
Silicon-Nanoparticles in Crop Improvement and Agriculture

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Abstract

Silicon (Si) is considered as quasi-essential for plant growth and development, and alleviates toxic effects caused by various environmental stresses in plants. Biogenic silica is also deterrent to various plant pathogens, insects and herbivores. The beneficial role of Si-nanoparticles (Si-NPs) is comparatively little explored and less characterized in plants. Green synthesis of Si-NPs is possible from plant sources and agricultural wastes, which are applied in hydroponics-form, soil supplementation or foliar spraying, following which they are transported by symplastic or apoplastic methods and from one cell to the other via plasmodesmata. The mesoporous nature of Si-NPs, presenting a wide surface area, makes them ideal candidates to act as unique carriers for pesticides and fertilizers, giving rise to the concepts like nanopesticides or nanofertilizers that may help adequately in improving the quality of the agricultural system. Si-NPs also facilitate the site-targeted controlled delivery of nucleic acids and nutrients with increased crop protection. Reckoning with all these facts, the present review highlights the process of green synthesis of Si-NPs, their application and uptake by the plants and their role in stimulating plant growth and development, their advantages over conventional fertilizers and pesticides, and their potentiality in mitigating the damages arising from biotic and abiotic stresses in plants. The innovative uses of Si-NPs in agriculture will certainly help to meet the rising demand for food and environmental sustainability in the near future.

Keywords: Silicon-Nanoparticles, Crop Improvement, Agriculture, Environmental Stress, Pathogen Infection, Nanoinsecticides and Nanofertilizers.

Introduction

Nanoparticles (NPs) are materials with size ranging between 1 and 100 nm. The use and application of NPs have ushered a revolution in the field of agriculture and plant quality improvement. The conventional chemical fertilizers, pesticides and other protective agents,

applied in the agricultural field via spraying and broadcasting, are maximally lost due to runoff, leaching or microbial and photolytic degradation, so that they do not reach in sufficient or desired concentrations to the targeted plants, leading to huge economic losses of crops. This in turn necessitates repeated and indiscriminate use of synthetic fertilizers in order to fulfill the nutritional requirements of the plants, which has led to inevitable nutritional imbalance of the soil and loss in soil microbiota and natural flora, and overall danger to the soil biodiversity. Increased probability of pest and pathogen resistance, together with bioaccumulation in food chain, as a result of using pesticides frequently at higher concentrations, is also an alarming signal for the environmental hazards. In this context, the use of NPs appear as an alternative solution, where the fertilizers or pesticides usually have a surface coating of NPs, which can strongly hold the chemicals due to high surface tension, leading to slow and controlled release of such chemicals, so that the bioavailability or the effective duration of activity of the chemicals is prolonged. The nutrients and pesticides are usually encapsulated by NPs coated with thin nanoscale polymeric film or delivered as nanoemulsions (Liu and Lal 2015).

Silicon is the second most abundant element on the earth crust and is a normal component in plants, ranging from < 0.1% to > 10.0%, mostly involved in strengthening the cell wall. Based on Si level, plant species are categorized into three groups, Si accumulators like rice (> 1.0 Si); intermediate types like *Urtica dioica* (between 0.5% and 1.0%) and Si excluder like tomato (lower than 0.5%). Such difference in Si content is mostly attributed to genotypic differences in Si uptake via transporters like Lsi1, Lsi2 and Lsi6, following absorption by the roots through aquaporin type channel proteins (Takahashi et al. 1990). Use of Si fertilizers has resulted in high plant growth rate, higher yield and protection against a wide range of pathogens and environmental stress factors (Liang et al. 2007). This has created a great interest among the researchers in isolation and synthesis of Si-NPs to study their effect on plant systems and improve the agricultural scenario. Such NPs have been synthesized artificially or have been extracted from the plant source itself. Since the discovery of mesoporous silicas, synthesized using cationic surfactants as templates, the templating method has been widely applied to prepare mesoporous silicas with high surface areas, tunable pore sizes, large pore volumes and rich morphology. In course of time, other methods like fast self-assembly, soft and hard templating, a modified Stober method, dissolving-reconstruction and modified aerogel have evolved (Wu et al. 2012). The present review focuses chiefly on the green synthesis of Si-NPs from plants, their mode of application and their widespread use in agricultural sector for betterment of plant production.

