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Effect of foliage applied chitosan-based silicon nanoparticles on arsenic uptake and translocation in rice (*Oryza sativa L.*)

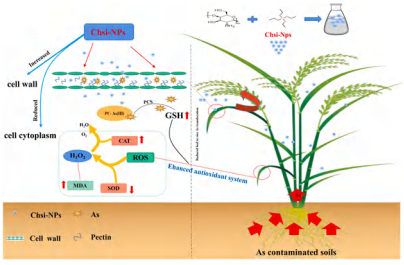
Yang Jia-Yi [a,b,1], Sun Meng-Qiang [a,1], Chen Zhi-Liang [a,*], Xiao Yu-Tang [b], Wei Hang [a], Zhang Jian-Qiang [a], Huang Ling [a], Zou Qi [a]

[a] Guangdong Engineering Technology Research Center of Heavy Metal Pollution Control and Restoration in Farmland Soil, South China Institute of Environmental Sciences, Ministry of Ecology and Environment, Guangzhou, Guangzhou 510275, PR China
[b] School of Environment, South China Normal University, Guangzhou 510006, PR China

HIGHLIGHTS

- Foliar Chsi-NPs were used to improve the As tolerance of rice in soils.
- Foliar Chsi-NPs application promotes the fixation of arsenic in the leaf cell wall.
- Foliar Chsi-NPs treatments reduced the As concentration in the grain by 61.2%.

GRAPHICAL ABSTRACT



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ABSTRACT

In this study, chitosan-based silicon nanoparticles (Chsi-NPs) are prepared that primarily consists of C (57.9%), O (31.3%), N (5.6%), and Si (3.5%) and are 10–180 nm in size. We then explore the effect on the foliage applied on rice planted on soil contaminated with 104 mg·kg^{-1} arsenic (As); low (3 mg·L^{-1})and high (15 mg·L^{-1}) doses of the foliar Chsi-NPs are administered during the rice grain filling stage. The results showed that the higher dose foliar Chsi-NPs treatment reduced the As concentration in the grain by 61.2% but increased As concentration in the leaves by 47.1% compared to the control treatment. The foliar spraying of the Chsi-NPs inhibited As transport to the grain by facilitating the attachment of As to the cell wall, with higher doses of the foliar Chsi-NPs treatment increased by 8.7%. The foliar spraying of Chsi-NPs increased the malondialdehyde levels by 18.4%, the catalase activity by 49.0%, and the glutathione activity by 99.0%. These results indicated that the foliar Chsi-NPs application was effective for alleviating As toxicity and accumulation in rice. This study provides a novel method for effectively alleviating As accumulation in rice.

1. Introduction

Humans are exposed to arsenic (As), a metalloid with a high carcinogenic risk, primarily through diet (González et al., 2020). Approximately 160 million hectares of rice cultivation area are maintained worldwide because rice is the staple food of more than half of the

* Correspondence to: South China Institute of Environmental Sciences, Ministry of Ecology and Environment, Guangzhou 510275, PR China.
E-mail address: chenzhiliang@scies.org (C. Zhi-Liang).
[1] These authors contributed equally

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world's population (Kumar et al., 2016; Samal et al., 2021). In Asia, an average of 200–600 g of rice is consumed daily by a single adult (Carey et al., 2010). However, the potential daily intake of As by an adult is highly variable depending on the region; for example, the daily intake is 19.6 μg in India (Kumar et al., 2016) and 69 μg in Cambodia (Pan et al., 2014). It has also been reported that the daily dietary intake is up to 2.32 μg/kg body wt./day of inorganic As from rice grain, and this exceeds the World Health Organization-recommended provisional tolerable daily intake (PTDI) value (2.1 μg/kg body wt./day inorganic arsenic) (Roychowdhury, 2008). In addition, rice in some rice-growing countries is contaminated with As to varying degrees; for example, the total As concentration in rice ranges from 16 $\mu g \cdot kg^{-1}$ to 630 $\mu g \cdot kg^{-1}$ in Australia (Maher et al., 2018). A study has shown that an increase in the As concentration in soil from 12 to 60 $mg \cdot kg^{-1}$ in conventional paddy fields of Bangladesh resulted in decreased rice yields from 7.5 to 2.5 $t \cdot ha^{-1}$ (Bakhat et al., 2017). It has been reported that rice plants grown in soils (containing >60 $mg \cdot kg^{-1}$ of total arsenic, arsenite (AsIII) is comprising 63%, arsenate (AsV) at 36%) As can cause toxicity symptoms of stunted growth, brown spots, and scorched leaves (Bakhat et al., 2017; Stoeva and Bineva, 2003). Hence, reducing the As content of rice planted on As-contaminated soil has become a major subject of interest.

