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Nanoparticulate Silica Internalization and Its Effect on the Growth and Yield of Groundnut (*Arachis hypogaea* L.)

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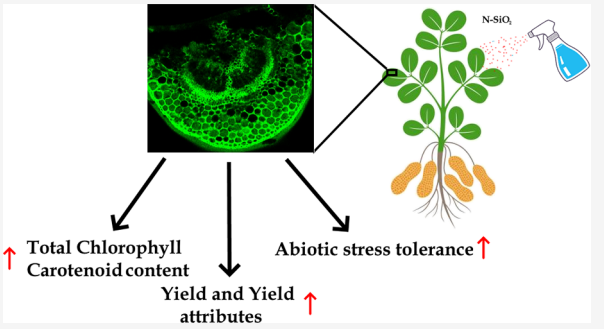
ABSTRACT: In recent years, foliar applications of nanoparticles are increasingly being employed in agricultural fields as fertilizers to enhance crop yields. However, limited studies are available on the foliar uptake of nanoscale nutrients and their interaction with plants. In this study, we reported the effects of foliar spray with varied concentrations of nanoscale silica (N-SiO_2) and bulk tetraethyl orthosilicate (TEOS at 2000 ppm) on the growth and yield of groundnut. Nanosilica was prepared by a sol−gel method and characterized by transmission electron microscopy, dynamic light scattering, and X-ray diffraction. The size and zeta potential of N-SiO_2 were found to be 28.7 nm and 32 mV, respectively. The plant height, number of branches, total dry weight, SPAD chlorophyll meter reading, photosynthetic rate, water use efficiency, number of nodules, and ascorbic acid content were increased significantly with the N-SiO_2 foliar application at 400 ppm over control. The number of filled pods increased significantly by 38.78 and 58.60% with N-SiO_2 at 400 ppm application over TEOS and control, respectively. The pod yield per plant in N-SiO_2 at 400 ppm increased by 25.52 and 31.7% higher over TEOS and control, respectively. Antioxidant enzyme activities enhanced significantly in N-SiO_2 at 200 and 400 ppm over control, indicating a stimulatory effect on the plant growth. In addition, confocal microscopy revealed that fluorescein isothiocyanate (FITC)-N-SiO_2 entered through stomata and then transported to vascular bundles via apoplastic movement. Our study for the first time demonstrated that N-SiO_2 can significantly modulate multiple complex traits in groundnut through an eco-friendly and sustainable approach.



KEYWORDS: *apoplast, foliar application, transport, nanoscale silica, stomata*

1. INTRODUCTION

In developing countries like India, agriculture is one of the most important economic pillars with loads of employment directly or indirectly. In recent times, continuing agriculture has become challenging due to unpredictable climate changes, labor costs, and soil contamination due to hazardous chemicals like industrial effluents, fertilizers, and pesticides.[1] A major drawback of sustainable agriculture is the lack of nutrients in the soil due to intensive cultivation.[1] Most of the fertilizers available in the market are unavailable to plants due to their compositional complexity, solubility, pH, etc. According to UN estimates, the world population would reach approximately 9 billion by 2050 and providing quality food to the ever-growing population would become impossible if the situation prevails in the world.[2] Thus, scientists are harnessing science to develop sustainable technologies to increase productivity.

Soils are the primary source of nutrients for plants, but in recent times, soil health has been impaired due to the indiscriminate use of chemicals like fertilizers and pesticides without lack of proper knowledge on land management systems; this in turn leads to the deterioration of soil health due to the accumulation of salts and toxins. Toxins accumulated in soil are detrimental to beneficial micro-organisms, which in turn worsen plant resistance toward endemic diseases and make them susceptible to pests. In light of this context, nanotechnology has emerged as a viable alternative to enhance agri-productivity with relatively less use of fertilizers in the form of eco-friendly nano-nutrients to attain economically sustainable cultivation. Numerous recent studies have reported that nanoparticles (NPs) significantly improved plant growth and yield and increased plant resistance toward different kinds of stressors.[3−7] Recent studies emphasized the

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uptake mechanism of NPs by plants using different techniques and successfully demonstrated nanoscale zinc uptake in soybean,[4] wheat,[5] coffee,[6] and silica in *Arabidopsis*.[7] In addition, NP-fortified plants and their products with essential micronutrients provide adequate amounts for proper nutrition to animals and humans.[8] Kolenčík et al.[9] showed that the foliar application of ZnO NPs stimulated physiological responses, but TiO_2 NPs increased quantitative parameters like oil content in sunflower. The foliar application of gold NPs, platinum NPs, and silver NPs modulated antioxidant responses and increased carotenoid content in oak leaf lettuce.[10] Hong et al.[11] reviewed the foliar application of several NPs on different aspects like transfer, absorption, and assimilation. Further, metal NPs have proved their efficacy in different plants by increasing plant growth and yield significantly.[12]

Currently, metalloid NPs like nanoscale silica are gaining importance in agriculture due to their beneficial effects with respect to abiotic stresses.[7] Silicon (Si) is the second most abundant available element on earth, available in the form of silicates.[13] Generally, Si is not considered as an essential element for plant growth and yield, but most of the recent studies showed that Si is beneficial to plants during stress.[14] Beneficial effects of Si have been observed in a wide variety of plant species.[14,15] Vladimir and Campbell[16] reported that plants per year removed 210 to 224 million tons of Si irreversibly. At present, monosilicic acid, orthosilicic acid, and inorganic complex forms are the primary forms of silica-based fertilizers and are being used in agriculture. Monosilicic ($Si[OH_4]$) and orthosilicic (H_4SiO_4) acid forms have characteristic higher solubility[17] and absorption rate, which may induce phytotoxicity in plants. This problem can be rectified by using nanotechnology, where the properties of nanoscale silica oxide differ drastically from their native forms in terms of size, thereby affecting its transport in plants. Many studies reported that nanoscale silica increased plant resistance in *Arabidopsis*,[7] increased photosynthetic rate and abiotic stress tolerance in sugarcane,[18] improved root formation in rice subjected to arsenic stress,[17,19] and increased yield in marigold.[20] Further, the application of Si increased the nodule numbers in legumes.[21,22]

The foliar application of nutrients proved to be beneficial than the soil application because nutrient deficiencies can be controlled efficiently, thereby increasing plant growth.[23] Lack of moisture on topsoil makes nutrients unavailable to plants during drought. During drought and root disease conditions, the foliar application of nutrients makes them viable to sustain abiotic and biotic stresses. Nutrients applied through foliar applications were known to be translocated rapidly through stomata[7,8] or cuticle[8] into the plant cell. But during the application, if the nutrients' grain size is larger than the stomatal pore, then utilization of these nutrient salts will be meager. Different microelements were reduced to nano-size to increase their efficiency and decrease their wastage to make nutrients readily available to plants.[24]

