# Designing Nanoparticles for Sustainable Agricultural Applications

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## Abstract

Progress towards achieving global food security continues to be hindered by several economic, geo-political and environmental variables which has led the United Nations to place emphasis on achieving Zero Hunger by 2030. Thus, it is important to invest in novel, eco-friendly, cost-effective solutions that will increase agricultural productivity. For this reason, nanoscale materials are increasingly being developed for use in agriculture with attention on controlling various properties such as size, shape, surface modifications and transformations for improved impact in plants. With continued interdisciplinary and collaborative efforts among nanoparticle experts and plant scientists, the research area will evolve to identify the best nanoparticle properties for foliar application to plants.

## Nanoscale materials to alleviate global food insecurity

Engineered nanoparticles (NPs) have drawn special attention for various medical, commercial, and now, agricultural, applications due to their emergent chemical and physical properties that are distinct from their bulk counterparts [1]. These properties can lead to enhanced ion dissolution and transformation as the large surface areas facilitate foliar attachment, chemical tunability, and plant uptake and transport [2-4]. In recent years, the use of NPs in agriculture has grown significantly, where NPs are being developed as sensors for monitoring plant health and pathogen detection [5-8], carriers to deliver beneficial cargo [9-13] and as disease-suppressing agents against various plant pathogens [14-19] with the overall goal of finding solutions to global food insecurity **(Box 1) [20].** The synthetic flexibility during NP design and synthesis enables scientists to use fundamental chemistry to design NPs with a desired size, surface charge, shape, surface coating and roughness, and the ability to transform (**Figure 1, Key Figure) [21-23]** . Depending on the NP type, plant, and the desired application (i.e., sensing, delivery, or pathogen control, etc.), certain NP design expectations can be set with the goal of improving their performance within the plant [5, 24].

In this review, we have assessed the recent literature to present the most promising design parameters that improve nanoparticle uptake and translocation as well as any notable increases in agricultural yield measures. We have limited the scope to foliar applied metal, non-metal, metal oxide and metalloid-based NPs that are likely to be successful in agricultural applications.

Metallic NPs, like gold- and silver-based NPs, are extensively used due to their established and tunable synthesis methods that allow for control over size and surface functionality, high mass contrast during analysis, and plasmonic features that allow for effective *in planta* characterization with low background signal in plants [25, 26]. Several metalloid and metal oxide NPs are similarly drawing attention for their tunable synthesis and because they appear to be outperforming conventional commercial products specifically in plant disease suppression [4, 27]. Farmers are being encouraged to incorporate various micro- and secondary macronutrients to better protect crops against disease and improve crop production [16, 27]. Using nanoscale forms of these nutrients (ZnO, CuO, and $SiO_2$ NPs) has been key to their success due to the increased, and in some cases controlled, ion dissolution as well as improved uptake and translocation in various plant species as is highlighted throughout this review. Since the field of nano-enabled agriculture is relatively new, it is challenging to be comprehensive and draw clear conclusions in this topic as the literature continues to develop. However, considerations of NP design rules prior to implementing experimentation can be invaluable towards propelling the field forward.

**Plant considerations for nanoparticle use in agriculture**

Before designing NPs for agricultural applications, it is critical to understand the application scenario and system of interest. Agriculture is an exceptionally broad field, including animal-based production, annual and perennial plant agriculture and aquaculture. The growth conditions and nutrient requirements can be orders of magnitude different depending on the specifics of the system and the mode of application. The use of inappropriate NPs, or perhaps use of appropriate NPs in inappropriate application regimens, could lead to low efficiency of use or even harm to target and non-target species. Importantly, this review will focus exclusively on plant-based agriculture and potential effective and sustainable strategies that can be designed according to the decision tree shown in **Figure 1.** Moreover, when designing NPs to interact with plants, it is important to recognize that these species have evolved strategies over tens of millions of years to minimize the impact of foreign materials and xenobiotic particles. As such, some subtlety and thoughtful design is warranted. Also, efforts should always be made to minimize dose and exposure, for both economic and health (human, environmental) reasons. Importantly, the design rules will always be a direct function of the exposure route, the intended target, and the desired material. Each exposure route presents unique barriers that must either be bypassed or perhaps taken advantage of, and how that advantage can be incorporated will depend on what is being delivered **(Box 2) [28-34].** The final plant growth conditions will be important as well; indoor or greenhouse-based, urban agriculture is distinct from acres of field production. Ultimately, only after a systems-level understanding is achieved (or at least recognized), can the desired material be appropriately designed.