Foliar fertilizers have been preferred because of their good ability to regulate the uptake of heavy metals or metalloids by crops planted on contaminated soil; for example, the foliar application of 2,3-dimercaptosuccinic acid reduces the levels of cadmium (Cd), lead (Pb), and As in rice grains by 47.95%, 61.76%, and 36.37%, respectively (Liu et al., 2014; Yang et al., 2021). Likewise, rice, as a typical silicon-philic crop, could be mitigated damage caused by polluted soil through the application of silicon fertilizer (Alshaal et al., 2017). Research has shown that Si fertilization decreased the total As concentration in grains by 16% (Li et al., 2012). However, it has been reported that the supplementation of foliar with silicon-like substances can significantly contribute to decrease As and Cd accumulation in rice grains, increase pectin synthesis and the mechanical force of the cell wall, improve resistance to diseases reduce production of reactive oxygen species in vivo and damage due to abiotic stresses (Guntzer et al., 2012). For example, foliar application of SiO_2 NPs can maintain the integrity of the cell, and increase the thickness of the cell wall (77.4%) and the ratio of As in the pectin (19.6%) (Cui et al., 2020). The foliar application of a nanoscale silica solution increased grain yield by 29.6% in field experiments (Liu et al., 2014). In general, the chemical synthesis of foliar fertilizers presents environmental risks due to toxic chemical components (Milewska-Hendel et al., 2019). Therefore, there is a need to explore new agricultural-friendly chemical synthesis methods.

Chitosan, an environmentally friendly natural polymer material, has been used in agriculture (Sivanesan et al., 2021). Great progress has been observed in the application of chitosan and chitosan-based materials in terms of crop resistance (Sathiyabama and Manikandan, 2021). Chitosan application improves growth, increases yield, and elicits defense mechanisms in plants (Divya and Jisha, 2018). However, chitosan nanoparticles (ChNPs) are highly soluble in aqueous media, and have increased activities compared to chitosan (Suhas et al., 2015). For example, the foliar application of ChNPs significantly enhanced Finger millet plants in dry weight (52%) and the mineral content of iron (Fe; 3%), zinc (Zn; 8%), manganese (Mn; 8%), phosphorus (P; 20%), calcium (Ca; 3%), and magnesium (Mg; 10%), when compared to chitosan (Sathiyabama and Manikandan, 2021). Similar studies have shown that foliar application of ChNPs can enhance 30–50% the chlorophyll content in coffee leaves and increase in the uptake of nutrients, such as nitrogen (N; 9.8–27.4%), P(17.3–30.4%), potassium (K; 30–45%) (Van et al., 2013). In addition, due to the unique physicochemical (e.g., size, shape, and surface area), biological and antimicrobial properties of ChNps, chitosan-based metal nanocomposites, such as Mg, silver (Ag), and copper (Cu), have been used to enhance the antimicrobial properties of plants (Ahmed et al., 2021; Rubina et al., 2017). ChNPs have primarily been studied for their crop growth and antimicrobial applications, but few studies have focused on regulating crop uptake of heavy metals or metalloids.

Therefore, in this work, chitosan-based silicon nanoparticles (Chsi-NPs) synthesized with the hydrothermal method are used to observe the effect of foliar application on As uptake and translocation in rice. Then, high and low-dose Chsi-NPs are used to regulate the migration of As in rice under anoxic (flooded) condition. The aims of this study are to examine (1) the ability of Chsi-NPs to regulate As and (2) the regulatory mechanism for As upon Chsi-NPs application.

2. Materials and methods

2.1. Soil samples

The soil was collected from the plough layer (0–20 cm) of a farmland (23° 62′ 22″N, 116° 85′ 65″ E) surrounding the Lianhuashan tungsten mine area in Shantou City, Guangdong Province, China. The soil was air-dried and put through a 2 mm mesh sieve before an analysis of the common physiochemical properties, which are provided in Table S1.

2.2. Preparation and characterization of Chsi-NPs

First, 6 g of chitosan was dissolved in 150 mL of 3% acetic acid solution, and the mixture was stirred at 45 °C for 1 h. Then, 100 mL of 4% H_2O_2 solution was added slowly, and the temperature was maintained at 60 °C for 4 h. After the mixture was cooled to room temperature, the pH was adjusted to a neutral value, and then the mixture was left to stand for 8 h, centrifuged, and freeze-dried. Next, 1 g of solid particles was dissolved in 600 mL of 1% acetic acid solution, and the product was named CS. Second, 10 mL of ethanol was blended with 1 mL of ammonia for approximately 1 h, and then 0.55 mL of tetraethyl orthosilicate was added to the mixed solution. The resulting mixture was heated and magnetically stirred for 2 h (40 °C, 300 rpm). Subsequently, 150 mL of CS and 60 mL of sodium tripolyphosphate (STPP) were added dropwise to the mixed solution at 30 °C for approximately 2 h. Finally, 2.5 mL of tween80 was added to the reaction solution, and this was stirred for 10 min and diluted to 250 mL for the production of the Chsi-NPs solution.

2.3. Characterization analysis

Transmission electron microscopy–energy dispersive spectroscopy (TEM–EDS, Tecnai G2 F20, GENESIS) was performed, and the specific functional groups of Chsi-NPs were determined using the infrared spectroscopy (FTIR) system (Thermo Nicolet iS5) and the X-ray photoelectron spectroscopy (XPS) system (Thermo ESCALAB 250 Xi.).

