). In a top-down synthesis (**Figure 3**), NPs are made from raw materials with large size (Meyers et al., 2006). Size reduction is achieved through a variety of physical and chemotherapy treatments. In a bottom-up synthesis, NPs are synthesized from atoms, compounds or smaller particles by chemical reactions. (Mukherjee et al., 2001).

2.2.1. Physical and chemical methods

In the top-down approach, the synthesis of NPs relies on chemical and physical methods, including mechanical milling, chemical etching, laser ablation, sputtering and explosion processes, which are very expensive and more likely to cause harm to the environment. Moreover, these

methods involve the use of toxic and dangerous chemicals that cause a variety of biological risks (Ahmed et al., 2016; Mittal et al., 2013).

2.2.2. Microorganism mediated synthesis

Synthesized with microorganisms (bacteria, actinomycetes, yeast, fungi, algae and viruses) has an advantage over other methods in that NPs can be synthesized at an environmental rate under artificial conditions (Salem and Fouda, 2021). Synthesized with microorganisms of metals and metal oxide NPs may occur in the intracellular or extracellular regions (Bandeira et al., 2020). In the case of intracellular synthesis, microorganisms absorb metal ions from their surroundings and convert them into elemental forms by enzyme reduction (Bandeira et al., 2020). In the case of extracellular synthesis, enzymes and proteins produced and released by microorganisms can reduce metal ions and stabilize particles. Kalishwaralal et al. (2008) conducted an experiment to reduce Ag^+ with nitrate reductase in the extracellular environment (Kalishwaralal et al., 2008). In addition, another study investigated the extracellular synthesis of Ag NPs with *Bacillus licheniformis* (Anil Kumar et al., 2007). Since nitrate reductase transfers electrons from nitrate to metal groups (He et al., 2007), microbial nitrate reductases can play a role in the synthesis of Ag NPs. Unlike extracellular biosynthesis, the intracellular pathway requires an extra cell lysis process to release NPs from the microorganism (Molnar et al., 2018). Therefore, the intracellular synthesis of NPs is more time-consuming and expensive than the extracellular synthesis.

2.2.3. Green synthesis

Plant-mediated synthesis of metal NPs has attracted extensive attention from researchers worldwide because of its environmental friendliness and stability. Using plants to synthesize metal NPs is similar to chemical reduction of metal ions, except that natural product extracts replace chemical reducing agents and blocking agents, avoiding the harm caused by chemical synthesis (Akintelu et al., 2020). The method is simple, convenient, and environment-friendly, which can effectively reduce the use of chemical substances and significantly improve efficiency (Mittal et al., 2013). Different parts of plants have been used for this purpose, for instance leaves, roots, seeds and fruits (Amina and Guo, 2020). The plant extract is added into the precursor metal solution, which reduces the metal ions to neutral atoms and aggregates them and then the plant extract is used as

capping agents to stably synthesize metal NPs (**Figure 4**). Notably, plants can be easily used to synthesize NPs compared to microbial synthesis techniques because it eliminates the process of cell culture and is not biohazardous (Rolim et al., 2019).

The underlying mechanism of using plants to synthesize NPs remains unclear. However, many researchers have proposed possible mechanisms (Armendariz and Gardea-Torresdey, 2002; Chandran et al., 2006; Gamez et al., 1999). It can be demonstrated that plant extracts are used as the main raw materials for the GS-MNPs because of their ability to reduce or chelate metal ions and act as stabilizers (Ahmed et al., 2017; Anjum et al., 2015). Previous studies reported that plants contain high concentrations of active compounds such as methylxanthine, phenolic acids, amino groups, proteins and saponins (Altemimi et al., 2017; Maisuthisakul et al., 2008; Xu et al., 2017). These compounds can neutralize reactive oxygen species (ROS) and free radicals and chelate metals (Flora, 2009). Phenol is one of them, which is a good natural active substance that can spontaneously synthesize NPs (Sebastian et al., 2018a). Previous studies have shown that *Euphorbia* root extract contains phenolic compounds, which allow it to react with $\text{Ti}(\text{OH})_2$ to synthesize very stable green synthetic TiO_2 NPs with a particle size of 17 to 45 nm. During the synthesis process, the hydroxyl group (OH^-) in the phenolic compound first acts as a reducing agent and reacts with $\text{Ti}(\text{OH})_2$ (Nasrollahzadeh and Sajadi, 2015b), and then acts as a capping agent to combine with metal NPs to stabilize it (El-Seedi et al., 2019). Li et al. (2007) proposed that proteins with functional amino groups can act as reducing agents in the synthesis process (Li et al., 2007). They selected *Capsicum annuum* L. extract that containing a large amount of reducing amino acids, such as *Lycopersicum esculantum*, β -carotene and β -cryptoxanthin for verification, and proposed a recognition-reduction-limited nucleation and growth model (Li et al., 2007). The initial recognition refers to the fact that Ag^+ are adsorbed on the protein of peppers by electrostatic interaction. Then, the Ag^+ are reduced by the protein. Immediately afterwards, the secondary structure of the protein is changed, forming an Ag core. The protein and biomolecules in the extract stabilize the Ag NPs. As time goes by, Ag NPs with an average size of 10.2 nm were formed (Li et al., 2007). It can be concluded that the size and shape of GS-MNPs are related to the reaction conditions. Therefore, some studies have discussed the effect of changes in reaction conditions during the synthesis of NPs (Makarov et al., 2014; Rahisuddin and Akrema, 2016; Sathishkumar et al., 2009b). The results show that some

182 synthesis parameters, such as temperature, pH, reaction time, type of extraction solvent and
183 concentration ratio of plant extract to precursor metal ions, have great effects on adjusting the size
184 and shape of NPs (Xu et al., 2021b).

185 Among all parameters, temperature is an important factor in the process of synthesizing NPs from
186 plant extracts (Apte et al., 2013; Das et al., 2011). Generally speaking, the increase of temperature
187 improves the reaction rate and efficiency of NPs synthesis (Makarov et al., 2014). The solubility of
188 hydrophobic materials in water generally decreases with decreasing temperature, and its solubility
189 affects the size of the synthesized NPs (Gröning et al., 2004). Vanaja et al. (2013) also proved the
190 influence of temperature on synthesis (Vanaja et al., 2013). Broader peaks of the UV-vis spectrum
191 indicate the formation of larger NPs and narrow peaks indicate smaller NPs (Vanaja et al., 2013).
192 At 20°C and 35°C, the absorption bands are 470 nm and 450 nm, respectively, suggesting the effect
193 of temperature on the property of the product. The shape of NPs also changes with temperature.
194 Gericke and Pinches reported that the shape of NPs formation was related to the incubation
195 temperature (Gericke and Pinches, 2006). Specifically, at low temperatures, the formation of
196 spherical particles was favored, while high temperatures resulted in the formation of rod and flake
197 shaped particles. Another study showed that Cu NPs of specific sizes can be synthesized by adjusting
198 the reaction temperature (Mott et al., 2007). The results show that within a certain range, the
199 temperature rises, the size of the NPs becomes larger, and the shape also changes. Abbasi et al.
200 (2015) suggested that the higher nucleation rate at high temperatures is due to the hindered execution
201 of the secondary reduction process NPs on the surface, leading to the formation of smaller size
202 particles (Abbasi et al., 2015). However, high temperature can lead to protein denaturation or
203 inactivation, which may affect the properties of NPs obtained. This has been rarely studied so far.

204 The pH value plays an important part in the formation of NPs (Armendariz et al., 2004; Gan and
205 Li, 2012; Ghodake et al., 2010; Sathishkumar et al., 2010), because the pH value affects the charge
206 of the active substance in the plant extract. The charge of the active material affects the reduction
207 and stabilization process of the metal ions, which in turn affects the size and shape of the synthesized
208 NPs (Makarov et al., 2014). Sathishkumar et al. (2009) synthesized Ag NPs from *cinnamon* extract,
209 and the size of Ag NPs observed in TEM was 15–20 nm. Notably, when the pH value increases,
210 then smaller size spherical Ag NPs were formed (Sathishkumar et al., 2009b). Interestingly, the pH

value also affects the reduction of Ag ions by the amino acid tyrosine. For example, tyrosine acts as a reducing agent under alkaline conditions because the phenolic group in tyrosine is ionized under alkaline conditions and it transfers electrons to the Ag ion (Swami et al., 2004). In the synthesis of *Coleus aromaticus* leaf extract-mediated NPs, similar to the effect of temperature above, a small and broad surface plasmon resonance (SPR) band was formed at low pH, indicating the formation of large NPs. At high pH, a narrow peak appears, which indicates the formation of smaller size spherical Ag NPs (Vanaja et al., 2013).