***Nanoparticle Size***

One common design strategy for controlling NP uptake involves tuning NP size. There are two main uptake mechanisms following foliar application of NPs: cuticular and stomatal pathways, with size limits of < 5 nm and 10-80 microns, respectively **(Box 2)** [31, 35]. Thus, NP size can dictate both the uptake mechanism and the amount taken up before translocation within plants.

*Metal Nanoparticles*

The uptake, translocation, and transformations of silver nanoparticles (AgNPs) has been previously reviewed and suggests that leaves can take up AgNPs in the size range of 10-40 nm, although precise size limitations for different plant species remains relatively unknown [36]. Su, *et al.* investigated AgNP foliar application in citrus trees [37]. Six weeks after application, the Ag recovered from the roots, branches, trunk, and leaves indicated uptake and translocation of the AgNPs with various coatings: polyvinylpyrrolidone (PVP), citrate (Ct), or gum Arabic (GA). The AgNPs sizes ranged from 9 to 29 nm for the metal cores [37], agreeing with previous reports that were within the 10-40 nm range [36].

To further probe this effect, Zhang, et al. applied PVP- and Ct-coated AgNPs to spinach leaves and found that leaf penetration was more dependent on size than surface coating [38]. The 40-nm-diameter AgNPs had a deeper penetration than the 100-nm-diameter AgNPs. Additionally, the estimated percentage of internalized AgNPs, 0.2-0.8%, was significantly smaller than that of the total Ag applied (9-12%), suggesting transformation of the NPs inside the plant. This agrees with previous studies which indicate that smaller AgNPs undergo greater dissolution, allowing $Ag^{+}$ ions to translocate or complex with other ions or biomolecules within the plant [36, 39-42].

More recent studies have suggested that AuNPs larger than 40-nm-diameter can enter through plant leaves. To explore AuNP transport, Avellan *et al.* synthesized AuNPs, coated with either Ct or PVP, that had diameters of 3, 10, and 50 nm and foliarly applied them to wheat [43]. For both coatings, 3-nm-diameter AuNPs had the best adhesion to the leaf surface after rinsing, followed by the 10-nm-diameter AuNPs, and then the 50-nm-diameter AuNPs. Hyperspectral microscopy images suggest all NPs sizes could enter the plant leaves via cuticular uptake pathways which was impacted by the coating used. Additionally, once inside the plant, similar transport to various plant compartments was observed for coated NPs of the same size. Another study led by Zhang *et al.* revealed that when AuNPs of various sizes (5 – 20 nm) were infiltrated into model *Nicotiana benthamiana* plant leaves, smaller NPs were able to travel through plant tissue and associate with cells [44]. Surprisingly, this study revealed that none of the spherical NPs were able to enter the intracellular plant space, noting that NP shape, rather than size, was integral for uptake. From these studies, it is evident that AgNP and AuNP size impacts the uptake within various plant models, with 50 nm or smaller NPs being ideal for plant uptake and transport.

*Metalloid, Metal Oxide and Non-metal NPs*

Metal oxides, carbon dots, and metalloid NPs follow similar trends as those observed for AgNPs and AuNPs, with smaller NPs improving leaf adhesion and plant uptake. In one of the most systematic studies published to date, Hu *et al.* synthesized hydrophilic carbon dots (CDs), cerium oxide nanoparticles ($CeO_2$ NPs), and silica nanoparticles ($SiO_2$ NPs) with hydrodynamic diameters ranging from 1.7 to 18 nm, and applied them to cotton (a dicot) and maize (a monocot) leaves [45]. NPs up to 18 nm penetrated cotton leaves via stomatal and cuticular pathways, whereas up to 8 nm NPs entered maize leaves entered using the stomata. This suggests a species-dependent and leaf anatomical difference for initial NP uptake and translocation. Additionally, NPs up to 16 and 8 nm had higher association with the leaf guard cells for cotton and maize, respectively. This size-based difference in guard cell penetration is likely due to the cell wall size exclusion limit that is also plant species-dependent. The authors also developed a nanoparticle-leaf interaction empirical model, based on hydrodynamic size and zeta potential, that predicts a 20 nm and 11 nm hydrodynamic diameter size limit for efficient NP delivery into cotton and maize guard cells, respectively [45]. However, other factors such as concentration, surface chemistry, and hydrophobicity would impact model outcomes; thus, there is a need for more systematic analyses of NP and leaf interactions to better model and predict the role of size in NP uptake.