Further, recent studies focused on potential routes of NP entry into the plant applied foliarly. NPs having a size less than the stomatal pore can easily enter through stomata[25] before transporting by apoplastic or symplastic movements into the vascular bundles of the leaf.[26] In addition, cracks, wounds, ion channels, protein carriers, and trichomes can absorb foliar NPs.[11] NP movement is bidirectional; therefore, it can accumulate in roots, stems, fruits, grains, and young leaves transporting through the xylem and phloem.[3] El-Shetehy et al.[7] reported that silica NPs (~50−70 nm) could enter the *Arabidopsis* leaf exclusively through stomata. After internalization, NPs usually distribute within the large extracellular spaces of the spongy mesophyll without penetrating cell walls. This study is aimed to understand the transport mechanism of N-SiO_2 applied on leaves and its effect on the growth and yield in *Arachis hypogaea*. In this study, we have synthesized and characterized nanoscale silica (N-SiO_2) and estimated its competence using several yield and biochemical parameters in groundnut. Further, we also studied the transport of N-SiO_2 by tagging fluorescein isothiocyanate (FITC) to understand its transport mechanism.

2. MATERIALS AND METHODS

2.1. Synthesis and Characterization of Nanoscale Silica (N-SiO_2). Nanoscale silica (N-SiO_2) was prepared by using the sol−gel method.[27] In brief, tetraethyl orthosilicate (TEOS) and CH_3COOH (acetic acid-glacial) were mixed on a magnetic stirrer for 30 min. The resultant mixture was rinsed with double-deionized water (DI water) and allowed to dry at room temperature. Finally, the fine powder was prepared from the mixture by crushing in a mortar−pestle, and subsequently, it was decomposed in a preheated muffle furnace for 90 min at 600 °C.

2.2. Characterization of Nanoscale Silica (N-SiO_2). *2.2.1. Particle Size and Zeta Potential Analysis.* The hydrodynamic diameter (size) and zeta potential of the NPs were measured by the principle of the dynamic light scattering (DLS) technique (using Nanopartica SZ-100, HORIBA). In brief, 5 mg of N-SiO_2 was suspended in 10 mL of deionized water using a magnetic stirrer for 15 min. After 15 min, the resultant suspension is used for hydrodynamic diameter (size) and zeta potential estimation.

2.2.2. Electron Microscopy Analysis. For TEM analysis, the samples were prepared by drop-casting the N-SiO_2 suspension on the carbon-coated copper grids and then the samples were air-dried. The N-SiO_2 NP surface morphology, shape, and size were studied by using transmission electron microscopy (TEM) [JEOL-30100] with a UHR (ultrahigh-resolution) pole piece using a lattice resolution of 0.14 nm and a point-to-point resolution of 0.12 nm.

Morphological and compositional analyses of N-SiO_2 and leaf sections of N-SiO_2 at 1000 ppm and control were performed using a high-resolution scanning electron microscope (HR-SEM) equipped with an energy-dispersive spectrophotometer (FEI Quanta 200 environmental scanning electron microscope).

2.2.3. X-ray Diffraction (XRD). XRD analysis was performed on an X-ray diffractometer (JEOL and model: JPX-8030) using Cu K_α radiation in the range of 40 Kv and 20 A to identify crystalline phases of the nanoscale particles. The built-in software program was used for identification of XRD peaks corresponding to Bragg's reflections and indexing.

2.3. Pot Culture Experiment. A pot culture experimentation was carried out at Regional Agricultural Research Station, Tirupati, during *rabi* in 2021 to study the efficacy of nanoscale silica and its transport mechanism in groundnut (*A. hypogaea*) (variety *Dharani*). The experiment was laid out in a completely randomized block design with seven treatments and replicated thrice. The treatment details are T_1, N-SiO_2 at 50 ppm; T_2, N-SiO_2 at 100 ppm; T_3, N-SiO_2 at 200 ppm; T_4, N-SiO_2 at 400 ppm; T_5, N-SiO_2 at 800 ppm; T_6, N-SiO_2 at 1000 ppm; T_7, N-SiO_2 at 1500 ppm; T_8, N-SiO_2 at 2000 ppm; T_9, TEOS at 2000

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ppm; and T_{10}, control (N-SiO_2 treatment suspensions are shown in Figure S1). The treatments were imposed at 30 days after sowing (DAS) and 50 days after sowing (DAS) as foliar spray. The experiment was carried out under controlled conditions with a temperature of 25 ± 2 °C and 95% relative humidity. T_9 treatment was selected with reference to Salim et al.[28]

2.3.1. Growth Parameters. The plant height was measured from the base of the plant to the shoot tip and expressed in cm. The number of branches per plant was counted after harvest. To determine dry weight, plant samples were collected after harvest. These plant samples were dried in an oven at 100 °C for 15 min followed by 80 °C for 2 days before estimating their dry weights. SPAD chlorophyll meter reading (SCMR) was measured by using of SPAD (SPAD-502, Minolta Corp., Ramsey, NJ) at 45 DAS. Three plants were selected randomly, and reading of every third leaf from the top of each plant was recorded. The number of nodules per plant was recorded after harvest. Yield and yield attributes like the number of filled pods per plant, number of unfilled pods, and pod yield per plant were recorded after the harvest of plants.

2.3.2. Biochemical Parameters. Biochemical parameters like chlorophyll contents (chlorophyll *a*, chlorophyll *b*, and total chlorophyll content) and carotenoid contents were quantified in the first fully expanded leaf blade from top measured after 15 days of treatments, i.e., 45 days after sowing (DAS). Leaf discs were grounded to a fine powder using liquid nitrogen, and contents were extracted with 10 mL of 80% acetone (v/v). The homogenate was centrifuged at 4000*g* at 4 °C for 10 min, and the supernatant was separated and used for the chlorophyll assay. Three replicates of individual samples were analyzed. The amounts of chlorophyll *a*, chlorophyll *b*, total chlorophyll, and carotenoids were determined spectrophotometrically, by reading the absorbance at 453, 505, 645, and 663 nm, respectively, as described previously by Hernández et al.[29]

2.3.3. Oxidative Stress Parameters. Peroxidase activity was estimated using *o*-phenyl diamine (OPD).[30] In brief, 0.2 g of leaf was thoroughly grinded with 5 mL of 50 μM citrate buffer (pH 6.4). The contents were centrifuged for 15 min at 10,000 rpm, and the supernatant was used for further analysis. The reaction mixture consists of buffer, OPD, and enzyme extract, and the reaction was initiated by adding H_2O_2. The increase in absorbance was measured at 450 nm for 5 min interval. Peroxidase activity was expressed as units/mg of proteins.