2.4. Experimental design

The rice seeds (Zhenghan 10) were sterilized in 30% H_2O_2 solution for 15 min, washed three times with pure water, soaked, and incubated at 28.0 °C. Healthy seeds were then selected and a placed in gauze cloth for germination. The rice seeds were germinated in As-free field soil in a greenhouse. Seedlings were transferred to potting soil at the three-to-four-leaf stage, and three seedlings were planted in each pot. The anoxic condition was maintained with a 2 cm water layer covering the soil surface. The treatments were denoted as CK (control), T1 (3 $mg \cdot L^{-1}$ Chsi-NPs), and T5 (15 $mg \cdot L^{-1}$ Chsi-NPs), and each treatment had three replications. Chsi-NPs (15 mL) were sprayed onto the leaves of the rice seedlings grown in the As contaminated soil at the filling stage (75 days after transplanting rice seedlings), continuously for three days. The control plants received an equal amount of pure water in the form of a foliar application on the same day, and the other plants received the Chsi-NPs treatments. During our experiments, we used geotextiles to cover the soil surface during chemical spraying to reduce the contact between the chemical and the soil. After 21 days, the rice samples were harvested after maturity, and some samples were dried in an oven at

65 °C for chemical analysis. In addition, some were cryopreserved at −80 °C for the biological analysis.

2.5. Analytical methods

2.5.1. Total as analysis

For the total As determination, 0.2 g of the dried samples was mixed with 10 mL of HNO_3 and $HClO_4$ (4:1, v-v) in a 50-mL of polyethylene tube overnight and digested on a graphite digestion apparatus at 120 °C until a clear digestion solution was obtained. The digested solution was diluted with 1% HNO_3 to 50 mL and filtered with a 0.22-μm filter. The As concentration in the solution was determined using an Agilent ICPMS 7800 instrument. Certified reference material (GBW(E)100353; composition of rice flour) and sample blanks were used for quality control, and the As recovery from the reference material was 100.2% ± 4.5 (n = 6). The As standard solutions (GNM-M330198–2013) were diluted for the standard calibration curve. The detection limit of As was 1 ug·L^{-1}.

2.5.2. As species analysis

Each rice grain or husk sample (1.0 g) was extracted with 20 mL of 0.15 M nitric acid (HNO_3). The mixture was left to stand overnight and heated at 90 °C in a heating block for 2.5 h and shaken for 1 min every 0.5 h. The digests were cooled to room temperature. The digests were centrifuged at 8000 r·min^{-1} for 15 min, the supernatant was collected and filtered with a 0.45-μm organic filter membrane prior to sampling.

As species in the rice grain and husk extracts were determined with an Agilent LC-ICPMS 7800 instrument. As species (arsenite, arsenate, dimethylarsinic acid [DMA], and monomethylarsonic acid [MMA]) were separated using an anion exchange column (PRP-X100, 250 × 4.1 mm, 10 μm, Hamilton Company). The mobile phase contained 20 mM $NH_4H_2PO_4$ (pH 5.6; the pH was adjusted with ammonia) that was pumped through the column at 1 mL·min^{-1}. Certified reference material (GBW(E)100353; composition of rice flour) was used to validate the method, The mean total recovery ((sum of species recovered from the HNO_3 extraction/total As from acid digestion) × 100%) ranged from 85% to 103%.

2.5.3. Total Si in the leaf analysis

The leaves (0.1 g of dried samples) were mixed well with 3 mL of 50% NaOH in a 50 mL polyethylene tube. The mixed samples were digested in a high-temperature sterilizing oven (40 min at 120 °C). The digested solution was diluted using ultrapure water to 50 mL in a plastic volumetric flask at 25 °C (Liu et al., 2009). Si was determined using the molybdate-blue method (Wei-min et al., 2005). The Si standard solutions (BW30024–100-J-50) were diluted for the standard calibration curve, the correlation coefficient was greater than 0.999, and the absorbance of the sample to be measured was within the standard curve.

2.5.4. As subcellular fractionation analysis

For the observation of the effects of Chsi-NPs on the subcellular As distribution, the leaves were separated into the cell wall, soluble portion, and organellar fractions (Wang et al., 2008). The separation process was as follows: first frozen leaves (0.8 g) were homogenized in pre-chilled extraction buffer containing 50 mM Tris-HCl (pH = 7.5), 250 mM sucrose, and 1.0 mM dithiothreitol. Then, the homogenates were centrifuged at 3000 rpm for 15 min and filtered through an 80-μm mesh nylon cloth to obtain the “cell wall fraction (F1).” Finally, the supernatant was centrifuged at 12,000 rpm for 30 min, and the resulting sediments and supernatants were obtained. The resulting sediments were identified as the “organellar fraction (F2),” and the supernatants were identified as the “soluble fraction (F3).”

2.5.5. Antioxidant enzyme systems analysis of the leaf

For the observation of the effects of the foliar Chsi-NPs application on the antioxidant enzyme systems in rice leaves, a catalase (CAT, EC 1.11.1.6), superoxide dismutase (SOD, EC 1.15.1.1), malondialdehyde (MDA), and glutathione (GSH) were analyzed with kits purchased from Suzhou Keming Technology Co., Ltd. The actual methods are in the SI.

2.5.6. Preparation of the transmission electron microscopy sections of the rice leaves

For transmission electron microscopy (TEM) slice preparation, the method of (Riaz et al., 2022) was used. First, the leaf tips (0–2 mm) were placed in 2.5% glutaraldehyde for fixation for 12 h above 4 °C. Then, the leaf tip samples were collected, washed four times with 0.1 mol·L^{-1} phosphate buffering solution (PBS), and washed three times with 0.1 mol·L^{-1} acid buffer for 15 min. Finally, a gradual dehydration of ethanol was completed that was first performed at 50%, 70%, 90%, and 100% ethanol dehydration for 15 min each time. Then, the samples were embedded and solidified. After staining, TEM was used to observe the representative images.