In addition, the metal concentration in experimental solution showed the greater influence on the size of synthesized NPs (Vanaja et al., 2013). The results of silver nitrate concentration on green synthesized Ag NPs were opposite to temperature and pH. The fastest NPs and the smallest NPs were synthesized in the lowest concentration of 1 mM silver nitrate solution. This is because the leaf extract contains many functional groups, and when the substrate concentration increases, the competition between the functional groups in the leaf extract increases and the NPs aggregate. The polyphenols and flavonoids in the extract were responsible for the reduction of Ag ions to zero-valent Ag NPs. The absorption spectra show that the absorbance also increases with time and becomes sharper due to the increasing concentration of Ag NPs. The SPR band around 400–407 nm confirms the formation of Ag NPs, and the sharpness of the peak corresponds to spherical NPs (Kreibig et al., 1999). At the same time, this study also emphasizes that the reaction time has a certain influence on the morphology and size of the synthesized NPs. In addition, many researchers have performed many time-dependent studies on the formation of NPs and their size. For example, in aqueous solution, Au rapidly bound to alfalfa sprouts and roots within the first 5 min and remained stable for 90 min, during which time the size of NPs changed (Herrera et al., 2003).

Subsequently, the synthesis of NPs with plant extracts is an effective method to reduce pollution and improve utilization efficiency. Therefore, we can synthesize the desired NPs by controlling the reaction conditions.

2.3. Plant mediated synthesis of NPs- state of art

Metallic NPs can be further divided into noble metal NPs and non-noble metal NPs (Chandra et al., 2014; Chen et al., 2014; Ghanta and Muralidharan, 2013), for example, zinc (Zn), copper (Cu), aluminum (Al), nickel (Ni), etc. NPs (Huang et al., 2017; Li-Er et al., 2018). Noble metal NPs are

consisting of Au, Ag, platinum (Pt), ruthenium (Ru), rhodium (Rh), iridium (Ir), osmium (Os) and palladium (Pd) NPs, among others. As we all know, noble metal NPs have attracted much attention due to their unique characteristics such as large specific surface area, high specific surface area, good optical and electronic properties, high stability, easy synthesis, and tunable surface functionalization (Tan et al., 2021). More importantly, noble metal NPs have excellent compatibility with biomaterials, which is why they are widely used in biological fields such as antibacterial (Tan et al., 2021). Therefore, the widely followed noble metal is selected to show the research status and advantages of green synthesis. Some examples of GS-MNPs are listed in **Table 2**.

3. Agricultural application of plant-based GS-MNPs

In recent years, the relationship between GS-MNPs and agriculture has attracted strong interest from researchers (Xu et al., 2021b). In this review, the application of GS-MNPs in agriculture is discussed in four main sections. First, GS-MNPs have different effects on plants by exposure methods, which are mainly divided into seed priming, direct contact with soil, and foliar spraying. Second, in the process of crop growth, due to the low application efficiency of traditional fertilizers, a lot of pollution and waste are caused. Promoting plant growth with GS-MNPs as nano-fertilizers is an important step towards green and sustainable development. Third, crop can be attacked by pathogens, which reduces yields. The use of GS-MNPs against various pathogens is a new and viable option. In addition, GS-MNPs used to encapsulate pesticides for controlled release can provide a wide range of benefits, including improving efficiency, durability and reducing the number of active ingredients required in its formulation (Kookana et al., 2014; Shang et al., 2019). Fourth, heavy metal stress in the soil leads to the reduction of crop yield and quality. The environmental problem that has plagued us for many years can be effectively solved by GS-MNPs. Therefore, the utilization of GS-MNPs is an inevitable trend of eco-friendly nanotechnology, and the promotion of nanotechnology is beneficial to improve the sustainability of agricultural production.

3.1 Application methods of GS-MNPs

3.1.1 Seed priming

Seed priming is a key process in the growth and development of crop (Chen and Arora, 2013). It alters the metabolism and signaling pathways within the seed, which directly affects seed

germination and seedling formation, and potentially the entire life cycle of the plant. In nano experiments, NPs suspension were used as initiator to improve seed germination and growth (Xin et al., 2020). The NPs penetrate the pores of the seed, diffuse into the interior and activate plant hormones that stimulate growth. Previous studies have shown that the application of NPs to seed priming can promote seed germination, as this process eliminates ROS and regulates plant growth hormones (Adhikary et al., 2022). In addition, during germination, seed priming activates various genes, especially those associated with plant resistance (An et al., 2020; Mahakham et al., 2017), leading to an increase in resistance. (Liu and Lal, 2015). Nanomaterials with unique physical and chemical properties are expected to save more energy than bulk chemicals (Kasote et al., 2019). Due to their inherent physicochemical properties, various nanomaterials have been used for seed priming (MS et al., 2021). Seed coating is formed because traditional seed priming uses mainly water or nutrients or hormones. However, in nano-seed priming, the large fraction remains on the seed surface as a coating regardless of whether they are absorbed (Duran et al., 2017; Falsini et al., 2019; Montanha et al., 2020). The resulting seed coating can be applied to stop pathogens from entering the plant. Seeds can absorb nanomaterials at the cellular level to minimize input and avoid molecular interactions. Seed priming enhances the defense mechanisms of seeds, enabling the seedling to overcome different environmental stresses (do Espirito Santo Pereira et al., 2021). Some researchers have found that seedlings induced by NPs are more resistant to stress, which is reflected in the activities of plant hormones and enzymes in the antioxidant system (Paul et al., 2022).

Drought is one of the common abiotic stresses that affected plant growth, development and metabolism activities, which caused by the inadequate water. Interestingly, drought stress affects plants at different growth stages to different degrees. The study by Amritha et al.(2021) showed that the use of nanomaterials under drought stress improved the germination rate of seeds (**Figure 5**) (Amritha et al., 2021). This is because, after seed priming with nanomaterials, there are two ways of mitigating stress. One is that nanomaterials regulate the activity of internal hormones in plants, strengthen the antioxidant system, and reduce the production of reactive oxygen species to relieve stress. Alternatively, seed priming induces stress tolerance gene expression and signaling mechanisms that enhance stress resistance.(Amritha et al., 2021). In addition, ZnO NPs increased the activation of phosphoglucomutase and cytoplasmic convertase, thus promoting the synthesis of

sucrose in leaves. Overall, ZnO NPs resisted salt stress by activating the antioxidant system, reducing ROS, improving plant photosynthesis, and promoting nutrient uptake (Wang et al., 2020). In another study, biocompatible FeO NPs were synthesized by using *Cassia occidentalis* L. flower extracts, and then used as nano-initiators to promote rice seed germination (Afzal et al., 2021). The results showed that seed priming with green synthesized FeO NPs promoted the growth and development of rice seedlings and increased the total soluble sugar content in the seeds by 24% compared with the control group. (Afzal et al., 2021). Additionally, onion extract were also used for the synthesis of Fe NPs (Kasote et al., 2019). The experimental results showed that the green synthetic Fe NPs not only had no toxic effects on seed germination and seedling development, but also continuously enhanced non-enzymatic antioxidant capacity and triggered or induced Jasmonic acid (JA)-related defense responses. Heavy metal concentration in the soil above environmental thresholds levels cause numerous harmful impacts on physio-chemical properties of soil (Barbieri, 2016). Previous study reported that plants were grown in heavy metal contaminated soil, accumulate the higher amount of heavy metals in root that generate the ROS and inhibited the plant growth and development (Salt et al., 1995). Cadmium (Cd) is a non-essential element for plant growth, and excessive levels of Cd can inhibit wheat (*Triticum aestivum*) growth (Rizwan et al., 2016). Rizwan et al. (2019) investigated the effect of adding ZnO and Fe NPs (seed priming) to Cd-contaminated soils on wheat (*T. aestivum*) growth. The results showed that both types NPs promoted the photosynthetic rate of wheat compared with the control, while reducing the accumulation of Cd in roots, shoots and seeds (Rizwan et al., 2019). ZnO NPs induced an increase in the activity of super oxide dismutase (SOD), ascorbate peroxidase (APX) and catalase (CAT) in plants, along with an increase in trapped energetic fluxes and electron transport fluxes, thus promoting photosynthesis in plants. Thus, it can be concluded that the seed priming has a positive influence on seedling growth by regulating plant metabolic activities.