Superoxide dismutase was estimated using the nitro blue tetrazolium (NBT) method.[31] A known (0.2 g) quantity of leaf samples was thoroughly grinded with 5 mL of 50 mM phosphate buffer (pH 7.0). The contents were centrifuged for 15 min at 10,000 rpm, and the supernatant was used for further analysis. The reaction mixture consisted of 13 μM methionine, 75 μM NBT, 2 μM riboflavin, 10 μM EDTA, and enzyme extract, which were exposed to fluorescent light for 30 min, and the absorption was measured at 560 nm. Test tubes without enzyme extracts were served as blank, and the activity was expressed as units/mg of proteins.

Ascorbic acid content was determined by using the 2,6-dichlorophenol indophenol titration method. About 5 mL of the ascorbic acid working standard (500 μg/5 mL) and 4% oxalic acid (10 mL) were pipetted out into a 100 mL conical flask. The contents in the flask were titrated against the dye solution (V_1) until the appearance of a color (pale pink color) that persisted for a few minutes. The test sample (5 mL) was similarly titrated against the dye solution (V_2). Ascorbic acid content present in the test samples was determined according to Karayannis et al.[32]

2.4. Fluorescent Labeling and Absorption Pathway of N-SiO_2 Particles. To track the distribution of silica NPs in the groundnut leaf, N-SiO_2 particles were labeled with FITC. In brief, 10 mg of SiO_2 NPs and 5 mg of FITC were dispersed in 25 mL of ethanol separately, and the mixture was subjected to continuous stirring on a magnetic stirrer for 24 h. After 24 h, 50 mL of ethanol containing FITC-tagged N-SiO_2 was pelleted out by centrifugation (at 10,000 rpm for 5 min). The pellet was air-dried for 30 min in vacuum, and subsequently, the pellet was washed twice with deionized water to remove the traces of ethanol present in the pellet, and then the resultant pellet was dissolved in deionized water. Supernatants were analyzed for FITC fluorescence using a fluorescence spectrometer (JASCO FP-8500), and fluorescence was not detected in the second wash supernatant. Suspension containing FITC-tagged N-SiO_2 was sprayed on the leaves of the groundnut plant with handheld spray bottles. Sampling was performed at different time points (0 min, 30 min, 1 h, and 2 h) after foliar application. Then, all the leaf tissues were mounted on microscope slides one by one after being rinsed with deionized water and dried. Before mounting on a confocal (Leica TCS SP8) and fluorescent (Nikon Eclipse Ti2) microscope, a drop of water was added on the leaf sample to prevent it from desiccation, and subsequently, a coverslip was placed on it.

2.5. Collection and Preparation of Plant Samples for Si Estimation. To understand the silica availability in N-SiO_2 treatments, higher growth and yield in groundnut along with TEOS and control were selected for ICP-OES studies. The plant samples were collected at the harvest stage from T_3-N-SiO_2 at 200 ppm and T_4-N-SiO_2 at 400 ppm, control, and TEOS at 2000 ppm. The samples were initially shade-dried and subsequently in a hot air oven at 65 °C for 2 days and grounded in a Willey mill and stored in labeled brown paper bags until use. The samples were analyzed for Si, by digesting 1 g of the powdered leaf sample with a diacid mixture (HNO_3:$HClO_4$ in a 9:4 ratio) in digestion glass bottles and kept it on a hot plate until ash is formed. This ash is diluted in 100 mL of deionized water and used for analysis by using ICP-OES (Teledyne Leeman Labs) after calibrating ICP-OES with a traceCERT multi-element standard.

2.6. Gas Exchange Parameters. Gas exchange parameters like net photosynthesis rate (Pn) and transpiration rate (Tr) were measured using a portable IRGA (infrared gas analyzer) (Li-6400XT, LICOR Inc., USA). The third leaf from the main axis was kept in the chamber by ensuring that the thermocouple touched it from the underside, and the measurements were recorded between 9:00 and 10:00 A.M. on a sunny day. The water use efficiency was calculated by dividing the photosynthetic rate (Pn) by the transpiration rate (Tr).

2.7. Statistical Analysis. The data was subjected to statistical analysis by applying one-way ANOVA using Statistical Package for Social Sciences (SPSS) version 15.[33] Differences between means were tested using Duncan's multiple comparison test, and significance was set at $p < 0.05$.

3. RESULTS AND DISCUSSION

3.1. Characterization of Nanoscale Silica (N-SiO_2). The hydrodynamic size and zeta potential of N-SiO_2 synthesized in this study were measured by using DLS and were found to be

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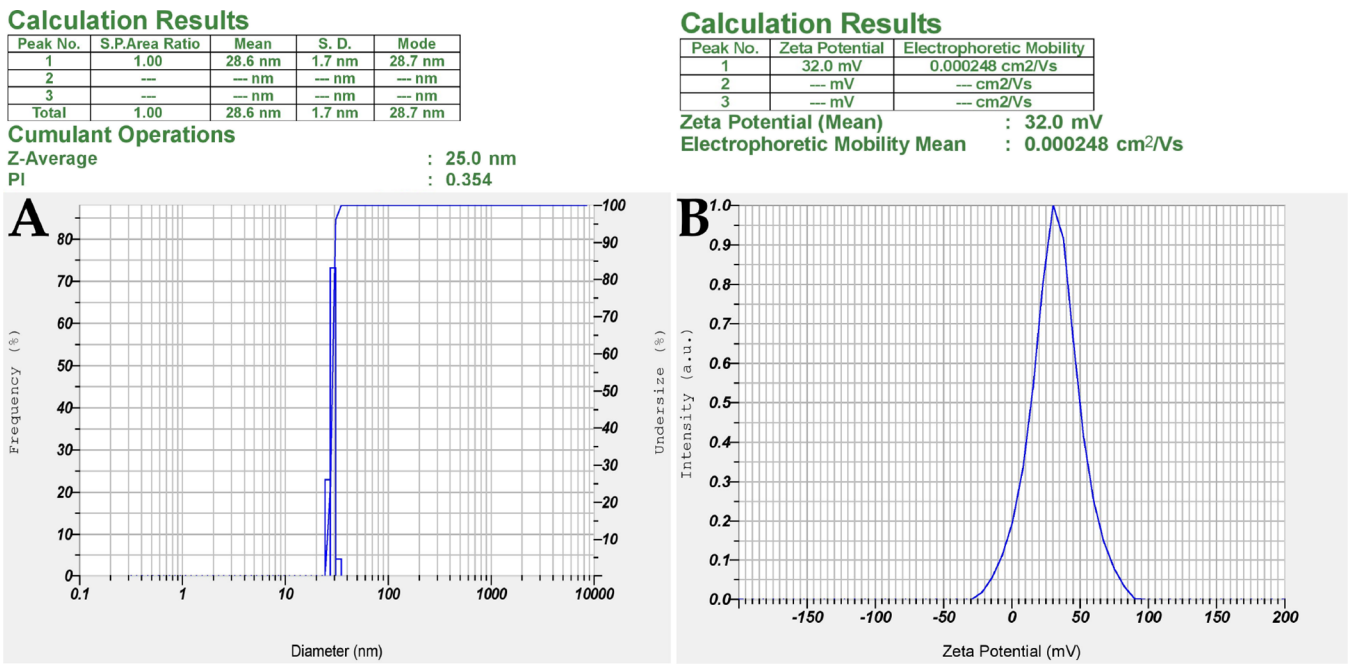

Figure 1. (A, B) Size and zeta potential of synthesized N-SiO_2.