2.6. Statistical analysis

Data are presented as the average ± standard deviation of the three replicates. The treatment effects were assessed using an analysis of variance, and the treatment means were compared using the least significant difference at p of < 0.05. All of the statistical analyses were performed using SPSS 22.0 (SPSS Inc., Chicago, Illinois). Graphs were plotted using Origin 8.5 (OriginLab, USA).

3. Results

3.1. Physicochemical properties of the Chsi-NPs

The physicochemical characteristics of Chsi-NPs were evaluated using the morphology obtained by the different analyses (Fig. 1). The Chsi-NPs were nearly spherical as determined by the TEM examination (Fig. 1[a] and [b]). The Chsi-NPs were 10–180 nm in size, and the average size was 166 nm (Fig. 1 [f]). Furthermore, we determined the distribution of an element using TEM–EDS. The EDS images showed that the Chsi-NPs were primarily composed of C (57.9%), O (31.3%), N (5.6%), and Si (3.5%) (Fig. 1[e]). The surface chemical composition of the Chsi-NPs was confirmed using XPS. The presence of a Si 2p peak in the spectrum demonstrated the successful synthesis of the silicon-based chitosan (Fig. 1[d]). Additionally, the C═C (1566.04 cm^{-1}), C═O (1550 cm^{-1}), and Si-O-Si (1091.66 cm^{-1}) stretching vibration peaks were found in the FTIR spectra (Fig. 1[c]).

3.2. Change in Si and As concentrations in the leaves

Fig. 2 shows the changes in Si and As concentrations in the leaves after Chsi-NPs foliar application. After foliar Chsi-NPs spraying, the concentration of Si in the leaves increased relative to that in CK (Fig. 2 [a]). The Si concentrations in the leaves subjected to the 3 mg·L^{-1} and 15 mg·L^{-1} Chsi-NPs foliar treatments were 15.0% and 16.5% higher than those of the control, respectively. However, Chsi-NPs treatments had no significant effect ($P > 0.05$) on Si concentrations in the leaves. The concentration of As in the leaves markedly increased after the foliar Chsi-NPs treatment (Fig. 2[b]). The As concentrations in the leaves after 3 mg·L^{-1} and 15 mg·L^{-1} Chsi-NPs of foliar application were 20.7% and 47.1% higher than those in the control ($P < 0.05$), respectively. The present results suggested that As and Si in the leaves played important roles in the reduction of As translocation from the shoots to rice. Ma and Yamaji (2006) showed that Si promoted the binding of heavy metal ions to the cell wall by deposited lignin.

3.3. As subcellular fractionation in the leaves

The As subcellular fractionation variations in the leaves treated with Chsi-NPs are shown in Fig. 3. After the Chsi-NPs treatment, the