Nano-seed priming is a new research field, which needs more research to explore the underlying mechanism. As well as the need to find out the optimum concentration of GS-MNPs that enhance the seed germination and reduce the microbial attacks on early growth of seedling.

3.1.2 Soil application

Root uptake is a major pathway for NP uptake by plants. After crossing the barrier layer in the plant through the symplast or apoplast pathway, NPs finally reach the xylem for longitudinal migration and transformation (Zhang et al., 2020).

Studies have shown that GS-MNPs can remediate heavy metal-contaminated soils. For example, superparamagnetic iron oxide NPs were synthesized with *Eucalyptus globulus* Extract and their effects on soil heavy metals were explored. The results show that the NPs exhibit excellent efficiency in remediation of agricultural soils, eliminating metals such as Cr-VI, Cd, and to a lesser extent Pb (Andrade-Zavaleta et al., 2022). Sebastian et al. (2018) synthesized iron oxide NPs using husk extract from *Cocos nucifera* L. *Chandrakalpa* and elucidates the effect of NPs on Ca and Cd tolerance in rice under sand culture conditions. Studies have shown that iron oxide NPs have adsorption properties for Ca and Cd and the efficiency of metal adsorption depends on temperature and pH (Sebastian et al., 2018b).

At present, nano-fertilizers have become one of the hottest topics. More and more researchers are exploring this, but there is currently no soil culture experiment of GS-MNPs on plant growth promotion, which requires researchers to further explore.

3.1.3 Foliar application

Foliar spraying of micronutrients is a common practice in agriculture. The use of NPs as nano-fertilizers for foliar spraying would be advantageous as it can potentially improve use efficiency of the nutrients by plants. (Patel et al., 2019). It has been reported that the reactivity, mobility, and bioavailability of NPs in soil is strongly hindered due to heterogeneous aggregation between NPs and soil particles (Usman et al., 2020). Therefore, foliar spraying would be a better method for NPs to quickly enter plant tissues and eliminate ROS directly.

In one study, used the green tea to synthesized copper oxide nanoparticles (CuO NPs) were realized. The results showed that 50 mg/L CuO NPs (13.4 ± 0.1 nm) were sprayed onto lettuce leaves caused a three-fold increase in lettuce dry weight (Pelegrino et al., 2021). In another study, Ag NPs and Cu NPs were synthesized from the aqueous extract of *Justicia spigera* and foliar sprayed on *Annona muricata* L. The results suggest that NPs can promote phenylpropanoid biosynthesis and antioxidant activation to protect *A. muricata* from oxidative stress (Jonapá-

Hernández et al., 2020). In addition, Ag NPs were synthesized from *Moringa oleifera* leaf extract, and then different concentrations (25, 50, 75 and 100 ppm) of Ag NPs were foliar applied to wheat plants inoculated with *Puccinia striiformis* to evaluate the incidence of wheat stripe rust disease. The results show that Ag NPs concentrations of 75 ppm were found to be most effective against wheat stripe rust (Sabir et al., 2022). Irshad et al.(2021) utilized leaf extracts of two plants (*Purslane*, *Quinoa*) for green synthesis of TiO₂ NPs and then sprayed on wheat(Irshad et al., 2021). It was found that the Cd concentrations in straw, roots and grains were decreased after TiO₂ NPs application compared with the control. Ultimately, the content of cereal Cd was below the recommended threshold for NPs exposure (0.2 mg Cd/kg grain dry weight).

3.2 GS-MNPs for plant growth

In the past decades, farmers faced the problem with the inefficiency and poor solubility of fertilizers. Farmers usually resorted to increasing the used of fertilizer to solve the problem, while excessive fertilizer application results in leaching and volatilization to the environment, which not only caused waste of fertilizer but also increased the risk of environmental pollution (Lowry et al., 2019; Zhao et al., 2020). Therefore, it is necessary to develop a new, green and sustainable agricultural technology to increase the yield. Nanotechnology can dramatically change agriculture by improving the productivity and quality of crops in the form of nano-fertilizers. (Figure 6). On the one hand, nano-fertilizers can enter the root and leaf cells of plants more easily than traditional fertilizers, and bring chemicals into these cells with better solubility and dispersibility without changing the physicochemical properties of the soil (Seleiman et al., 2020). On the other hand, NPs can promote plant metabolism and enhance rhizosphere microbial activity (Acharya et al., 2019). GS-MNPs as nano-fertilizers promote the activity of soil microorganisms and did not change the physicochemical properties of soil, which is an inevitable trend for sustainable agriculture.

Phosphorus (P) is an essential element for all living organisms. Soil contains large amount of P, while most of them are in the form that are not available for plant uptake (Syers et al., 2008). The high application rate and low efficiency of phosphate fertilizers increase the pollution and eutrophication of water bodies on the one hand, and increase the waste of resources on the other hand (Syers et al., 2008). Therefore, how to improve the utilization efficiency of traditional

phosphate fertilizers has received extensive attention. Taşkın et al. (2018) found that lettuce yields increased after nano-hydroxyapatite treatment compared to plants treated with conventional phosphate fertilizers (Taşkın et al., 2018). Theoretically, nano-hydroxyapatite interacts with soil constituents weaker than the charged ions in conventional phosphate fertilizers and has a smaller size and larger specific surface area. Therefore, it can promote the uptake of P by plants better than conventional phosphate fertilizers. Ullah et al. (2020) explored the effect of TiO₂ NPs on the content of plant available P in soil. It was found that the concentration of plant available P in the soil was significantly increased to 63.3% in the treatment group of 50 mg/kg TiO₂ NPs compared with the control (Ullah et al., 2020). In addition, nano-hydroxyapatite has slow-release properties, which can provide nutrients to plants in a sustainable way (Raliya et al., 2018). Similarly, iron (Fe) is an essential nutrient required by all living organisms. In the process of plant growth, Fe promotes chlorophyll synthesis, respiration, and more (Mimmo et al., 2014; Zargar et al., 2015). Conversely, Fe deficiency can affect plant growth (Rui et al., 2016). Therefore, improving the efficiency of Fe fertilization is an issue that must be addressed. Rui et al. (2016) added different concentrations of Fe₂O₃ NPs and EDTA-Fe to peanut soil. The results showed that both Fe₂O₃ NPs and EDTA-Fe could promote the growth of peanut plants. This may be because Fe₂O₃ NPs can be adsorbed on sandy soils, thereby enhancing the utilization of Fe by plants (Rui et al., 2016). In addition to boosting nutrient absorption and reducing fertilizer use, NPs can also boost antioxidant systems and enhance the ability to resist stress, resulting in increased yield. These antioxidant enzymes quench ROS during seedling growth and reduce ROS damage (Ye et al., 2019). Although NPs promote plant growth to a certain extent, it is related to the concentration. Above a certain concentration, NPs may show toxic effects. It should not be overlooked that NPs used for seed priming process, for mitigation of various stresses (heavy metals, drought, salt, etc.), for resistance to pathogens, can indirectly contribute to plant growth and development (Alghanem et al., 2021; Hussain et al., 2017).

3.3 GS-MNPs acting as antibacterial agents

Over the past decade, plant diseases have been affecting plant growth and causing losses in agricultural production. Currently, crop production relies on synthetic agrochemicals to minimize plant pathogens and ensure crop yields (Athanasios et al., 2018). Obviously, the use of pesticides,

fungicides and bactericides is growing rapidly worldwide (Fu et al., 2020). However, excessive and indiscriminate use of agrochemicals contributes to global warming and leads to multiple adverse effects, including increased resistance to pesticides (Jang et al., 2014), toxicity to non-target organisms, and a serious threat to the economy and health of humans (Deshpande et al., 2017). This raises concerns about the toxicity of environmental residues (Manish and Sunder, 2013), which requires economical, environmentally compatible, and rapid plant disease control strategies and advanced technologies to improve the effectiveness of disease control and reduce environmental damage. At this critical juncture, nanotechnology appears to be a new way of controlling plant diseases (Agrios, 2005). GS-MNPs have shown an active role in crop disease management. For example, Ag NPs, Cu NPs, ZnO NPs and Fe₂O₃ NPs have been shown to protect plants from bacterial and fungal infections (**Table 3**).