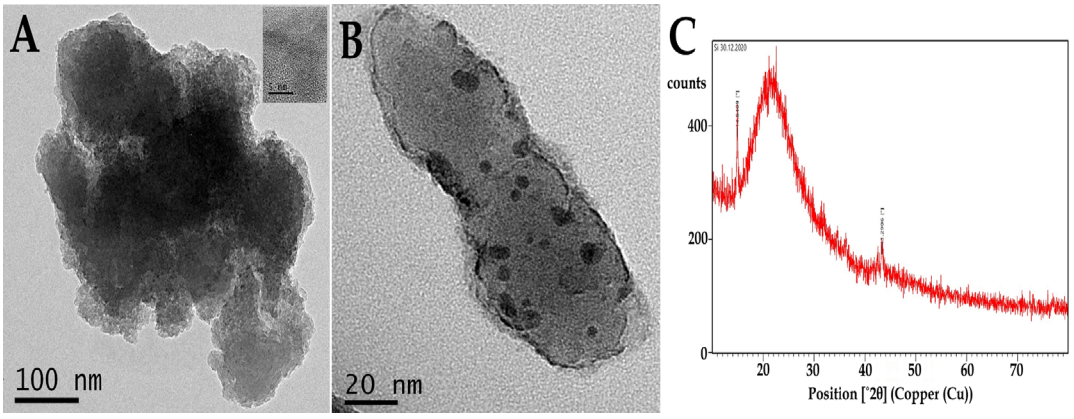

Figure 2. (A–C) Morphometric and crystal structure analysis of synthesized N-SiO_2 using TEM and XRD. Diffraction peaks were observed at 14.0409 and 43.2096.

28.70 ± 1.7 nm with a Z-average of 25 nm (Figure 1A) and 32 ± 15.3 mV (Figure 1B), respectively. N-SiO_2 was agglomerated in the absence of dispersion medium, i.e., water. In a recent study, N-SiO_2 was subjected to XRD through a range of 2θ angles (0–80 degrees) and all possible diffractions and spacings were recorded, which helped in the identification of the crystalline structure of N-SiO_2. 2θ diffraction peaks were identified by computer-based "Search–Match" algorithms of ICDD (International Centre for Diffraction Data, USA). XRD showed a characteristic diffraction broad pattern at 23° (2θ) that indicates the amorphous nature of N-SiO_2 (Figure 2C). Morphometric and composition analysis of N-SiO_2 was investigated using TEM (Figure 2A,B) and HR-SEM (Figure 3), respectively. Agglomeration of N-SiO_2 is clear from TEM analysis (Figure 2). The composition of N-SiO_2 primarily consists of silica and oxygen, which is evident from EDS analysis (Figure S2). Plants sprayed with N-SiO_2 at 1000 ppm were used for SEM analysis, and SEM analysis clearly showed the silicification or deposition of silica below the epidermal layers in N-SiO_2-sprayed leaves (Figure 3B), whereas such prominent thickenings below the epidermis were not identified in the control leaves (Figure 3A). A similar type of silicification was observed in grass family members (reviewed in Kumar et al.[34]).

3.1.1. Effect of N-SiO_2 on Growth Parameters like Plant Height, Number of Branches, Dry Matter, and Nodule Number. The foliar application of N-SiO_2 at 400 ppm recorded the highest plant height (37.88 cm) and number of branches (5.07) compared to TEOS (33.68 cm, 4.53) and control (32.89 cm, 4.00) treatments (Table 1). These kinds of growth-promoting effects of silica NPs were already reported in marigold,[20] sugarcane,[18] and rice.[19]

The total dry matter was recorded maximum in N-SiO_2 at 400 ppm (32.80 g) compared to TEOS (27.50 g) and control (22.46 g) (Table 1). SCMR increased significantly in plants sprayed with N-SiO_2 at 100, 200, and 400 ppm. SCMR was higher in N-SiO_2 at 200 ppm (43.30) compared to TEOS (42.18) and control (38.46) (Table 1). These results were in line with Dung et al.,[35] who reported that 60 ppm nanosilica increased the total dry matter and chlorophyll content in chili

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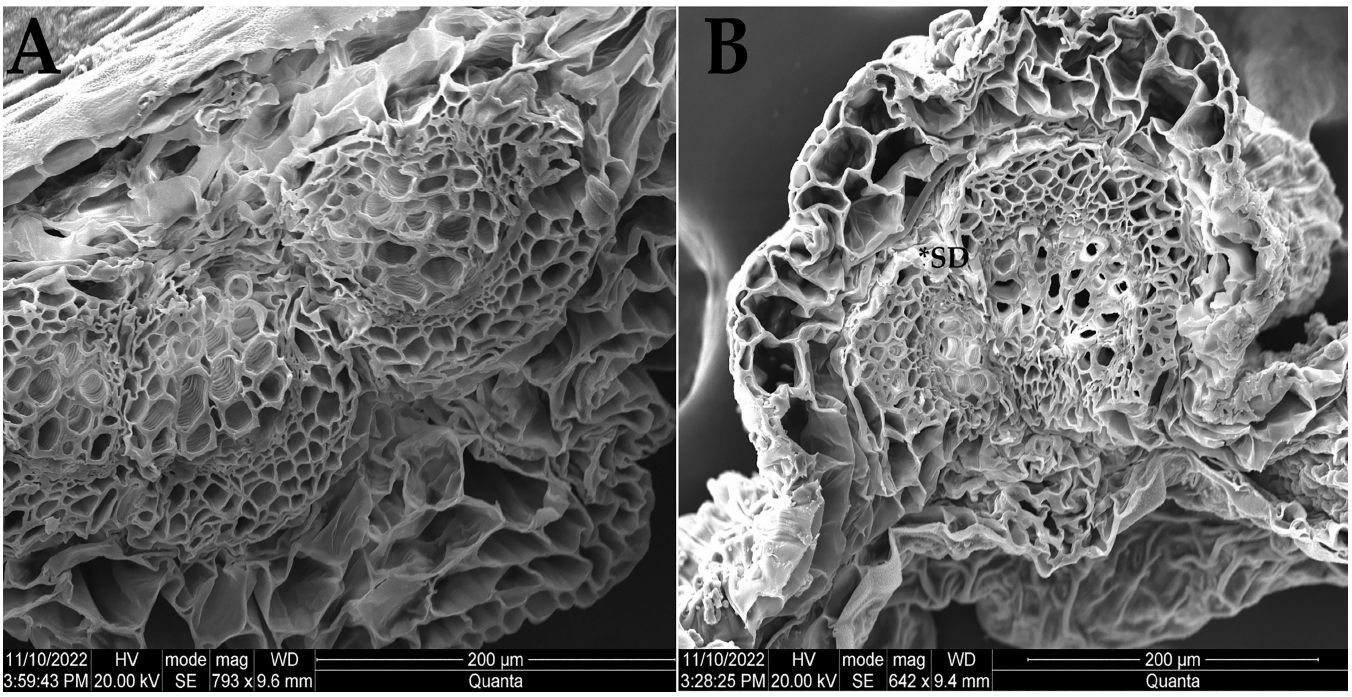