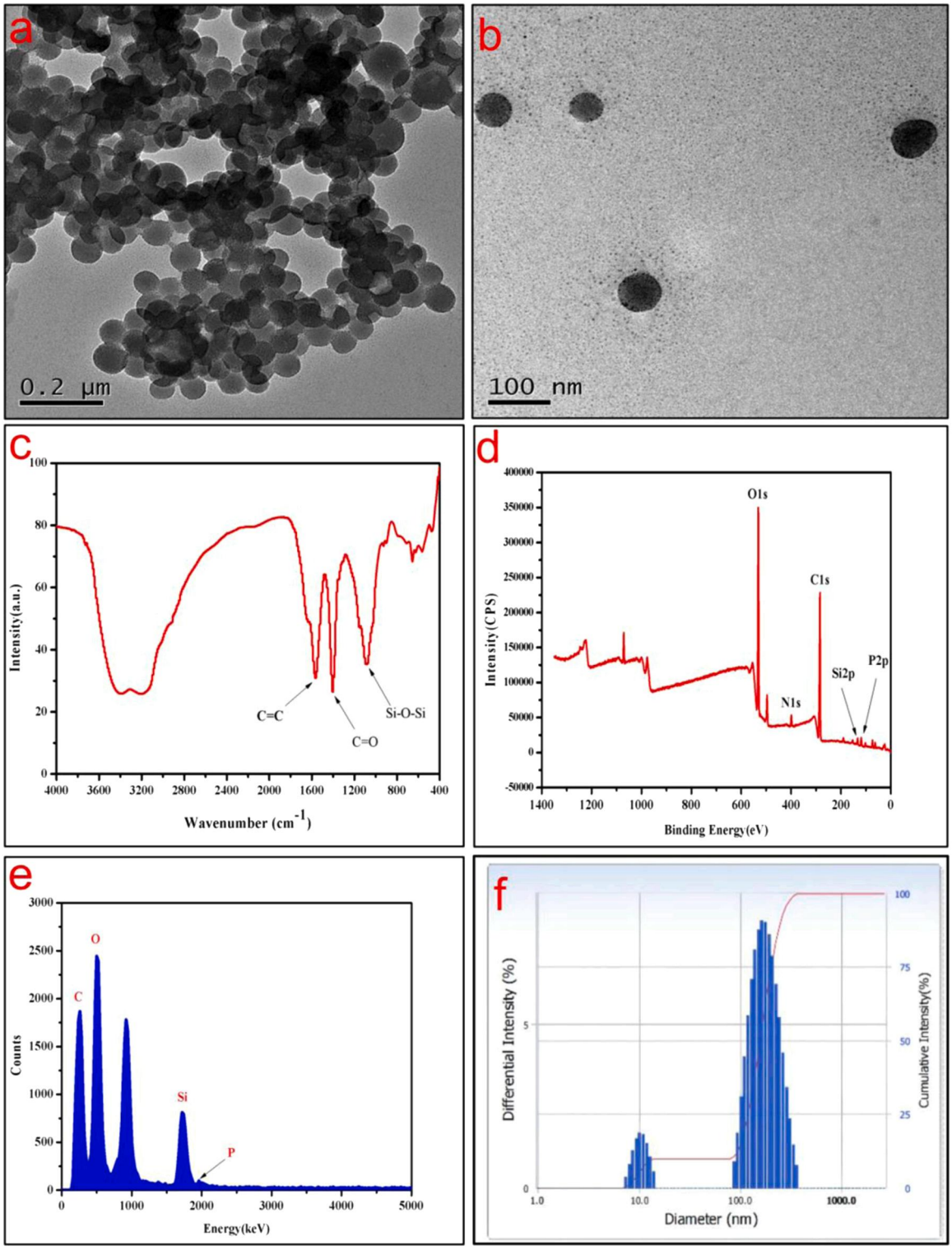

Fig. 1. Characterization of Chsi-NPs. a) and b) TEM images of Chsi-NPs, c) FTIR images, d) XPS patterns of Chsi-NPs, e) TEM–EDS images, and f) size of the nanoparticles.

proportion of As in the cell wall fraction (F1) of the leaves increased, whereas the proportion of As in the soluble fraction (F2) decreased relative to those of the CK. Specifically, F1 for the 3 mg·L-1 and 15 mg·L-1 Chsi-NPs treatments significantly ($P < 0.05$) increased by 5.7% and 8.7%, respectively. Conversely, F2 for the 3 mg·L^{-1} and 15 mg·L^{-1} Chsi-NPs treatments decreased by 2.7% and 3.4%, respectively, compared with the control. Thus, after the Chsi-NPs treatment, the F2 fractions were converted into F1 fractions, and As was retained in the cell wall and its movement in the leaves was inhibited. In addition, the percentage of As in the leaf cell wall significantly increased after the foliar Chsi-NPs treatment. Similarly, the thickness of the cell wall increased after the SiO_2 NP treatment (Cui et al., 2020). The possible reason was that the As in the cell wall was bound to aliphatic polyols and fromed As-O-C bonds.

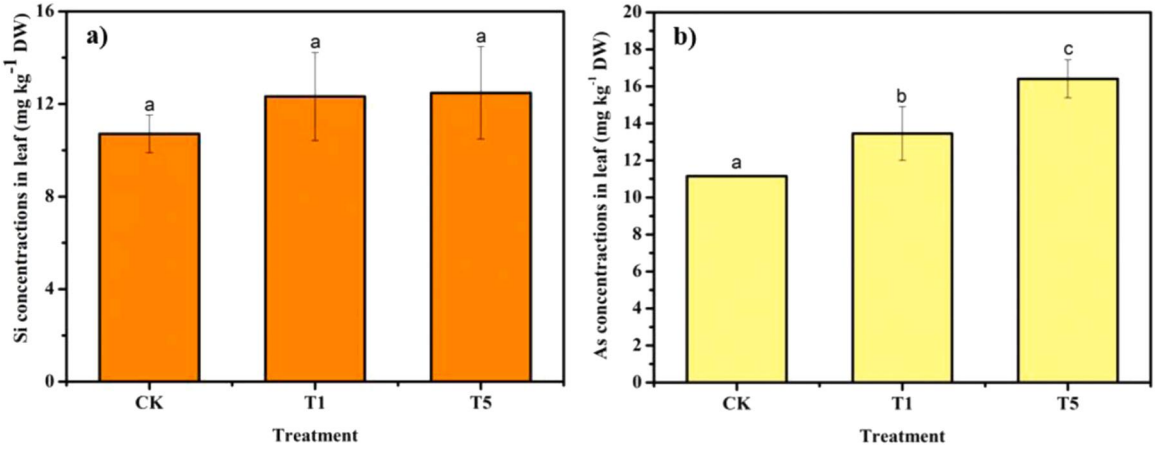

Fig. 2. Effects of foliar Chsi-NPs spraying on the leaves, a) concentration of Si in the leaves, b) concentration of As in the leaves.

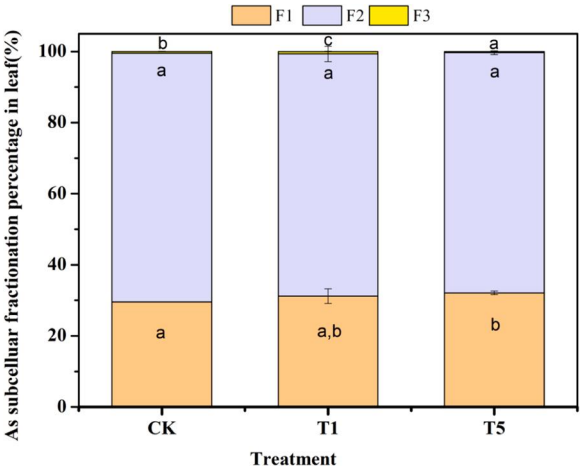

Fig. 3. Effects of foliar Chsi-NPs spraying on subcellular As distribution in the leaves (F1 is cell wall fraction, F2 is soluble fraction, and F3 is organelle containing fraction).