Plant sources for the synthesis of Si-NPs

The production of plant-derived NPs has emerged as an efficient biological source of green NPs that draw an extra attention of scientist due to their eco-friendly nature and simplicity of production process compared to the other routes. Green synthesis of silica nanoparticles has been possible from various plant sources. The chopped pieces of the inner portions of the

bamboo stem or culm, when subjected to pyrolysis at extremely high temperature (1250°C) for 12 hours in argon atmosphere, self thermochemical decomposition results, with the removal of some organic compounds and water from bamboo pieces, forming charcoal biotemplates. Cooling of such biotemplates to 200°C followed by shutting off the inert gas environment created by argon, leads to Si-NP formation (Vinay et al. 2016). Another source of Si-NP is the sugarbeet bagasse, calcinated at 500°C for 12 hours, following which the bagasse ash is subjected to acid hydrolysis with HCl: HNO₃ (1:3) at 35°C for two hours and oven-dried. Subsequent alkalization of the aqueous extract of the residue overnight with concentrated NaOH, followed by acid neutralization and filtration will separate out nanoparticle solution from the fibers (Nalan et al. 2014). Rice husk, containing 60% silica, has also been used for extracting NPs. Following boiling of rice husk in HCl for two hours and washing with de-ionized water, it is dried at 100°C for one day and then pyrolysed at 700°C, for two hours. The NPs thus formed is ultrasonicated in KNO₃ solution (0.2 M) coupled with stirring for one hour. The solution is filtered and dried at 105°C for four hours. The filtered and dried sample is pyrolysed again at 800°C for four hours which results in semi crystalline porous silica nanoparticle (Weining et al. 2012). X-ray diffraction studies revealed that amorphous silica nanoparticles are formed from rice hull biomass at 923-1023 K, whereas crystalline particles at 1073-1173 K. The optimised processing temperature (1023 K) enabled amorphous silica nanoparticles to have high-specific surface area (Palanivelu et al. 2014). Thus, waste management is intricately associated with NP synthesis, since agricultural wastes like rice husk are directly utilized in NP synthesis. The synthesised NPs, either in powder or dispersion forms need to be stored at room temperature or refrigerated condition before being utilized. The three-dimensional NPs (which have 0 dimension at the nanoscale and three dimensions at the macroscale) have recently attracted considerable research interest owing to their large surface area and other superior properties like absorption sites for all involved molecules in a small space which lead to a better transport of the molecules (Tiwari et al. 2012).

Mode of application of Si-NPs and their uptake by the plants

Mesoporous silica-NPs, usually 20 nm in size are normally applied to the plants via different modes. In the hydroponics mode, the powdered NP is added to the nutrient solution at the appropriate concentration and the uptake is mediated by the roots immersed in nutrient solution. The other method is direct soil supplementation with NPs, whose success depends on soil texture, soil pH, salt content in the soil and the duration of agrochemical release by the NPs. Foliar application constitutes another method where liquid Si-NPs are sprayed on the leaf surfaces, and the uptake occurs by stomata or leaf epidermal cells. A binary film is formed at the epidermal cell wall following absorption, imparting a structural color to the plants (Strout et al. 2013). However, soil-applied SiNPs were reported to be more effective than foliar-applied silica nanoparticles (Suriyaprabha et al. 2014). The factors governing uptake, translocation and accumulation of NPs include plant species, age of the plant,

growing environment, size, shape and chemical composition of NP and its stability in solution (Rico et al. 2011). The NPs mostly form complexes with root exudates and bind to membrane transporters or carrier proteins and pass through ion channels, aquaporins or endocytosis. The size of the NPs should be such that it is less than the pore diameter (5-20 nm) of the cell wall. Si-NPs are mostly transported to the aerial system through xylem via apoplastic pathway, whereas specific aquaporins like nodulin intrinsic protein 2 (NIP2) are required for symplastic entry (Fleischer et al. 1999). Sun et al. (2014) used combination of confocal laser scanning microscopy, transmission electron microscopy and proton-induced X-ray emission (micro-PIXE) elemental analysis to locate and quantify mesoporous Si-NPs in tissues and in cellular and sub-cellular locations. They showed that MSNs penetrated into the roots via symplastic and apoplastic pathways and then via the conducting tissues of the xylem to the aerial parts of the plants including the stems and leaves. It is to be noted that there should be a fine tuning between the pH and surfactant concentration for efficient uptake of NPs through the pores present in the cell wall.