Several related studies also provide evidence for NPs outperforming their bulk counterparts upon plant application. A study performed by Zhu *et al.* found that large 200 nm and 500 nm zinc oxide (ZnO) bulk particles were more easily removed from wheat leaves with washing than their 40 nm counterparts. Additionally, the 40 nm ZnO NPs were taken up through the stomatal pathway for leaf entry, excluding the larger particles. Once inside the leaves, the 40 nm ZnO NPs were also able to cross the cell wall into the cytoplasm, demonstrating the small size needed to readily cross the cell wall [46]. In a similar study, Zhang *et al.*, compared 20 nm ZnO NPs to $ZnSO_4$, an ionic control. The concentration of Zn within the wheat grain was increased significantly and to a greater extent than $ZnSO_4$-treated plants. Higher uptake efficiency is likely due to the smaller size increasing adhesion on the leaf surface and slow dissolution of the ZnO NPs that provide a sustained Zn pool as a nutrient for plant growth [47].

Similar trends were observed when comparing 8 nm $CeO_2$ NPs to a 5-micron cerium acetate control [48]. Lastly, El-Shetehy et al., investigated $SiO_2$ NPs with a size range of 50 to 70 nm that entered the leaf through the stomata and were able to distribute within the large extracellular air spaces of the mesophyll. Successful uptake induced bacterial pathogen resistance in Arabidopsis plants by activating the plant's natural defense response [49]. While several mechanisms remain unknown for NP uptake and for improving plant health and yield, smaller NPs (often <50 nm) have beneficial impacts on several plant species.

NPs have relatively large surface areas that impact their leaf adhesion, uptake, and translocation and transformation within the plant. NP sizes in the range of 1-40 nm are ideal for foliar application; however, some studies do indicate that larger NPs (~50-70 nm) may still enter plant leaves through the stomata. Still, more systematic studies are needed for modeling and predicting NP uptake and translocation based on a NP's chemical and physical properties to allow for optimal design of NPs for various plant species. NP shape [19, 50-57] and surface charge [33, 45, 58-60] are also design factors to consider because they can impact NP adhesion, uptake, translocation, and dissolution when applied to plants. Overall, these two factors appear to have a smaller impact than size; detailed analysis can be found in the Supporting Information.

### *Nanoparticle Surface Modifications*

NP surface modifications may be incorporated to introduce new chemical or physical properties for a desired purpose. As the NP surface is the first point of contact with plant leaves, surface coatings have the potential to drive the impact and performance of NP in the context of transport and overall impact on plant yield. This section will analyze recent literature trends on the intentional surface coatings of metal, metal oxide, metalloids, and non-metallic nanoparticles with a continued analysis presented in the SI [61-64].

#### *Metal Nanoparticles*

As discussed above, PVP, an amphiphilic coating, and Ct, a hydrophilic coating, have been commonly used to modify Au and Ag NPs to evaluate their uptake, translocation, and biodistribution in plants as a function of surface hydrophobicity. For example, when Avellan *et al.* applied PVP- and Ct-coated AuNPs to wheat leaves, the hydrophobic moieties present in PVP allowed for better adhesion and improved interaction with the hydrophobic cuticle, making uptake more likely because the amphiphilic PVP-coated Au NPs are able to diffuse within the cuticle. On the other hand, the Ct-coated AuNPs were easily rinsed off the leaf surface; yet, even with the limited contact time, some uptake occurred via stomatal openings. Interestingly, the performance of PVP- and Ct-coated nanoparticles is reversed in the context of translocation, where the PVP-coated nanoparticles were trapped in the mesophyll while the Ct-coated nanoparticles had better translocation which improved overall plant health [43]. This more efficient delivery of Ct-coated NPs was also seen in a study that used AgNPs in the distinct plant system of citrus trees. Foliarly applied NPs allowed for uptake and translocation to various parts of the tree such as leaves (other than dosed leaves), branch/trunk, and roots based on the coating type. In terms of transport, the Ct coating allowed for more delivery to the tree branch/trunk than the PVP coating [65].