3.4. Change in the antioxidant enzyme systems in the leaves

The primary toxicity effects of metal or metalloids in the plants resulted in the injury of lipid peroxidation and a loss of the membrane integrity, which destroyed cell membrane lipids, proteins, enzymes, and other molecules (Tripathi et al., 2013). Fig. 4 shows the effects of the Chsi-NPs foliar treatment on the antioxidant enzyme systems in the leaves. Compared with CK, however, Chsi-NPs treatments had no any significant effect ($P > 0.05$) on the MDA, CAT and SOD. MDA is considered an important indicator of cell oxidative damage (Riaz et al., 2022). The MDA levels in the leaves subjected to the 3 mg·L^{-1} and 15 mg·L^{-1} Chsi-NPs foliar treatments were 13.5% and 18.4%, respectively, higher than those of the control (Fig. 4[c]). This indicated an accumulation of free radicals and reactive oxygen species (ROS) in the leaves.

SOD and CAT play important roles in ROS accumulation in leaves. First, excessive superoxide (O_2^-) can be converted to H_2O_2 by superoxide dismutase (Hussain et al., 2016). Then, CAT rapidly degrades H_2O_2 into H_2O and O_2 (Liu et al., 2014). We found that foliar Chsi-NPs treatment reduced the SOD activity in the leaves, and after the 3 mg·L^{-1} and 15 mg·L^{-1} foliar treatments, it decreased by 7.7% and 9.3%, respectively (Fig. 4[d]). The results indicated that the O_2^- content in the cells was converted into H_2O_2. Dynamic change in the SOD activity in the plants is closely related to O_2^- in cells (Hussain et al., 2016). However, we found that CAT activity after the 3 mg·L^{-1} and 15 mg·L^{-1} Chsi-NPs foliar treatments increased by 33.0% and 49.0%, respectively (Fig. 4[b]), indicating that when CAT mediated H_2O_2, the rate of the removal process in the leaves increased with As content.

GSH can chelate with As(III) in the vacuole and cytoplasm, thereby protecting plants (Mendoza-Cozatl et al., 2011). GSH activity after the 15 mg·L^{-1} Chsi-NPs foliar treatments significantly ($P < 0.05$) increased by 101.7% and 3 mg·L^{-1} Chsi-NPs foliar treatments increased ($P > 0.05$) by 99.0% (Fig. 4[a]). In the present study, the increase in the As content in the leaves after the foliar Chsi-NPs treatment was associated with the upregulation of GSH metabolism, showing potential as a foliar Chsi-NPs application strategy for improving the As tolerance of rice.

3.5. Changes in the As concentrations in the husk and rice

After foliar Chsi-NPs spraying, the concentration of As in the husk markedly increased (Fig. 5[a]), whereas the concentration of As in the grain markedly decreased (Fig. 5[b]). The 3 mg·L^{-1} treatments increased the concentration of As in the husk by 36.5% ($P > 0.05$) and the 15 mg·L^{-1} treatments significantly ($P < 0.05$) increased by 61.2%. Conversely, the 3 mg·L^{-1} and 15 mg·L^{-1} treatments significantly ($P < 0.05$) decreased the concentration of As in grain by 27.8% and 35.4%, respectively, relative to that of the control. In addition, the As concentrations of the husk and rice are shown in Fig. 5(c) and Fig. 5(d), respectively. After the 3 mg·L^{-1} and 15 mg·L^{-1} foliar Chsi-NPs spraying, the proportions of As(III) in the husk decreased by 8.6% and 11.3%, respectively, relative to the proportion in the control. However, the proportions of As(V) in the husk significantly increased by 8.1% and 8.8%, respectively. The ratio between the DMA and MMA in the husk slightly changed. The As fractions of the husk decreased in the order As (V) > As(III) > MMA > DMA. However, there was no significant difference in the different As species concentrations in the husk among different Chis-NPs treatments. The As fractions of the grain decreased in the order As(III) > As(V) > MMA > DMA. After the 3 mg·L^{-1} and 15 mg·L^{-1} foliar Chsi-NPs spraying, the proportions of As(III) in the grain significantly ($P < 0.05$) decreased by 10.1% and 20.0%, respectively. However, the proportions of As(V) in the grain significantly ($P < 0.05$) increased by 73.6% and 144.5%, respectively. The ratio of the DMA and MMA in the grain slightly changed and did not significantly ($P > 0.05$) change.

3.6. TEM analysis of the rice leaves

Fig. 6 shows the changes in the leaf ultrastructure and the subcellular level after Chsi-NPs foliar treatment. It can be seen from Fig. 6 that the cell wall in the leaves subjected to the foliar Chsi-NPs spraying thickened, and starch granules were deposited. After the Chsi-NPs treatments,