In terms of the sterilization of NPs, as shown in the **Figure 7**, there may be two mechanisms: one is that NPs cause oxidative stress to generate ROS (Besinis et al., 2014). Then, the generated ROS damage the internal structure of bacteria, such as DNA damage, DNA replication inhibition, protein denaturation and enzyme destruction. The other is the free metal ions resulting from metal dissolution on the surface of NPs enter bacteria through direct physical contact or assimilation, and then destroy the internal structure of bacteria or destroy the cell membrane to achieve sterilization. In addition, the morphology and physicochemical properties of NPs have been shown to affect their antibacterial activity (Mohammadi et al., 2011; Seil and Webster, 2012). Smaller NPs are known to have a stronger bactericidal effect (Besinis et al., 2014; Fellahi et al., 2013; Mohammadi et al., 2011). The positive surface charge of metal NPs helps them bind to the negatively charged surface of bacteria, which may lead to an enhanced bactericidal effect (Seil and Webster, 2012). The shape of NPs can also affect their antibacterial effect (Bera et al., 2014; Pal et al., 2007). In addition to sterilization, NPs enhance the tolerance of plants, so that plant can resist the invasion of germs well enough. El-Shetehy et al. (2021) explored that nano-silica enhanced the disease resistance of *Arabidopsis thaliana* plants (El-Shetehy et al., 2021). The functions of SiO₂ NPs are: (a) slowly releasing Si(OH)₄ into cells, in which Si(OH)₄ is a form of Si that can be absorbed by cells, which can enhance the stress resistance of plants and promote the growth of plants; (b) blocking pores, triggering salicylic acid(SA), causing local resistance. However, the transmission of SA in the

extracellular space stimulated the SAR signal and triggered the subsequent overall defense (SAR can prevent pathogens from invading). Rahisuddin and Akrema synthesized Ag NPs using an extract of the leaves of *Callistemon viminalis* and demonstrated the antibacterial properties of Ag NPs (Rahisuddin and Akrema, 2016).

Crop diseases resulting from fungal pathogens appear at specific stages of plant growth and limiting the development of agricultural economy. Fungi have two sources of nutrients from plant, one is to absorb nutrients directly from the plant and the other is to destroy the plant cells to absorb the released nutrients (Xu et al., 2021a). The new approaches are that exposure of GS-MNPs to remove the fungi or inhibit the growth of fungi. *Dahlia verticillium* is a widespread fungal pathogen, which can cause serious diseases in many crops. *Solanum melongena* L.(eggplant) is considered as among the vegetables with high economic value. However, it is vulnerable to various diseases and pathogens, especially *Verticillium* wilt (Collonnier et al., 2001). Jebril et al. (2020) used *m. zedarach* aqueous extract to prepare Ag NPs as antifungal agent for *Solanum melonal*. In vivo, the presence of Ag NPs reduced the severity of *verticillium* wilt by 87% compared to controls. The results showed that Ag NPs synthesized by plants could inhibit the growth of *Dahlia verticillium* and have positive effects on plant growth (Jebril et al., 2020). *Beauveria bassiana* has a wide host range, with plants in 32 plant families and 188 genera having been infected (Gangopadhyay and Chakrabarti, 1982). It is well known to cause stem and leaf blight, one of the most devastating fungal diseases of rice (Gangopadhyay and Chakrabarti, 1982). The antifungal activity of Ag NPs was evaluated on mycelia and sclerotia of *rhizoma solani* by poisoning food technique and dilution of *rhizoma solani* broth. The results showed that the effective inhibition rate of mycelia growth was dose-dependent. Treatment with 10 mg/L Ag NPs enhanced seedling vigor index by 1.5 times. In addition, Ag NPs treatment at 20 mg/L completely inhibited disease development. Therefore, Ag NPs can be used to control various fungal diseases of crops and enhance the plant growth (Kora et al., 2020). Chikte et al. (2019) stated that the minimum inhibitory concentration (MIC) of traditional ZnO NPs against *Xanthomonas oryzae pv. oryzae* was 20 mg/L (Chikte et al., 2019). However, Abdallah et al. (2020) found that the green synthesized ZnO NPs showed substantial significant inhibition effects against *Xanthomonas oryzae pv. oryzae* strain at a concentration of 16.0 mg/L, for which the antagonized area was 17 mm and the biofilm formation was decreased by 74.5%

(Abdallah et al., 2020).

In addition to fungal pathogens, bacterial pathogens can contribute to many plant diseases and limit the agricultural production. In general, most of these pathogens live on plants and can also be in the soil. Some bacteria can cause damage to plant cell walls and have a series of negative effects on plants (Xu et al., 2021a). *Parthenium hysterophorus* L. is a kind of poisonous and harmful weeds and invasive. Different sizes of ZnO NPs were synthesized and their resistance to plant fungal pathogens were explored by Rajiv et al. (2013). The results demonstrated that *Parthenium*-mediated synthesis of ZnO NPs showed the highest zone of inhibition against *Aspergillus flavus*. This opens up the possibility of ZnO NPs as antimicrobial agents with excellent biocompatibility (Rajiv et al., 2013). In general, bacterial diseases of plants infect a wide range of plants and thus cause huge losses worldwide (Nazarov et al., 2020). In addition, the antibacterial mechanism of NPs is to cause apoptosis of bacterial cells, the production of ROS, destruction of biofilm, cell wall, and eventually cell death. *Solanacearum* known as bacterial wilt, which influence widespread latent host plant in subtropical and temperate zones of the tropics (Champoiseau et al., 2009). The main characteristic of *Solanacearum* is that once formed, it is difficult to remove from the soil (Yuliar et al., 2015). As a result, it has a strong ability to survive in soil. Tortella et al. (2019) synthesized the Ag NPs from the leaf extracts of *Chilean native* weeds, and measured their antibacterial activity by disk diffusion method, and measured their MIC and minimum bactericidal concentration (MBC). The results revealed that MIC (30 mg/L) and MBC (40 mg/L) showed high antibacterial activity of Ag NPs against bacterial wilt (Tortella et al., 2019). In addition, Jamdagni et al. (2018) compared the antimicrobial properties of chemically synthesized and green synthesized Ag NPs. It was concluded that the MICs of traditional Ag NPs against *A. alternata*, *A. niger*, *B. cinerea*, *F. oxysporum*, and *P. expansum*, were 64, 8, 32, 64, and 64 mg/L, respectively. While the MICs of green synthesized Ag NPs against *A. alternata*, *A. niger*, *B. cinerea*, *F. oxysporum*, and *P. expansum*, were 32, 8, 32, 32, and 64 mg/L, respectively. This suggests that GS-MNPs have superior performance in antibacterial (Jamdagni et al., 2018). In the future, more studies are needed by using other GS-MNPs as antibacterial agents that are highly used in the agricultural field.

3.4 GS-MNPs for alleviating heavy metal stress

Heavy metal contamination is not only harmful to biota, but also related to global environment (Fan et al., 2016). Recently, due to various human activities, such as mining and burning of the fossil fuels, more and more heavy metals have been released into the environment (Munzuroglu and Geckil, 2002), especially in the soil. Excessive heavy metal contamination seriously endangers the growth of crops and human health through the accumulation of food chain (Onakpa et al., 2018). Sufficient studies have shown that NPs can effectively alleviate various stresses on plants. Here, some common mechanisms of stress mitigation by NPs are summarized (**Figure 8**). For the typical heavy metal stress, the following strategies can alleviate the heavy metal stress in plants.

NPs usually have a large specific surface area and have unique properties in reducing the negative impact of heavy metals on natural resources (Dickinson and Scott, 2010; Shen et al., 2009). NPs can directly affect soil properties, for example changing soil pH value, adjusting soil water holding capacity, microbial community structure, which can indirectly reduce the bioavailability of heavy metals in soil (Zhou et al., 2021). In addition, NPs may directly affect stress sources (heavy metal), including adsorption, complexation, and other reactions (Zhang et al., 2022). Since some NPs contain essential elements that required by plants, such as Fe, Zn and Se, the supplement of these elements can effectively improve the stress resistance of plants. It should be noted that Fe supplementation contributes to the formation of root Fe plaque, which can block most pollutants (Deng et al., 2010). Some signal-inducing mechanisms of NPs on plants are also considered essential strategies to alleviate stress. Some researchers found that NPs can promote the synthesis of some plant protective agents (including root exudates, phytochelin and organic acids) (Verma et al., 2018). Moreover, some NPs can regulate the expression of heavy metal transport genes and genes related to plant hormone synthesis in plants. Interestingly, NPs can enhance the ability of the plant antioxidant system, and some NPs can directly remove excess ROS in plants because of their unique properties (Wu et al., 2017). For example, CeO₂ NPs can directly remove ROS to alleviate stress and promote biological growth (Wu et al., 2017). Briefly, excess light causes electron transfer from Photosystem I (PSI) to oxygen to form superoxide anion (O²⁻). SOD reduces superoxide anion to produce hydrogen peroxide (H₂O₂). The H₂O₂ reacts with ascorbic acid (AsA) and anti-APX to produce MDA and H₂O on the one hand, and produces hydroxyl radicals that are difficult to scavenge through Fenton reaction on the other hand. In the presence of NPs, ROS such as O²⁻, H₂O₂

and hydroxyl radicals are eliminated.