Applications in crop improvement

Si-NPs in plant growth and development

Si-NPs (12 nm) improved germination in a known Si-excluder, tomato with higher fresh weight and dry weight of seedlings (Siddiqui and Al-Whaibi 2014). Si-NPs enhanced the expression of phenylalanine ammonia lyase and lignifications in leaves and roots and enhanced plant growth in oat (Asgari et al. 2018). Leaf thicknesses and development of the vascular system (xylem and phloem) were reinforced in *Astragalus fridae* following seed priming with cold plasma in conjunction with manipulation of culture medium with silica-NPs (Moghanloo et al. 2019). Application of SiO₂-NPs increased the average mass of potato tuber, stimulated the length of roots and sprouts and enhanced the chlorophyll and carotenoid content (Mushinskiy et al. 2018). Sun et al. (2016) observed that mesoporous Si-NP application appears as a smart delivery system in wheat and lupin plants to improve growth and development, seed germination, plant biomass, total chlorophyll and photosynthetic activity without causing oxidative damage and membrane damage. Nazaralian et al. (2017) observed increase in endogenous Si in fenugreek (*Trigonella foenum-graceum* L.), xylem cell wall lignification, cell wall thickness, PAL activity and protein concentration in seedlings. Nanostructured SiO₂ was shown to be useful when applied to the roots of 1-year old *Larix olgensis* seedlings, which promoted lateral root growth, main root length and chlorophyll content (Bao-shan et al. 2004). Seed germination and root elongation in maize was also enhanced upon Si-NP application (Karunakaran et al. 2016). Another interesting study by Karunakaran et al. (2013) showed that seed germination percentage in maize was promoted by increase in biomass or population of plant growth promoting rhizobacteria, leading to doubling of colony forming unit along with increase in uptake of silica and nutrient value of the soil, with increase in nanosilica concentration. Flowering in *Vicia faba* was also improved by applying Si-NPs (Roohizadeh et al. 2015).

Si-NPs in mitigating environmental stress

A study by Abdelazim et al. (2017) observed that foliar spray of SiO₂ NP mitigated the effect of salt stress in cucumber by increasing growth and yield, together with increasing nitrogen and phosphorus content. Exogenous nano-silicon alleviated the salt stress in soybean seedlings by increase in K⁺ concentration, antioxidant activities, non-enzymatic compounds and decreasing of Na⁺ concentration, lipid peroxidation, and reactive oxygen species production (Farhangi-Abriz and Torabian 2018). Alsaeedi et al. (2018) used silica NPs for improving germination and vegetative growth of cucumber seedlings under elevated salt stress through proper maintenance of K⁺/Na⁺ homeostasis. Likewise, Alsaeedi et al. (2019) also observed that Si-NPs boosted growth and productivity of cucumber seedlings under both water deficit and salt stress by increasing plant height, yield and chlorophyll content, maintaining ion homeostasis and osmotic balance by regulating high K⁺ content and controlling stomatal opening. Even in case of common bean (*Phaseolus vulgaris*), Si-NPs have proven to be highly effective in ameliorating the detrimental effects of Na⁺ ions and causing increase in germination percentage, vigor index and germination rate of seeds (Alsaeedi et al. 2017). The alleviation of salinity stress in tomato was reported by Haghghi et al. (2012) and Haghghi and Pessarakli (2013) by application of Si-NPs leading to improvement of several physiological attributes. A dose-dependent impact on alleviating drought stress was observed in *Crataegus aronia* by increases in plant growth properties and photosynthetic pigment concentrations and decreases in xylem water potential and MDA content (Ashkavand et al. 2015). Nano-silicon layer may reduce plant transpiration and, thus, make plants more resistant to drought, high temperature and humidity (Strout et al. 2013). Tripathi et al. (2017) observed that pre-addition of Si-NPs protected wheat seedlings against UV-B stress through nitric oxide-mediated triggering of antioxidant systems that counteracted ROS-induced damages of photosynthesis. Foliage supplementation with Si-NPs alleviated Cd and Pb toxicity in rice seedlings by reducing the endogenous metal concentration, and improving growth, biomass, grain yield and nutritional quality (Hussain et al. 2020). Si-NP treatment reduced oxidative stress in wheat seedlings exposed to Cd stress by reducing hydrogen peroxide, electrolyte leakage and lipid peroxidation, along with enhanced activity of antioxidative enzymes like superoxide dismutase and peroxidase. Moreover, the Cd accumulation within the grains was also lowered, the effect was most pronounced with the highest concentration of NPs (Khan et al. 2020). Ali et al. (2019) showed that Cd-stressed wheat seedlings treated with Si-NPs improved tissue biomass, chlorophyll, leaf gas exchange attributes by lowering damages, electrolyte leakage and Cd accumulation, and activating the superoxide dismutase and peroxidase enzymes. Cui et al. (2017) reported that the expression of *OsLsi1*, responsible for Si uptake and *OsHMA3*, responsible for vacuolar transport of Cd, were upregulated, whereas expression of Cd-uptake genes like *OsLCT1* and *OsNRAMP5* were downregulated by applying Si-NPs to rice seedlings facing cadmium toxicity. Even seed priming with Si-NPs positively affected the growth of soil-grown wheat seedlings by diminishing oxidative stress, decreasing Cd