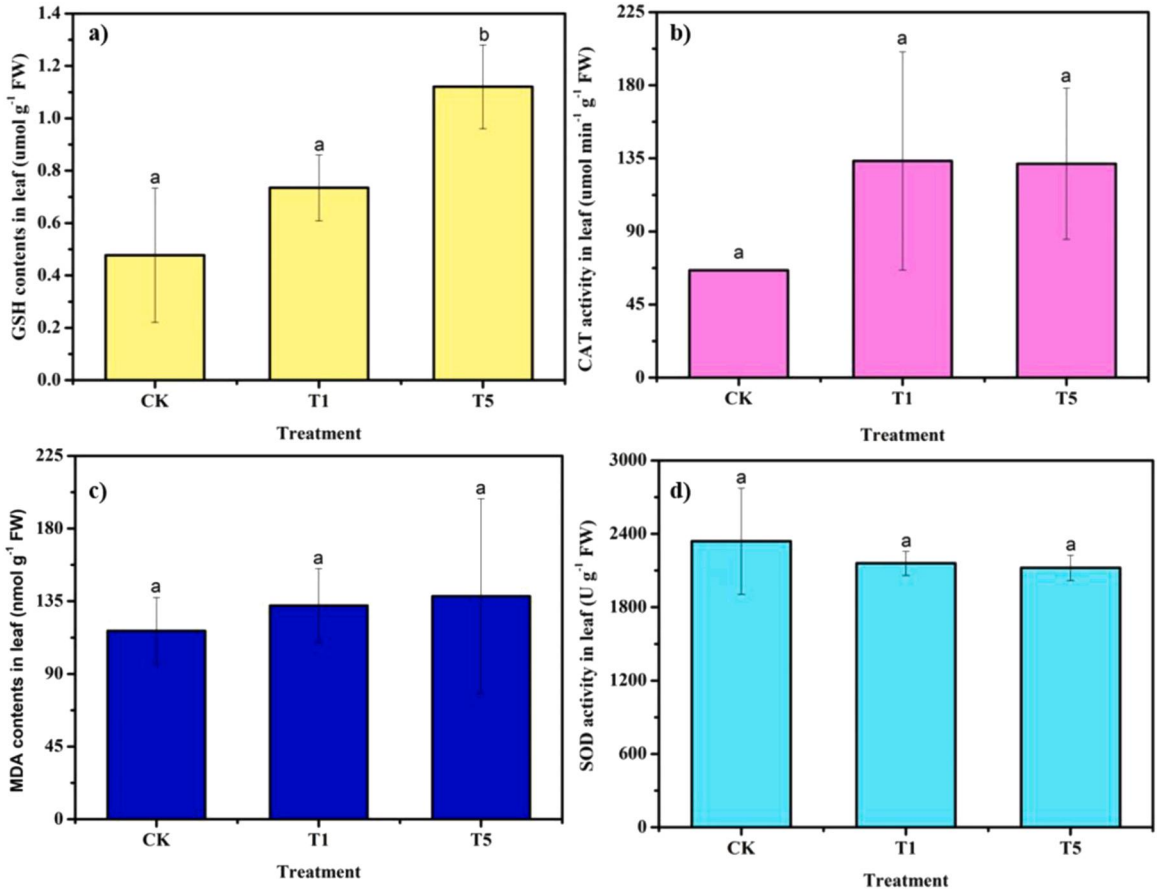

Fig. 4. Effect of the antioxidant enzyme system in the leaves: a) GSH content in the leaves, b) CAT activity in the leaves, c) MDA content in the leaves, and d) SOD activity in the leaves.

the cells were tightly arranged and had regular shapes, indicating that the Chsi-NPs reduced the As toxicity. In addition, it can be seen from Fig. 6[e] and Fig. 6[f] that the cytoplasm and the bottom of the cell wall of the rice leaves after the foliar Chsi-NPs spraying treatment have uneven granular substances that may have been induced by the Chsi-NPs. The results also indicated that the Chsi-NPs were distributed in the cells.

4. Discussion

As is a nonessential and toxic element in rice. It can severely inhibit plant growth and chlorosis in leaves (Zeng et al., 2016). Arsenite, comprising 63% of the total As in soil, is taken up by root cells and enters through OsLsi1 and then OsLsi2 for upward transporting to the shoots and grain (Abedin et al., 2002; Li et al., 2009). It has been reported that over 90% of the AsIII entering the grain is transported by the phloem (Carey et al., 2010). In this research, the foliar Chsi-NPs treatment improved the concentration of Si and As in the leaves (Fig. 2[a], Fig. 2 [b]). In addition, we observed that the As percentage in the leaf cell wall significantly increased after foliar Chsi-NPs treatment, and decreased in soluble fraction (Fig. 3). Similarly. Liu et al. (2014) found that over 50% of As was combined on the root cell walls of rice seedlings after foliar Si application. Omar et al. (2022) also found that Si was deposited in the cell walls by binding with hemicellulose and aliphatic polyols via Si-O-C bonds. Singh et al. (2016) also found that arsenite can bind with many functional groups in the cell walls of bacteria, such as the C–N group, the hydroxyl group, and alkanes. This demonstrates that As and Si are supposed to co-bind to the aliphatic polyols in the cell walls. We used TEM analysis to characterize the content in the leaves, and this indicated that the Chsi-NPs penetrated through the leaf cuticle or stoma on the leaf surface (Fig. 6). Wang et al. (2015) reported that nano-Si fertilizers can easily penetrate the leaf and build a thick silicated layer on the leaf surface. Hussain et al. (2020) also found that SiNP can enter the plant through the plant cell wall, depending on the type, and size of the nano-material. Cui et al. (2017) reported that the presence of SiNPs considerably improved the proportion of live cells to 95.4%, 78.6%, and 66.2% having sizes of 19 nm, 48 nm and 202 nm, respectively. In addition, we conducted FTIR analysis of the Chsi-NPs to obtain more information regarding the important functional groups, and we found C═C (1566.04 cm^{-1}), C═O (1550 cm^{-1}), and Si-O-Si (1091.66 cm^{-1}) stretching vibration peaks (Fig. 1[c]). These represented that the plant cell wall increased the carboxyl and pectin molecules for the adsorption of As after foliar application. Previous studies have found that stomata on the leaf surface have sizes in the tens of microns (e.g., 5 × 13 μm on spinach leaves and 16 × 6 μm on lettuce leaves) (Larue et al., 2014; Zhao et al., 2017). In our study, the average size of the Chsi-NPs was 166 nm (Fig. 1[f]), and the Chsi-NPs were deposited on the leaf surface and penetrated through the leaf cuticle or stoma. Chsi-NPs were then transported within the plants via the xylem and phloem.