Figure 3. SEM analysis of *A. hypogaea* leaf, (A) control leaf and (B) N-SiO_2-treated leaf at 1000 ppm showing N-SiO_2 precipitation below the cuticle. SD, silica deposition.

Table 1. Effect of N-SiO_2 on Growth Parameters in Groundnut[a]

treatment	plant height (in cm)	no. of branches	no. of nodules	SCMR	total dry matter (g)
T_1: 50 ppm	$33.10^{a} \pm 1.77$ (0.63%)	$4.00^{a} \pm 0.00$ (0%)	$27.91^{a} \pm 0.44$ (0.83%)	$40.80^{a} \pm 0.42$ (6.08%)	$29.90^{a} \pm 1.26$ (33.12%)
T_2: 100 ppm	$35.20^{b} \pm 1.83$ (7.02%)	$4.00^{b} \pm 0.57$ (0%)	$31.98^{b} \pm 0.49$ (15.53%)	$42.12^{b} \pm 0.26$ (9.52%)	$30.06^{a} \pm 1.4$ (33.83%)
T_3: 200 ppm	$37.11^{c} \pm 0.88$ (12.83%)	$5.20^{c} \pm 0.33$ (30%)	$33.59^{c} \pm 0.18$ (21.35%)	$43.30^{c} \pm 0.24$ (12.58%)	$30.23^{a} \pm 2.15$ (34.59%)
T_4: 400 ppm	$37.88^{c} \pm 0.79$ (15.17%)	$5.07^{c} \pm 0.33$ (26.8%)	$34.28^{d} \pm 0.33$ (23.84%)	$42.79^{d} \pm 0.22$ (11.26%)	$32.80^{b} \pm 2.7$ (46.04%)
T_5: 800 ppm	$35.54^{bc} \pm 1.95$ (8.05%)	$4.00^{ab} \pm 0.00$ (0%)	$33.24^{ce} \pm 0.33$ (20.08%)	$40.38^{a} \pm 0.52$ (4.99%)	$29.90^{a} \pm 1.26$ (33.12%)
T_6: 1000 ppm	$36.68^{bc} \pm 1.27$ (11.52%)	$4.00^{ab} \pm 0.00$ (0%)	$32.87^{e} \pm 0.16$ (18.75%)	$39.83^{e} \pm 0.29$ (3.56%)	$27.36^{a} \pm 2.39$ (21.82%)
T_7: 1500 ppm	$35.42^{b} \pm 1.21$ (7.69%)	$4.00^{ab} \pm 0.00$ (0%)	$28.78^{f} \pm 0.46$ (3.97%)	$39.33^{f} \pm 0.44$ (2.26%)	$25.53^{c} \pm 2.45$ (13.67%)
T_8: 2000 ppm	$32.46^{b} \pm 1.26$ (−1.31%)	$4.00^{ab} \pm 0.00$ (0%)	$27.00^{g} \pm 0.54$ (−2.45%)	$38.08^{g} \pm 0.48$ (−0.98%)	$23.83^{cd} \pm 3.62$ (6.09%)
T_9: bulk	$33.68^{ab} \pm 1.22$ (2.40%)	$4.53^{d} \pm 0.00$ (13.3%)	$30.26^{h} \pm 0.83$ (9.32%)	$42.18^{b} \pm 0.28$ (9.67%)	$27.50^{ac} \pm 2.68$ (22.44%)
T_{10}: control	$32.89^{a} \pm 1.23$	$4.00^{ab} \pm 0.00$	$27.68^{a} \pm 0.42$	$38.46^{g} \pm 0.42$	$22.46^{d} \pm 2.73$

[a]Values are represented in mean ± standard deviation; $n = 15$. Values sharing same alphabet as superscript do not vary significantly from each other.

plants. It was already reported that Si constituted to 0.1 to 10% total dry weight of the plant, as it is absorbed by roots in the form of monosilicic acid and then transported to different parts of the plant through xylem.[36] Si potentiates leaf dry mass by decreasing biotic and abiotic stress impacts.[37]

N-SiO_2 treatment increased the nodule numbers significantly compared to control (Table 1). N-SiO_2 at 400 ppm recorded the highest number of nodules per plant (34.28) compared to TEOS (30.26) and control treatments (27.68). An increase in the nodule number can be correlated to higher nitrogen fixation and availability, thereby facilitating growth and yield in *A. hypogaea*. Putra et al.[21] showed that Si enhanced root nodulation in Leguminosae plants, *Medicago truncatula*. Similarly, Si supplementation increased nodulation, when commercially available rhizobia strain is applied to *Medicago sativa*.[38] From these results, it is evident that N-SiO_2 increases the chlorophyll content, dry weight, and nodule number by strengthening the plant physical barriers to cope up abiotic and biotic stresses in groundnut.

3.1.2. Effect of Nanosilica on Biochemical Parameters. N-SiO_2 treatment increased the chlorophyll and carotenoid content significantly compared to control and bulk. N-SiO_2 at 400 ppm recorded higher chlorophyll *a* (48.93 mg/100 g fresh weight^{-1}) content compared to TEOS (35.24 mg/100 g fresh weight^{-1}) and control (33.12 mg/100 g fresh weight^{-1}) (Figure 4). On the other hand, chlorophyll *b* content was significantly higher in N-SiO_2 at 1000 ppm (12.20 mg/100 g fresh weight^{-1}) compared to TEOS (9.43 mg/100 g fresh weight^{-1}) and control (7.61 mg/100 g fresh weight^{-1}) (Figure 4).