Cd is considered to be a common toxic trace metal in the environment because of its persistence and high mobility (Das et al., 1997). Cd is easily absorbed into the roots of crops in soil or water medium and then transported to buds (Liu et al., 2009). A recent soil survey in China reported that at least 13,330 hectares of agricultural land are currently contaminated with Cd (Liu et al., 2009). It is well known that Cd accumulates in the soil and subsequently transfers through the food chain, ultimately posing a threat to human health (Jarup et al., 1998). Therefore, reducing the absorption and accumulation of Cd by crops is very important to ensure food security. Wang et al.(2019) used CeO₂ NPs to add nutrient solution of rice seedlings under Cd stress, salt stress and both (Wang et al., 2019). The results showed that the presence of CeO₂ NPs reduced chlorophyll damage in rice under Cd stress conditions. CeO₂ NPs can reduce the content of corresponding heavy metal elements, which may be due to the competition for calcium channels in rice roots (Wang et al., 2019). In recent years, one of the popular means of arsenic (As) remediation is using low-cost Fe adsorbents, including Fe NPs and Fe₂O₃ NPs. These adsorbents remove As by adsorption, co-precipitation, ion exchange and reduction (Virgen et al., 2018). However, a majority of Fe adsorbents are chemically prepared, which are costly and not environmentally friendly. Therefore, various green synthetic Fe NPs have received increasing attention. A study showed that Fe₂O₃ NPs can resist various kinds of heavy metal stress at different concentrations by absorbing heavy metal ions and improving wheat's own antioxidant system (Konate et al., 2017). The results showed that the content of heavy metals and malondialdehyde (MDA) decreased significantly compared to the control group, while the activities of SOD, POD and other antioxidant enzymes increased. Francy et al.(2020) synthesized Fe NPs by using the leaves of *Mentha longifolia* (mint) (Francy et al., 2020). Then, the NPs were used to remove Pb and Ni from contaminated soil. The results showed that the chemically synthesized NPs were the least efficient, and the NPs synthesized from mint leaves were more effective for the removing both metals, with 62.3% for Pb and 50.6% for Ni (Francy et al., 2020). In addition, chronic exposure to chromium (VI) (Cr (VI)) in human can damage health which can lead to kidney failure. Due to these harmful effects, it is important to remediate Cr (VI) from the environment. According to the previous study, green synthesized Fe NPs used for Cr (VI) removal from soil medium (Rao et al., 2013). Similarly, Madhavi et al.(2013) used *E. globulus* leaf extracts

to synthesize Fe NPs for the removal of Cr (VI) (Madhavi et al., 2013). This may be due to the effective adsorption of Cr (VI) by a polyphenolic compound present in *E. globulus*. The adsorption isotherm demonstrates the occurrence of adsorption, which is instructive for the use of Fe NPs as green adsorbents. In addition to adsorption of Cr (VI), Fe NPs can also reduce Cr (VI) availability. Mystrioti et al.(2015) synthesized Fe NPs from green tea extract and trivalent iron solution (Mystrioti et al., 2015). The polyphenols in green tea extract acted as reducing and capping agents. Remediation potential of the Fe NPs produced by the green tea method against Cr (VI) was confirmed by column testing.

Undoubtedly, additional research is in need to removal or change the available to unavailable form of heavy metals in plant growing medium. The complete life cycle of plants is also required with exposure of GS-MNPs in heavy metals contaminated medium.

4. Summary and future perspectives

Due to the constraints of agricultural development, nanotechnology has emerged as a solution to achieve a sustainable agriculture. In recent years, the synthesis of NPs from plant extracts has increasingly become a research hotspot. This review summarizes the methods, influencing factors of GS-MNPs, and compares the agricultural advantages of GS-MNPs over conventional NPs. The applications of GS-MNPs in agriculture, such as seed germination, plant growth, antibacterial, and mitigation of heavy metal stress, are also highlighted.

However, the role of GS-MNPs in sustainable agricultural is not fully developed and further studies needed to be in this context. More recommendations are:

1. More research is needed to elaborate the impact of GS-MNPs on plant physiology and biochemical and GS-MNPs uptake by plant as a micronutrient at molecular level.
2. Further research is needed on full life cycle of plant species in various medium for expecting the GS-MNPs used as biofertilizer for plant growth and production.
3. The toxic effect of GS-MNPs on soil microorganisms, plant, and animal health for long exposure requires additional inquiries since it is closely associated with shapes, sizes, capping agents, types and surface charges of GS-MNPs.

4. To fulfill the demand for GS-MNPs for large-scale/field applications, we may use market vegetable residue or rotten fruits (juices) to synthesize GS-MNPs.
5. Most of the previous documented studies used noble metals (Au, Ag and Pt) for GS-MNPs but there is no GS-MNPs made of Ru, Rh, Ir and Os metals that has been synthesized. For a long time, these metals are considered stable, with a low environmental impact and non-toxicity to humans. Therefore, green synthesis of such metal NPs is beneficial to the sustainable development of agriculture.
6. The changes in plant physiology and metabolites that caused by different exposure methods of GS-MNPs need to be further explored, because various exposure methods lead to different absorption of NPs by plants, and the transformation of NPs in media (soil/hydroponic) is also different.

After improving these aspects, GS-MNPs will be able to better serve agriculture and become a frontier method for sustainable agricultural development.

Author contributions

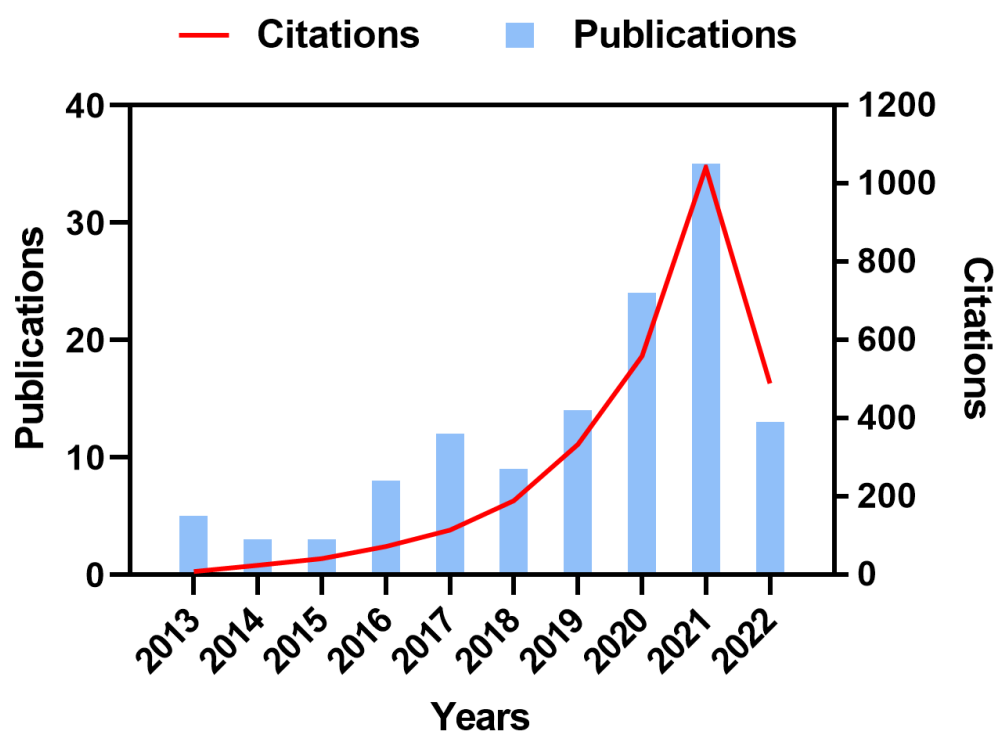
Yaqi Jiang: Writing - Original Draft, Visualization, Conceptualization. Pingfan Zhou: Writing - Review & Editing, Conceptualization. Peng Zhang, Muhammad Adeel, Noman Shakoor, Yuanbo Li, Mingshu Li, Manlin Guo, Weichen Zhao, Benzhen Lou, Lingqing Wang, Iseult Lynch: Writing - Review & Editing. Yukui Rui: Writing - Review & Editing, Supervision.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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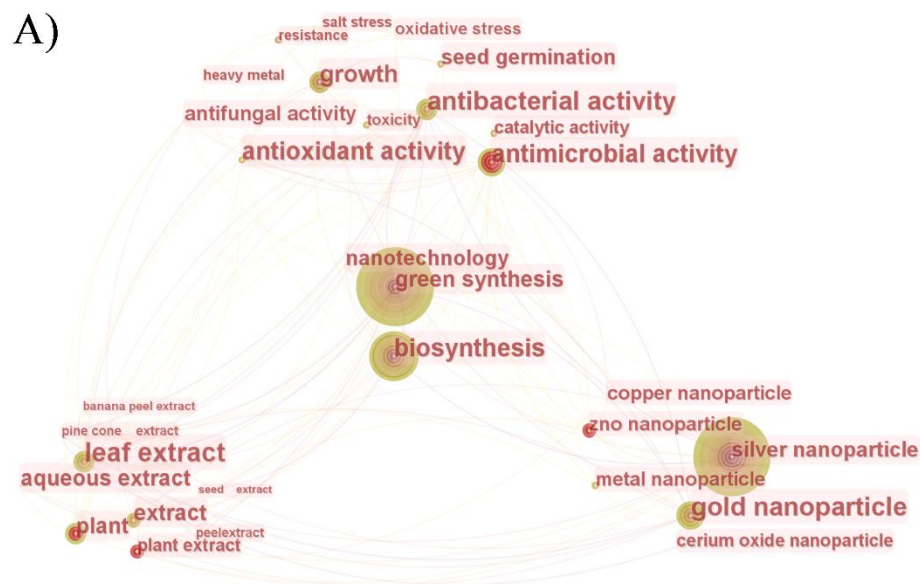
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611 **Figure 1** Number of publications and citations in the literature on the application of GS-MNPs in