concentration in grains, and improving plant biomass and chlorophyll content. Silicon dioxide-NPs ameliorated Al toxicity in maize seedlings by reducing the activity of photorespiratory enzymes and NADPH oxidase, stimulating the antioxidant defense systems at enzymatic (ascorbate and glutathione peroxidases, catalase, superoxide dismutase) and non-enzymatic (ascorbate, glutathione, flavonoids, polyphenols, tocopherols) levels and metal detoxification via glutathione-S-transferase activity (de Sousa et al. 2019). Chromium phytotoxicity in *Pisum sativum* seedlings was also overcome by application of Si-NPs by reducing Cr accumulation and oxidative stress and upregulating antioxidant defense system and nutrient elements (Tripathi et al. 2015). Silica-NPs have also been shown to significantly absorb atmospheric Pb in the polluted environment, implicating their potential utility in treating heavy metal pollution from contaminated sites, thereby enabling phytoremediation (Yang et al. 2013).

Si-NPs in protection against pathogen infection

Application of Si-NPs to seedlings of *Panax ginseng* Meyer., suffering from root rot disease, caused due to infection by the devastating fungus *Ilyonectria mors-panacis*, could confer protection by reducing the disease-severity index, reducing the expression of PgSWEET, leading to regulated sugar efflux into apoplast and enhanced tolerance against the pathogen, thereby improving root quality and yield (Abbai et al. 2019). Silica-NPs were shown to act as strong antifungal agents in maize against several phytopathogens like *Fusarium oxysporum* and *Aspergillus niger*, by inducing higher expression of phenolic compounds and lower expression of stress-responsive enzymes like phenylalanine ammonia lyase, peroxidase and polyphenol oxidase (Suriyaprabha et al. 2014). Ecofriendly approach of controlling gray mold disease of table grapes caused by *Botrytis cinerea* was shown by Youssef et al. (2019) by applying both silica-NPs as well as chitosan-silica nanocomposites, which could preserve bunches from mass loss due to pathogen infection. This may serve as alternative control means and reduce/substitute the use of fungicides. SiO₂-nanospheres loaded with Ag-NPs displayed antibacterial effect in rice by controlling bacterial leaf blight caused by *Xanthomonas oryzae* pv. *oryzae* (Xoo). The nanocomposite acted as bactericides by inducing reactive oxygen species production and inhibiting DNA replication (Cui et al. 2016).