The success of Ct coatings for internal transport seems promising; however, a similar study by Spielman-Sun *et al.* found that the Ct-AuNPs applied to broad bean leaves were randomly distributed around the leaf surface rather than achieving stomatal association as reported by Avellan *et al.* [66]. Both studies used the same design and synthesis strategy but show contrary results, which could be due to differences in the plant models used. In addition to the Ct-coated

NPs, Spielman-Sun *et al.* also employed NPs coated with an anti-pectic polysaccharide antibody (LM6-M), which has specific affinity to, and can thus target, the stomata of broad bean leaves. This work reports the successful design of NPs with specific targeting moieties that were able to strongly adhere to the stomata [66]. Herein, we can infer that a targeted delivery approach, rather than surface hydrophobicity, may be more effective; however, follow-up translocation studies of LM6-M-coated NPs would further test this claim.

The complex biological environments within plants make it difficult to extract definitive reasons for translocation differences for Ct vs PVP coatings. Hence, identifying potential biomolecules that could interact with nanoparticles and their respective coatings can enable a better understanding of NP transport. Like the studies above, PVP- and Ct-coated AgNPs were used in a study that used surface-enhanced Raman spectroscopy mapping to identify the amino acid cysteine as a significant biomolecule that interacts with AgNPs in spinach leaves [38]. The Ct coating showed a rapid interaction with cysteine while the PVP coating had a delayed interaction due to the bulkier nature of PVP preventing access to the Ag surface which caused it to mask the NP surface from cysteine. Future studies need to focus on elucidating the unique role of biomolecular corona on plant uptake and translocation.

*Metalloids and Metal Oxides Nanoparticles*

As the usage of metalloid- and metal oxide-based NPs increases, new application-driven surface modifications of NPs have emerged with a focus on tailoring NP uptake and localization as well as controlled release of target ions and other beneficial cargo for disease suppression and improved plant health.

For instance, Buchman *et al.* coated mesoporous silica nanoparticles (MSNs) with chitosan to aid in suppressing *Fusarium wilt* in watermelon through the dual delivery of beneficial silicic acid and chitosan [18]. Chitosan-coated MSNs resulted in a 70% increase in watermelon yield in healthy plants which is an exciting outcome toward increasing global food supply. The well-developed and versatile synthesis methods for $SiO_2$ NPs allowed them to also serve as a NP coating in two similar studies that used $SiO_2$ NPs to encapsulate the pesticide azoxystrobin [67] and ZnO NPs [68]. Both studies showed that the presence of a silica coating allowed for a slow and continuous release of azoxystrobin and $Zn^{2+}$ ions that were distributed towards the stem > leaves > roots of tomato plants, in each study. More interestingly, both studies characterized the uptake and translocation of nanoscale forms of $SiO_2$ and ZnO, and both NPs were present in stems, roots, and other leaves. In both cases, the silica coating was regarded as the source of success where Gao *et al.* concluded preferential uptake for $SiO_2$-coated nanoparticles (as the uncoated nanoscale ZnO nanoparticles remained in the leaf).

*Nanoparticle Surface Roughness*

Strength and number density of NP adhesion onto leaf surfaces can greatly influence leaf entry by NPs and the overall impact NPs may have on plants. While not widely studied, tuning the NPs' surface roughness has been investigated to improve leaf adhesion.