612 agriculture over the past decade.

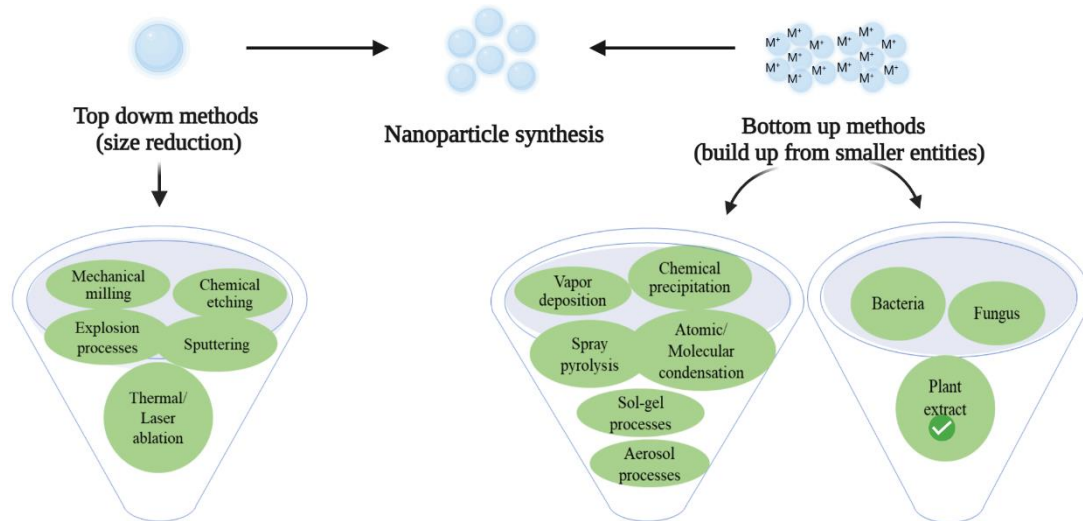


B) Top 15 Keywords with the Strongest Citation Bursts

| Keywords | Year | Strength | Begin | End | 2013 - 2022 |
|---------------------------|------|----------|-------|------|------------------------|
| escherichia coli | 2013 | 1.06 | 2013 | 2016 | <div><div></div></div> |
| gold nanoparticle | 2013 | 0.66 | 2013 | 2015 | <div><div></div></div> |
| cerium oxide nanoparticle | 2013 | 0.75 | 2014 | 2018 | <div><div></div></div> |
| ag | 2013 | 0.66 | 2014 | 2017 | <div><div></div></div> |
| green nanotechnology | 2013 | 1.75 | 2015 | 2016 | <div><div></div></div> |
| biological technique | 2013 | 1.07 | 2016 | 2017 | <div><div></div></div> |
| antimicrobial activity | 2013 | 1.03 | 2017 | 2020 | <div><div></div></div> |
| biochemical profiling | 2013 | 0.8 | 2017 | 2019 | <div><div></div></div> |
| nanotechnology | 2013 | 1.19 | 2018 | 2019 | <div><div></div></div> |
| zno nanoparticle | 2013 | 1.82 | 2019 | 2022 | <div><div></div></div> |
| plant extract | 2013 | 1.82 | 2019 | 2022 | <div><div></div></div> |
| cytotoxicity | 2013 | 1.23 | 2019 | 2020 | <div><div></div></div> |
| antibacterialactivity | 2013 | 0.95 | 2019 | 2020 | <div><div></div></div> |
| plant | 2013 | 0.75 | 2019 | 2020 | <div><div></div></div> |
| acid | 2013 | 1.14 | 2020 | 2022 | <div><div></div></div> |

Figure 2 (A) Graph of high frequency keywords over time and keyword clustering from 2013 to 2022. The size of the nodes indicates the frequency of the keywords in the studied literature. (B) The top 15 most cited keywords.

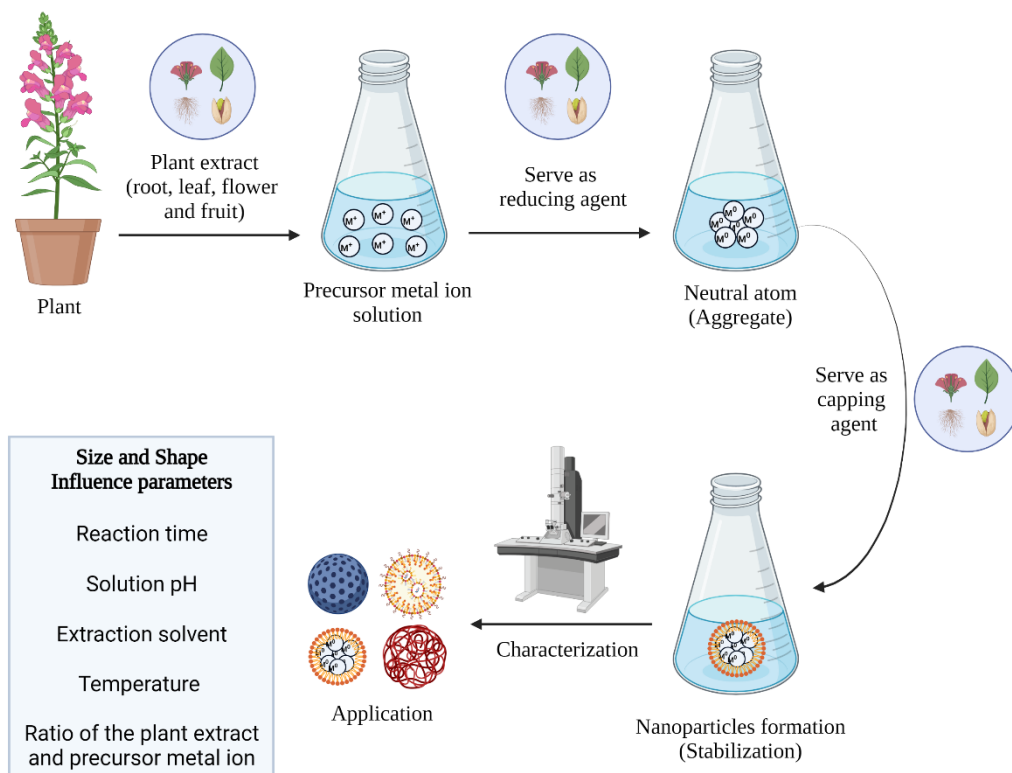
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619 **Figure 3** Various approaches for making NPs.

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622 **Figure 4** Schematic diagram for synthesis of NPs by using plant extracts.