The total chlorophyll and carotenoid content was higher in N-SiO_2 at 400 ppm (55.98 mg/100 g fresh weight^{-1} and 28.85 mg/100 g fresh weight^{-1}) compared to TEOS (44.67 mg/100 g fresh weight^{-1} and 22.41 mg/100 g fresh weight^{-1}) and control (40.73 mg/100 g fresh weight^{-1} and 21.85 mg/100 g fresh weight^{-1}) (Figure 4). It is evident from the literature that an increase in the chlorophyll content is directly proportional to the photosynthetic rate, which enables the plant to synthesize an adequate amount of starch to complement the

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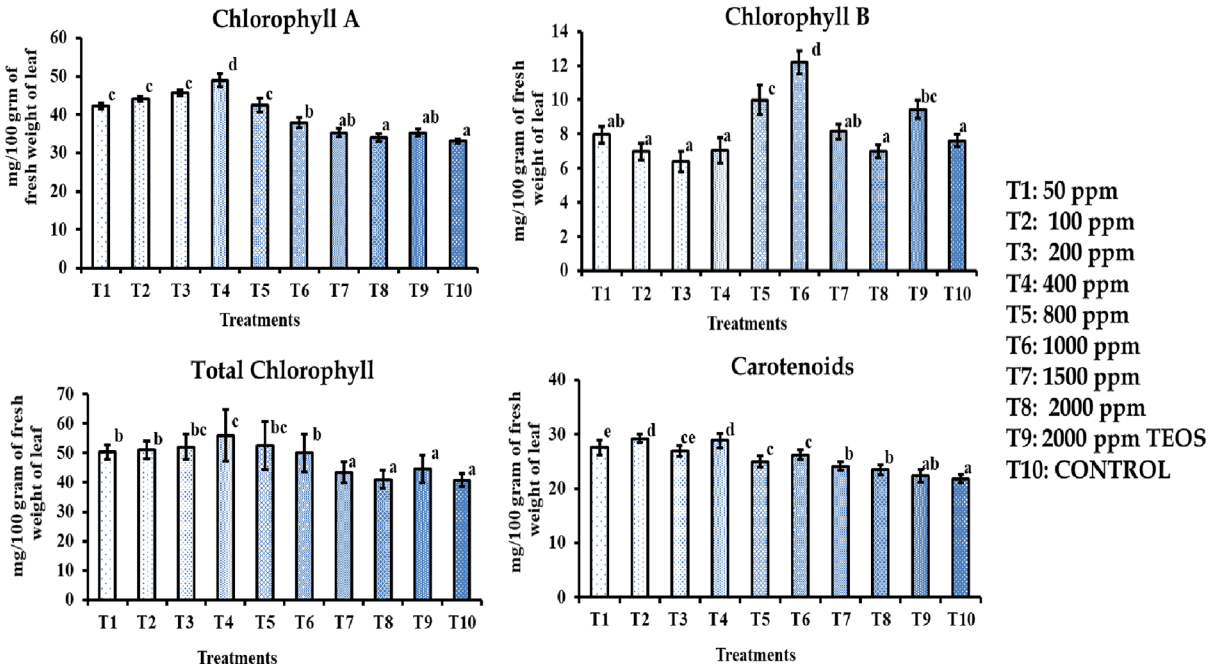

Figure 4. Effect of N-SiO_2 on biochemical parameters. Footnotes: Values are represented in mean ± S.D. of 15 plants; bars sharing the same superscript do not vary significantly from each other.

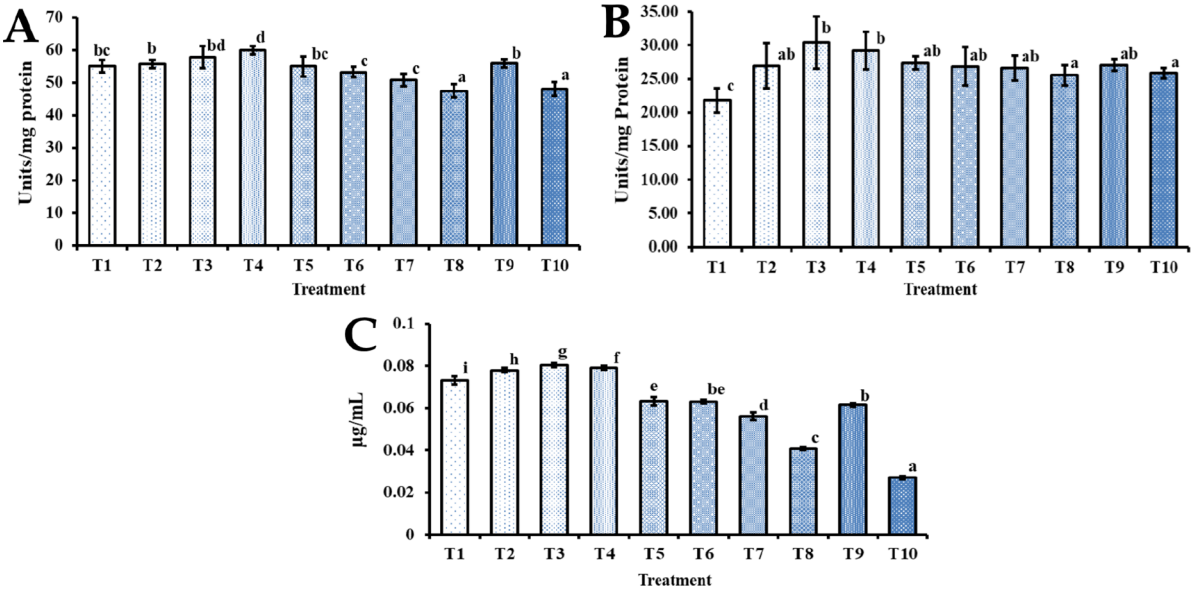

Figure 5. (A–C) Effect of N-SiO_2 on oxidative stress parameters. Footnotes: Values are represented in mean ± S.D. of 15 plants; bars sharing the same superscript do not vary significantly from each other.

growth and yield of groundnut plants as Si diminishes the effects of abiotic and biotic stressors.