Li *et al.*, investigated sea urchin-like micro-nanostructured hollow silica spheres (SUH-Si) that had a 500-nm-thick uniform shell that was covered with a large number of silica urchin-like nanotubes **(Figure 2C & 2F, top panel),** increasing their surface roughness [69]. Compared with traditional foliar nitrogen fertilizers, the nitrogen fertilizer-loaded SUH-Si increased the adhesion on peanut and maize leaves by 5.9 times and 2.2 times, respectively. This increased adhesion allowed for a more efficient delivery of the nitrogen fertilizer and promoted the maize plants growth and development [69]. The same group also designed a pompon-like magnesium foliar fertilizer **(Figure 2B, bottom panel)** that consisted of thin fold-like curled nanosheets on a hollow silica structure to increase leaf adhesion [70]. The pompon-like structure resulted in a sustained release of magnesium and the foliar adhesion efficiency on tomato leaves was improved by 10.4 times when compared to traditional magnesium foliar fertilizers [70]. Both studies indicate that increasing surface roughness positively impacts leaf adhesion and can result in more efficient delivery of common nitrogen- and magnesium-based fertilizers.

**Uptake, translocation, and biodistribution is dependent on NP properties**

NPs encounter a complex biotic and redox-sensitive environment within plants, The literature has shown that the uptake, translocation, and distribution of NPs in plant tissues are highly related to the NP properties discussed above. In addition, exposure time [61, 71, 72], aging and/or transformation processes NPs [73, 74], and species [75, 76] all affect uptake processes.

When designing NPs, the role of exposure time to plants is an important consideration. Questions such as how fast the NPs should dissolve or release their ions, and what is the optimum interaction time between NPs and the plant after the application are important factors that control NP usage efficiency. Wang *et al.* reported that the uptake and translocation of sulfur nanoparticles was highly time dependent, highlighting a time-sensitive window of physiological opportunity where these nanoscale crop protection strategies were successful [61, 62]. Importantly, surface functionalization of the material could be used to optimize activity as that impacts dwell time on and in plants. The effect of NP residence time or aging must also be considered when designing NPs. For example, rutile titanium dioxide nanoparticles ($nTiO_2$) were weathered in field soil for four months prior to planting carrots for cultivation to full maturity [74]. The aging of $nTiO_2$ was highly dependent on the initial NP chemical properties, especially the surface charge, and the resulting differences in transformation processes can have overt impacts on biota. Specifically, the increases in taproot biomass, leaf fresh biomass, plant height, and nutrient element accumulation in the roots and leaves highlight the age-dependent loss of phytotoxicity as a function of $nTiO_2$ surface properties [63, 74].

After accumulation in plant tissues, NPs encounter a complex chemical environment that may vary greatly in terms of pH, moisture, metabolite contents, and endophytic microbiome activity. For example, the accumulation of Cu content after nanoscale CuO exposure in Rosie bok choy was correlated with its higher anthocyanin than Green bok choy. Similarly, more Cu was translocated to the grain of wild rice than cultivated rice after nCuO exposure [76]. If the mechanisms behind these plant-specific differences could be understood, nanomaterials could be specifically synthesized to take advantage of the differences.

**Biotransformation is dependent on NP properties**

The biotransformation of NPs after plant uptake is largely dependent on the chemical composition of the NPs. With high surface-area-to-volume ratios, NPs such as nanoscale Ag, ZnO, CuO, and $CeO_2$ are thermodynamically unstable, as the Gibbs energies of synthesis reactions are often positive [77]. Therefore, these materials may undergo biologically driven dynamic transformations including aggregation, dissolution, adsorption, recrystallization, and redox reactions; these processes will be critical to controlling NP fate and distribution.

For example, the partial oxidation of AgNPs in the root tissues of ryegrass was attributed to two possible pathways: direct uptake by roots followed by oxidative transformation in root tissues or dissolution outside the root surface followed by the uptake of ionic species by roots [78]. With hydroponic ZnO NP exposure, Lv *et al.* found that the majority of Zn accumulated in maize roots and shoots was in forms such as $ZnPO_4$, primarily due to the enhanced dissolution of ZnO NPs in the rhizosphere and plant uptake and translocation in the ionic form [79]. It has been reported that for ZnO NPs, the uptake, transport and accumulation of Zn is primarily in the form of dissolved $Zn^{2+}$ from the NPs. Consequently, surface modification could be employed to minimize rapid dissolution of ZnO, as well as to potentially control the rate of uptake and translocation. Interestingly, the *in planta* reduction of Cu(II) to Cu(I) has been reported in soil-cultivated rice and maize. Peng *et al.* found that CuO NPs were transported from rice roots to shoots and that dissolved Cu(II) was mainly combined with cysteine, citrate, and phosphate ligands, but importantly, a fraction of the Cu(II) was reduced to $Cu_2O$ [80].