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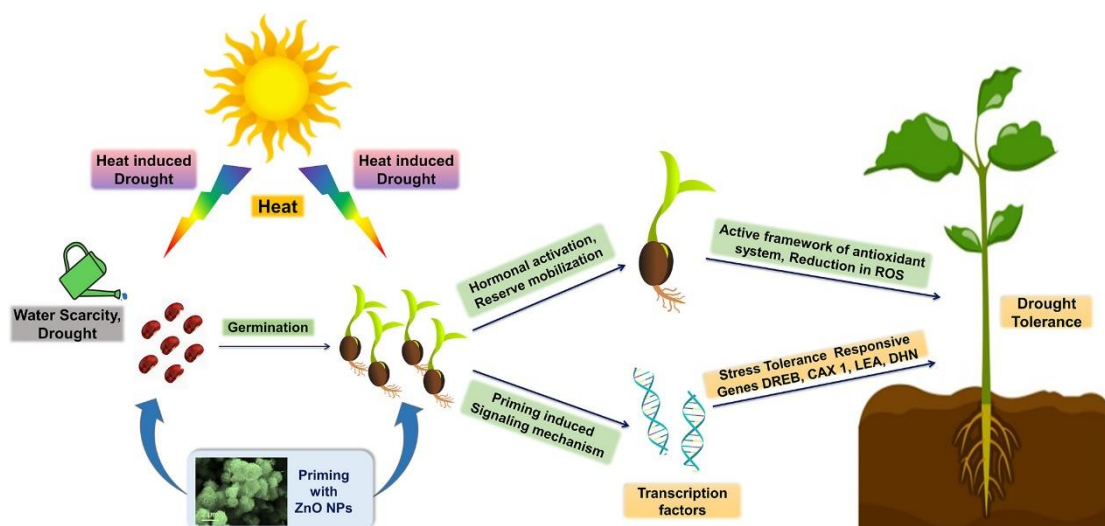


Figure 5 Schematic diagram of priming with nanoscale ZnO NPs to improve their tolerance for growth under drought stress .Reproduced with permission from ref (Amritha et al., 2021).

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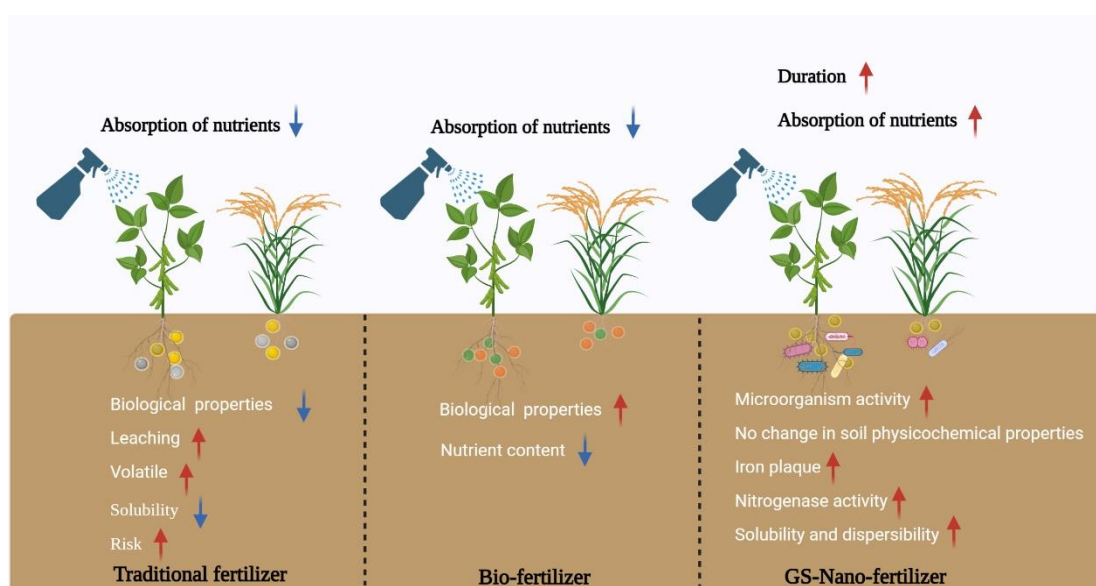


Figure 6 Comparison between nano-fertilizer and traditional fertilizer.

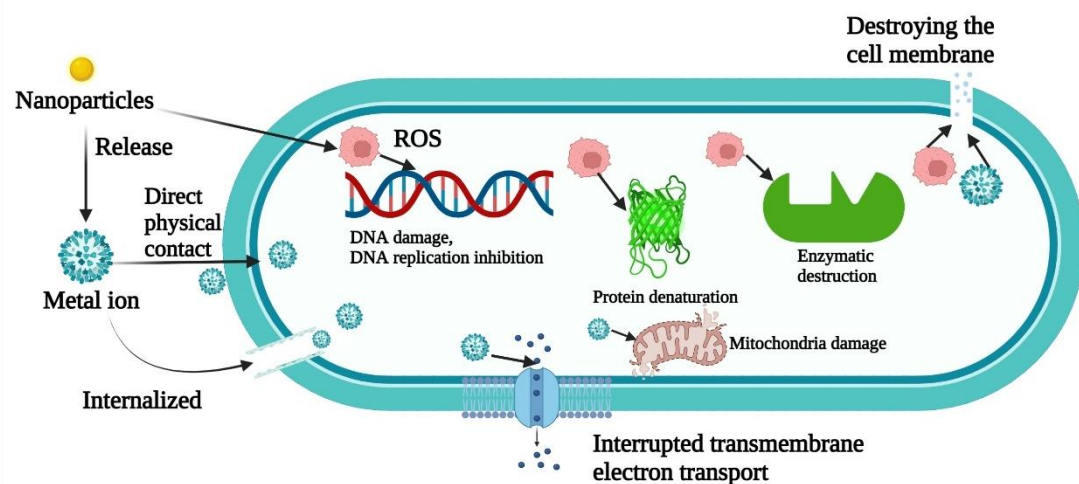


Figure 7 Antibacterial mechanism of NPs.

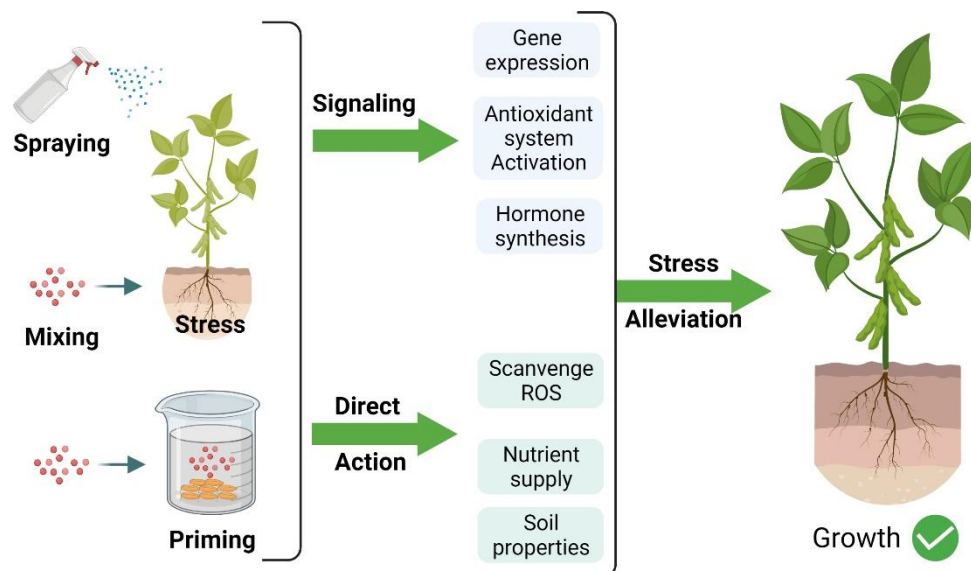


Figure 8 A schematic model figure is showing how exogenous GS-MNPs application improves the stress tolerance in plants.