3.1.3. Effect of N-SiO_2 on Oxidative Stress Parameters. Abiotic stress and stress induced by application of N-SiO_2 can be evaluated by estimating enzyme activities of superoxide dismutase and peroxidase. Stress (both abiotic and biotic) induces the generation of free radicals, and these free radicals were transformed into hydrogen peroxide by superoxide dismutase (SOD). Hydrogen peroxide generated will be transformed into oxygen and water by peroxidase (POD). Apart from stress, SOD and POD play a crucial role in the maintenance of free radicals during rapid growth or cell division in plants. In this study, SOD and POD increased significantly in N-SiO_2-treated groups compared to control. Among the treatments, N-SiO_2 at 200 and 400 ppm showed a significant enhancement of SOD and POD activities compared to control (Figure 5). Ascorbic acid content in N-SiO_2-treated plants were significantly higher in N-SiO_2 at 200 ppm (0.0804 μg/mL) compared to control (0.0270 μg/mL) and TEOS (0.0613 μg/mL) treated plants (Figure 5). Silicification of cell walls generates oxidative stress in plants, and antioxidant enzymes decrease oxidative stress by transforming the superoxide radicals into oxygen. Hence, increases in antioxidant enzyme activities and antioxidants provide protection to plant cells from oxidative stress generated by silicification process. These results are on par with Ismail et al.[39] Increased

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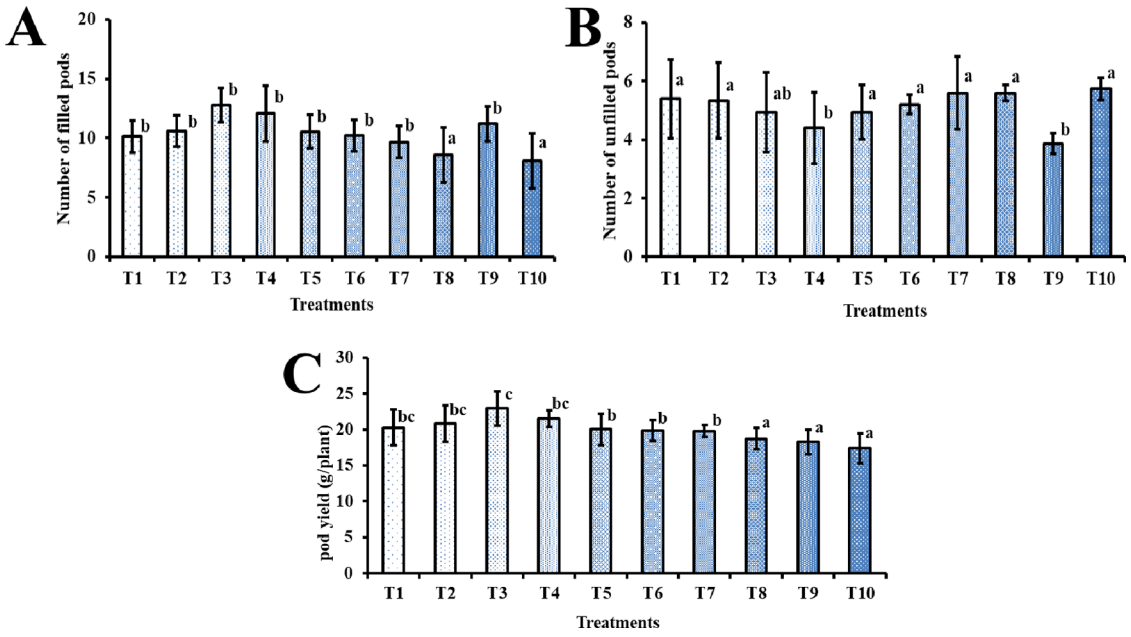

Figure 6. (A–C) Effect of N-SiO_2 on yield and yield attributes. Footnotes: Values are represented in mean ± S.D. of 15 plants; bars sharing the same superscript do not vary significantly from each other.

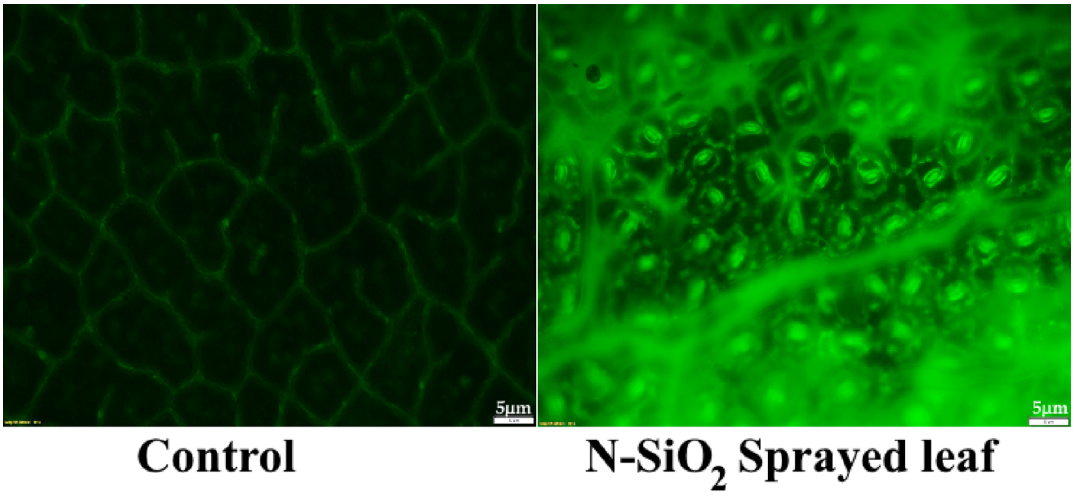

Figure 7. Stomatal entry of FITC-tagged N-SiO_2.

ascorbic acid reflects the plant antioxidant status and higher photosynthetic rate as ascorbic acid is a co-factor for many important enzymes involved in photosynthesis.[40] Antioxidant enzyme activities improve plant growth and yield in response to N-SiO_2 by decreasing the oxidative stress caused during rapid growth.[41]

3.1.4. Effect of N-SiO_2 on Yield and Yield Attributes. N-SiO_2 increased yield and yield attributes in groundnut up to 400 ppm. Application of N-SiO_2 above 400 ppm showed a decline in yield and yield attributes compared to 400 ppm. The control plants had the lowest filled pods (8.07), which is increased by 58.16 and 38.78% in N-SiO_2 at 200 ppm (12.80) and TEOS at 1000 ppm (11.20) treated plants (Figure 6A). Unlike filled pods, the number of unfilled pods was lower in TEOS at 1000 ppm (3.87) over N-SiO_2 at 200 ppm (4.93) and control plants (5.73) (Figure 6B). The pod yield per plant increased by 25.52% in N-SiO_2 at 200 ppm (22.93 g/plant) over TEOS (18.26 g/plant) and 31.7% over control (17.39 g/plant) (Figure 6C). Similar results were obtained with marigold,[20] sugarcane,[18] and rice after N-SiO_2 treatment.[19]