Conversely, Au and $SiO_2$ NPs are present largely in their pristine form within plants [81]. However, Kang *et al.* used synthesis conditions to control the $SiO_2$ NP dissolution **(Figure 3)**; greater dissolution correlated with enhanced activity against *Fusarium* wilt in watermelon [17, 18, 82]. This correlated with higher Si concentrations in the roots of plants that had been treated with faster dissolving NPs, indicating more effective silicic acid delivery. These findings suggest that NPs can be intentionally designed to control and take advantage of subsequent *in planta* transformation processes.

## Concluding remarks and future perspectives

The motivation for this review is clear: our society continues to suffer from lack of global food security, and we need to invest in long-term and sustainable solutions to mitigate this impact. Innovations such as nano-enabled agriculture is providing us with an opportunity to overcome food insecurity. As with biomedical applications, NPs in agriculture require careful attention to NP properties that will determine their impact. Some properties include size, shape, surface modifications and transformations of example metal, non-metal, metal-oxide, and metalloid-based NPs that are applied to plant leaves, many of which are outlined in **Table S1.**

This assessment of the current field of research reveals that it is difficult to identify optimal NP characteristics, but we can draw some conclusions that may guide future research. In terms of NP size and surface charge, the studies presented here show that smaller NPs (generally < 50 nm) and positive surface charge seem to improve NP uptake into leaves. Perhaps surprisingly, novel analytical tools have revealed that NPs larger than 50 nm can travel throughout the plant vasculature. On the other hand, studies that systematically evaluate the role of NP shape are lacking, but changing morphologies seems to improve disease and stress tolerance in some plants with no clear understanding (yet) of the underlying mechanism. Surface coatings add another layer of complexity as hydrophobic coatings may improve leaf adhesion and thus uptake, but once inside the plant, the impact of NP hydrophobicity on translocation is nuanced due to the complex biological environment present within plants. When incorporating coatings, it is important to include the coatings as part of the control treatments for greenhouse and field studies to properly elucidate any individual impact of the NP and/or coating. Lastly, NP transformations are generally considered a post-synthesis characteristic, yet the design properties mentioned throughout this review can facilitate a desired transformation. Future researchers should consider NP residence time within the plant when considering intentional control over transformations.

Despite the wide array of NPs available to us, it is important to account for the difficulty of synthesizing some novel NP systems with controlled properties as well as the need for efficient characterization methods to understand the system before plant application. Additionally, several studies highlighted in Table S1 show commercial nanoparticles that often lack extensive material characterization which eventually leads to no clear method of determining which property had the most valuable impact. Once inside the plant, there are several complex questions (see Outstanding Questions) related to plant biology, growth and plant species variation that need to be accounted for, and unfortunately, is the part of this challenge we do not currently have much control over. Lastly, for future commercialization, the cost, scalability, and acceptance of nanotechnology within the public needs to be taken into careful consideration. Towards these efforts, life cycle assessments (LCA) of NPs, with a focus on the material parameters mentioned above, can help us better identify the datapoints needed to conduct a complete analysis of NPs in agriculture and thereby inform insights towards the sustainable implementations of these systems. Figure 4 shows some steps that need to be considered which range from data collected from scientists at the bench to social scientists interfacing with the public that would consume the agricultural products. In conclusion, we hope this work emphasizes the need for more cohesive and systematic studies and thoughtful collaboration among researchers focused on nanoparticle preparation and the plant sciences.

## Glossary

**Biotransformation:** changes to nanoparticles in complex biological environments.

**Dicot:** flowering plants that contain two cotyledons (embryonic leaf).

**Foliar application**: spraying formulations directly to plant leaves as opposed to the soil.

**Food insecurity:** lack of consistent access to enough food for every person in a household.

**Food security:** always having physical and economic access to enough food.

**Monocot:** flowering plants that contain one cotyledon.

**Nanoparticle:** particle with one dimension with a size of 1–100 nm.

**Protein corona:** biomolecules adhering to the nanoparticle surface.

**Transformation:** changes to nanoparticles when introduced to different media

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