Table 1 Comparison of GS-MNPs and conventional MNPs for agricultural applications

| Strengths | Traditional MNPs | GS-MNPs |
|------------------------|--|--|
| Toxicity | Toxic waste is produced. | It has little or no toxic effect on the follow-up. |
| Cost | Chemicals are expensive. | Cheap raw materials. |
| Antibacterial property | The MIC (minimum inhibitory concentration) of ZnO NPs against <i>Xanthomonas oryzae pv. oryzae</i> was 20 mg/L (Chikte et al., 2019). | GS-ZnO NPs showed substantial significant inhibition effects against <i>Xanthomonas oryzae pv. oryzae</i> strain at a concentration of 16.0 mg/L, for which the antagonized area was 17 mm and the biofilm formation was decreased by 74.5% (Abdallah et al., 2020). |
| Antifungal property | The MICs (minimum inhibitory concentrations) of Ag NPs against <i>A. alternata</i> , <i>A. niger</i> , <i>B. cinerea</i> , <i>F. oxysporum</i> , and <i>P. expansum</i> , were 64, 8, 32, 64, and 64 mg/L, respectively (Jamdagni et al., 2018). | The MICs (minimum inhibitory concentrations) of Green Ag NPs against <i>A. alternata</i> , <i>A. niger</i> , <i>B. cinerea</i> , <i>F. oxysporum</i> , and <i>P. expansum</i> , were 32, 8, 32, 32, and 64 mg/L, respectively (Jamdagni et al., 2018). |
| Oxidation resistance | DPPH removal rate of 76.9% for 100 mg conventional TiO ₂ NPs (Karunakaran et al., 2013). | Over 81% DPPH removal by 100 mg of synthesized TiO ₂ NPs (Santhoshkumar et al., 2014). |

Table 2 Synthesis of different MNPs by using various plant extract.

| Plant | Type of NPs | Size (nm) | Shape | Reference |
|--|--------------------------------|-----------|-----------------------|------------------------------------|
| Lemongrass (sprouts) | Au | 200-500 | Spherical, triangular | (Shankar et al., 2005) |
| <i>Psidium guajava</i> (leaves) | Au | 25–30 | Spherical | (Raghunandan et al., 2009) |
| <i>Dioscorea bulbifera</i> (fruits) | Au | 11–30 | Spherical | (Ghosh et al., 2011) |
| <i>Geranium</i> (leaf) | Au | 16–40 | / | (Shankar et al., 2003) |
| <i>Mucuna pruriens</i> (whole) | Au | 6–17.7 | Spherical | (Arulkumar and Sabesan, 2010) |
| <i>Parthenium</i> (leaf) | Au | 50 | Cubic | (Parashar et al., 2009) |
| <i>Anogeissus latifolia</i> (fruit) | Ag | 5.5–5.9 | Spherical | (Kora et al., 2012) |
| <i>Pinus densiflora</i> (fruit) | Ag | 30-80 | Oval, few triangular | (Velmurugan et al., 2015a) |
| <i>Nigella sativa</i> (leaf) | Ag | 15 | Spherical | (Amooaghaie et al., 2015) |
| <i>Azadirachta indica</i> (leaf) | Ag | 41–60 | / | (Poopathi et al., 2015) |
| <i>Red ginseng</i> (root) | Ag | 10–30 | Spherical | (Singh et al., 2016) |
| <i>Abutilon indicum</i> (leaf) | Ag | 5–25 | Spherical | (Ashokkumar et al., 2015a) |
| <i>Euphorbia prostrata</i> (leaf) | Ag | 10–15 | Spherical | (Zahir et al., 2015) |
| <i>Cacumen Platycladi</i> (root) | Pt | 1.6-3.2 | Spherical | (Zheng et al., 2013) |
| <i>Punica granatum</i> 's(peel) | Pt | 16–23 | Spherical | (Dauthal and Mukhopadhyay, 2015) |
| <i>Prunus Xyedoensis tree</i> (fruit) | Pt | 10-50 | Spherical and oval | (Velmurugan et al., 2016) |
| <i>Maytenus royleanus</i> (leaf) | Pt | 5 | Cubic crystalline | (Ullah et al., 2017) |
| <i>Psidium guajava</i> (leaf) | TiO ₂ | 32.58 | Spherical | (Santhoshkumar et al., 2014) |
| <i>Annona squamosa</i> (peel) | TiO ₂ | 21-25 | Spherical | (Roopan et al., 2012) |
| <i>Moringa oleifera</i> (peel) | CeO ₂ | 40 | Spherical | (Surendra and Roopan, 2016) |
| <i>Leucas aspera</i> (leaf) | CeO ₂ | 4–12.8 | Spherical | (Malleshappa et al., 2015) |
| <i>Laurus nobilis</i> (leaf) | CuO | 90-250 | Spherical | (Bulut Kocabas et al., 2020) |
| <i>Abutilon indicum</i> (leaf) | CuO | 16.78 | Spherical | (Ijaz et al., 2017) |
| <i>Anisochilus carnosus</i> (leaf) | ZnO | 30-40 | Hexagonal wurtzite | (Anbuvaran et al., 2015) |
| <i>Artocarpus Heterophyllus</i> (leaf) | ZnO | 10-25 | Spherical | (Vidya et al., 2017) |
| <i>Ixora Coccinea</i> (leaf) | ZnO | 14.5 | Hexagonal wurtzite | (Yedurkar et al., 2016) |
| <i>Asparagus racemosus</i> (root) | Fe ₂ O ₃ | 30–40 | Spherical | (Sharma et al., 2020) |
| <i>Citrus sinensis</i> (leaf) | Fe ₂ O ₃ | 60 | Spherical | (Ahmmad et al., 2013) |
| <i>Plantain</i> (peel) | Fe ₃ O ₄ | < 50 | Spherical | (Venkateswarlu et al., 2013) |
| <i>Ginkgo biloba</i> (leaf) | Cu | 15–20 | Spherical | (Nasrollahzadeh and Sajadi, 2015a) |
| <i>Cocos nucifera</i> (leaf) | Pb | 47 | Spherical | (Elango and Roopan, 2015) |

Table 3 Plant NPs as antibacterial agents.

| Types of NPs | Plant | Pathogens | Result | Reference |
|--------------------------------|---------------------------------|---|--|------------------------------------|
| Fungicide | | | | |
| Ag | <i>Melia azedarach</i> | <i>Verticillium dahlia</i> | Under in vitro conditions, the presence of Ag NPs significantly reduced the growth of <i>Verticillium dahliae</i> | (Jebril et al., 2020) |
| Ag | Rice leaf | <i>Rhizoctonia solani</i> | At 20 mg/mL, Ag NPs treatment completely inhibited the disease. | (Kora et al., 2020) |
| Fe ₂ O ₃ | <i>Azadirachta indica</i> | <i>Fusarium oxysporum</i> | At 100 ppm, the growth inhibition rate was 88% | (Ali et al., 2021) |
| ZnO | <i>Allium sativum</i> | <i>Colletotrichum sp. and Mycena citricolor</i> | At 12 mmol/L, the growth inhibition rate of anthrax was 3%, and the growth inhibition rate of citrus mold was 97% | (Arciniegas-Grijalba et al., 2019) |
| Bactericide | | | | |
| Ag | <i>Hypericum perforatum</i> | <i>Ralstonia solanacearum</i> | 45 mm corrosion inhibitor, 99% reduction at 30 ppm | (Tortella et al., 2019) |
| Ag | <i>Nyctanthes arbortristis</i> | <i>E. coli</i> MTCC 443 | The clear zone of inhibition suggests the antibacterial activity of Ag NPs. | (Gogoi et al., 2015) |
| Ag | <i>Abutilon indicum</i> | <i>S. typhi</i> and <i>S. aureus</i> | The decrease in the size of Ag NPs will lead to an increase in the precise surface of sterilized samples, which indicates that their ability to enter the cell membrane is increased, thus improving the antibacterial activity. | (Ashokkumar et al., 2015b) |
| Ag | <i>Pinus densiflora</i> | <i>B. linens</i> , <i>P. acnes</i> , <i>B. cereus</i> and <i>S. epidermidis</i> . | The synthetic Ag NPs showed the largest zone of inhibition of the skin pathogen <i>Brevibacterium linens</i> compared to other treatments | (Velmurugan et al., 2015b) |
| Ag | Sumac | <i>Pseudomonas syringae</i> | The minimum inhibitory concentrations of green synthesized Ag NPs and Cs-Ag nanocomposites are 12 ppm and 9.2 ppm Cs/4 ppm Ag NPs, respectively. | (Shahryari et al., 2020) |
| ZnO | Green tomatoes | <i>Xanthomonas oryzae pv oryzae</i> | The inhibition rate was 25% at 16 ppm. Better antimicrobial effect with both applications compared to chitosan and zinc oxide alone. | (Abdallah et al., 2020) |
| ZnO | <i>Parthenium hysterophorus</i> | <i>Fusarium culmorum</i> | <i>Parthenium</i> -mediated synthesis of ZnO NPs showed the highest zone of inhibition against <i>Aspergillus flavus</i> and <i>Aspergillus niger</i> compared to the control. | (Rajiv et al., 2013) |

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