3.1.5. Absorption and Transport of N-SiO_2 Particles. In the foliar application of NPs, NPs can enter in two ways, i.e., through the stomatal opening[23] and lipophilic pathway.[42] Groundnut stomata are kidney-shaped with unique geometric structures and complex physiological functions. To understand the entry point of N-SiO_2 NPs into the leaf, N-SiO_2 was tagged with FITC to visualize their entry with a fluorescent microscope. Hydrophilic N-SiO_2 particles tagged with FITC are absorbed rapidly through kidney-shaped stomata (Figure 7). We observed internalization of FITC-N-SiO_2 after 30 min from the foliar application of FITC-N-SiO_2 (Figure S3). After 2 h from the foliar application, fluorescence of FITC-N-SiO_2 was observed throughout the leaf section, indicating homogeneous spreading of N-SiO_2 in apoplastic regions from the epidermis to vascular bundles (Figure 8), which is on par with SEM analysis (Figure 3). In SEM analysis, we

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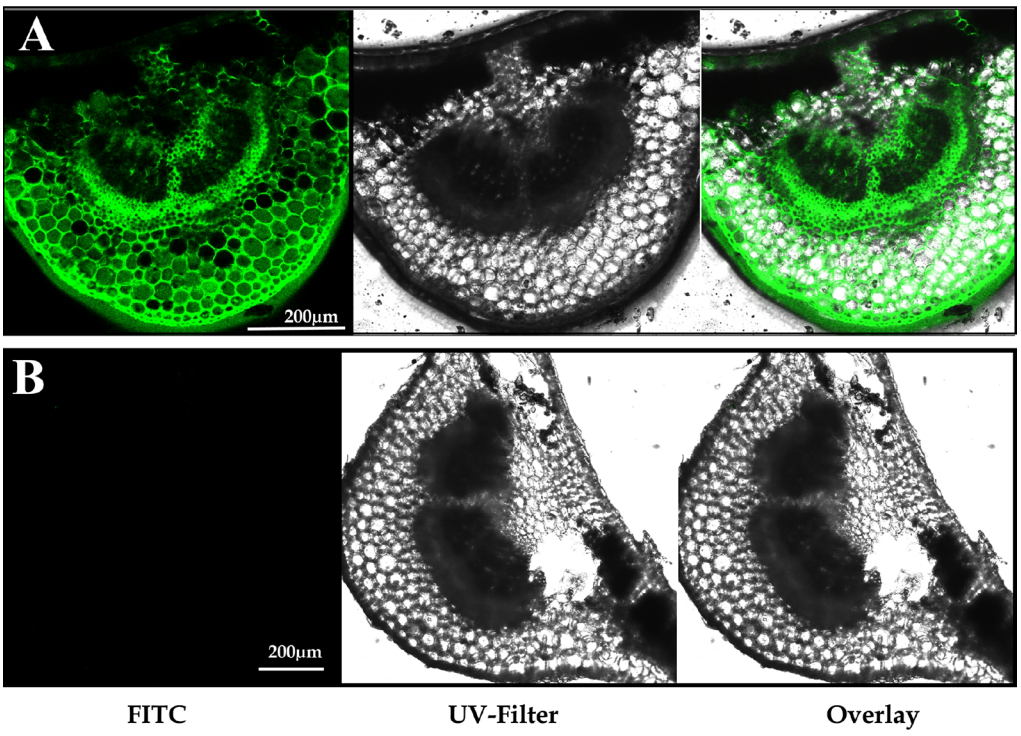

Figure 8. (A, B) Longitudinal section of the groundnut leaf showing transport and accumulation of FITC-tagged N-SiO_2 in the apoplastic space after 2 h.

found the homogeneous spreading of N-SiO_2 through apoplastic spaces and thickening of cell walls (Figure 3). In this study, N-SiO_2 was able to enter easily through the stomatal pore because of its size and charge. Hu et al.[43] reported that silica NPs of 18 nm can enter through the stomatal pore in maize and cotton. Polymeric NPs of 43 nm and 20 nm Fe_3O_4 NPs were able to enter through stomata of *Vicia faba*[44] and *Nicotiana benthamiana*,[45] respectively.

In this study, the majority of the NPs are positively charged (32 mV), which facilitates easier entry of N-SiO_2 into the groundnut leaf through the stomatal pore. Studies also reported that positively or negatively charged NPs with zeta potential magnitudes higher than 20 or 30 mV are absorbed by plants.[43] In contrast, neutral nanomaterials cannot penetrate lipid bilayers of plants.[46] Nanosilica is converted into the insoluble silicic acid layer through polymerization, which mostly deposits beneath the leaf cuticle and in cell walls, where it tightens the cell wall to improve resistance to biotic and abiotic stresses in chili plants.[47]

3.1.6. Estimation of Si in Leaves of N-SiO_2-Treated Plants. Estimation of Si in leaves of groundnut treated with N-SiO_2 at 200 and 400 ppm, TEOS at 2000 ppm, and control (water-treated plants) was carried out to understand Si deposition, i.e., silicification of plant cells. ICP-OES analysis showed that Si content increased significantly in leaves of N-SiO_2 at 200 ppm (0.73 ± 0.23) and N-SiO_2 at 400 ppm (0.76 ± 0.19) treated plants when compared to control (0.24 ± 0.12) and TEOS at 2000 ppm (0.39 ± 0.13) treated plants. These results clearly indicate the deposition of Si in leaves in the form of silicified layers, which provide an extra-physical barrier to decrease the transpiration rate and pest incidence in plants.[44] These results are in correlation with SEM analysis and FITC-N-SiO_2 experiments.

3.1.7. Effect of N-SiO_2 on Leaf Gas Exchange Parameters. The photosynthetic rate increased significantly in N-SiO_2-treated plants at 200 ppm (27.87 ± 1.53) and 400 ppm (28.27 ± 0.96) when compared to control (23.20 ± 1.53) and TEOS at 2000 ppm (24.67 ± 1.17). The transpiration rate decreased significantly in N-SiO_2-treated plants at 200 ppm (1.46 ± 0.05) and 400 ppm (1.63 ± 0.09) when compared to control (2.01 ± 0.07) and TEOS at 2000 ppm (1.87 ± 0.06). From this, it is clear that the water use efficiency is higher in N-SiO_2-treated plants at 200 ppm (19.1) and at 400 ppm (17.34) compared to control (11.54) and TEOS at 2000 ppm (13.19). Silica gets accumulated in the cell walls to form phytolith-like structures, thereby reducing transpiration rate and increasing water use efficiency in plants.[48]

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.est.3c00327.

N-SiO_2 treatment suspensions at different concentrations, compositional analysis of synthesized N-SiO_2 using high-resolution scanning electron microscopy equipped with energy-dispersive X-ray spectroscopy, and longitudinal section of the groundnut leaf showing transport and accumulation of FITC-tagged N-SiO_2 in the apoplastic space after 30 min (PDF)

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Notes

The authors declare no competing financial interest.

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