Si-NPs as nanozeolites, nanoinsecticides and delivery agents for fertilizers and herbicides

Improved soil quality with abundant reserves of water for conduction in plants is vital for crop productivity. Due to their porous and capillary properties, Si-NPs act as natural wetting agents and water distributors in the soil. They facilitate water infiltration and retention in the soil, helping in slow-release of water, thereby increasing water holding capacity and improving soil quality, especially under drought conditions (Ghanbari and Ariafar 2013). The insecticidal property of Si-NPs is attributed to the dehydrating properties of silica, which leads to disruption of digestive tract, blockage of respiratory trachea and spiracles and

damage to the waxy protective covering on the cuticle, particularly in the adult insects. Nanosilica works by breaking the protective lipid water barrier via sorption of silica. SiO₂-NPs exhibited lethal properties for *Callosobruchus maculatus* (Rouhani et al. 2012). Mesoporous silica-NPs can also be used as nanocarriers that encapsulate commercial pesticides and release them in a controlled manner only at the targeted site, with enhanced durability, stability against adverse environmental conditions, and efficiency of pesticides (Li et al. 2007; Chen et al. 2011). Herbicides like chloroacetanilide, anilide and benzimidazole were linked to nanocarriers, and mesoporous Si-NPs with a specific pore size (2-10 nm) served as an efficient delivery vector for urea-, boron-, and nitrogenous-based fertilizers (Waynika et al. 2012). Sabir et al. (2014) demonstrated that nanocalcite (CaCO₃-40%) application with nano SiO₂ (4%), MgO (1%), and Fe₂O₃ (1%) not only improved the uptake of Ca, Mg, and Fe, but also enhanced the intake of P with micronutrients, Zn and Mn.

Si-NPs in developing genetically modified plants

Mesoporous Si-NPs can host a number of guest molecules like DNA, proteins and agrochemicals because of their large surface area, adjustable pore sizes, three-dimensional open pore structure and well-characterized surface properties (Torney et al. 2007). The delivery of DNA and small-interfering RNA with surface-coated MSNs (Xia et al. 2009), and Cre-recombinase through gold-plated MSNs via particle bombardment method in maize (Martin-Ortigosa et al. 2014) have proved the potential of MSNs to develop genetically modified plants. Nanobiologics is emerging as a novel approach of plant genetic transformation, which however requires optimization for broad scale implementation (Cunningham et al. 2020).

Safety issues

Si-NP application to plants is considered safe, since silica is widely distributed in plants in leaf epidermal layer, epidermal cells of inflorescence bracts and root endodermis. However, there are a few reports where Si-NPs are known to exert negative impact on plants. Si-NPs of size 50 nm and 200 nm caused decreased growth in *Arabidopsis* due to a high negative zeta-potential and hence, pH-change in the growth media (Slomberg and Schoenfisch 2012). Le et al. (2014) observed decrease in plant height and biomass in *Bt*-transgenic cotton due to Si-NP transport. The root meristem cells of *Allium cepa* also showed concentration-response association in increased cytotoxicity and genotoxicity, with the highest concentration (100 µg/mL) of Si-NPs inducing significant DNA damage (Liman et al. 2020). Therefore, Si-NPs, only of appropriate size, used at the specific standardized concentration, appear beneficial to the plants, while may cause severe toxicity if they are of improper size or used at too high concentrations. Moreover, the positive impacts also vary from species to species. These factors need to be critically considered to derive the maximum benefits from Si-NPs in agriculture.

Conclusion

The synthesis and emergence of Si-NPs and their actions within the frame of sustainable agriculture have revolutionized world agriculture and provided a new window to meet the projection of global food demand. Waste management through recycling is also simultaneously possible because of the utilization of agricultural waste materials in Si-NP production. Since silica is abundant on earth, normal component of a plant tissue and has numerous positive effects on plants, the use of Si-NPs is considered safe and will also restrict the use of agrochemicals, pesticides and chemical fertilizers, responsible for large-scale pollution. However, there are still gaps in our proper understanding of the uptake mechanism, proper size and dosage of Si-NP to be used for a particular plant, and the permissible limit and ecotoxicity, which are not adequately standardized. Further research needs to be encouraged to unravel the interaction of Si-NPs with the different biomolecules and cell signaling elements in plant systems and also Si-NP mediated delivery of DNA and other molecules, for their broader application in agricultural improvement.

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