The re-translocation of As from flag leaves to the rice grain during grain filling is an important process. At the filling stage, the node plays a vitally important role in controlling As transport to the leaf and grain (Yamaji and Ma, 2017). After the anthesis, the expressions of OsLsi6, OsLsi2, and OsLsi3 were simultaneously reactivated, and the As in the flag leaf and other portions of the rice plant was transported to the grain (Yamaji et al., 2015). Zheng et al. (2011) reported that the nodes of rice distributed 40% of the As received to the closest leaf, and then a significant amount of As in the leaf was re-translocated to the grain. In this study, we observed that foliar Chsi-NPs treatment improved the concentration of As in the husk (Fig. 5[a]) and reduced the concentration of As in the grain (Fig. 5[b]). Pan et al. (2020) found that the OsLsi6 and

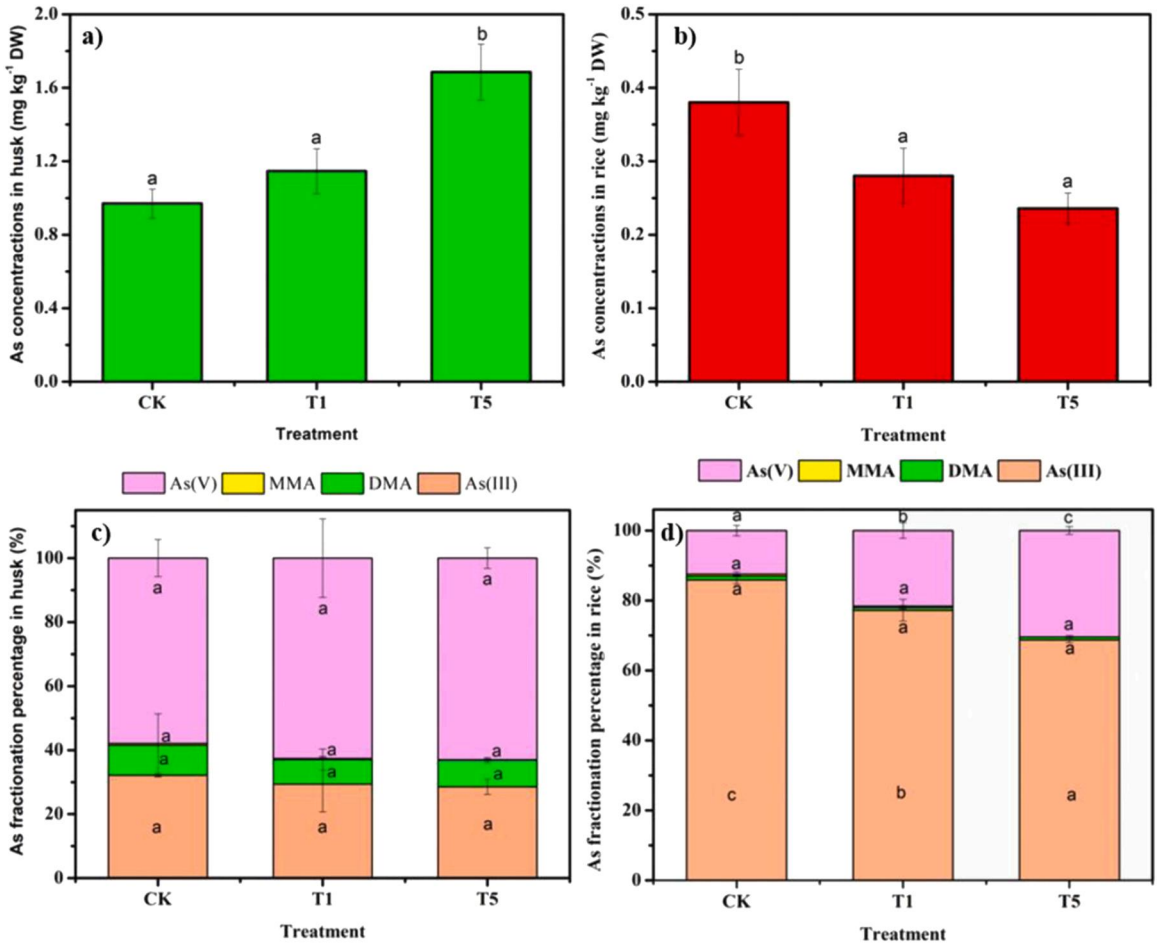

Fig. 5. Effects of foliar Chsi-NPs: content of As in the husk (a) and grain (b), chemical forms of As in the husk (c) and grain (d).

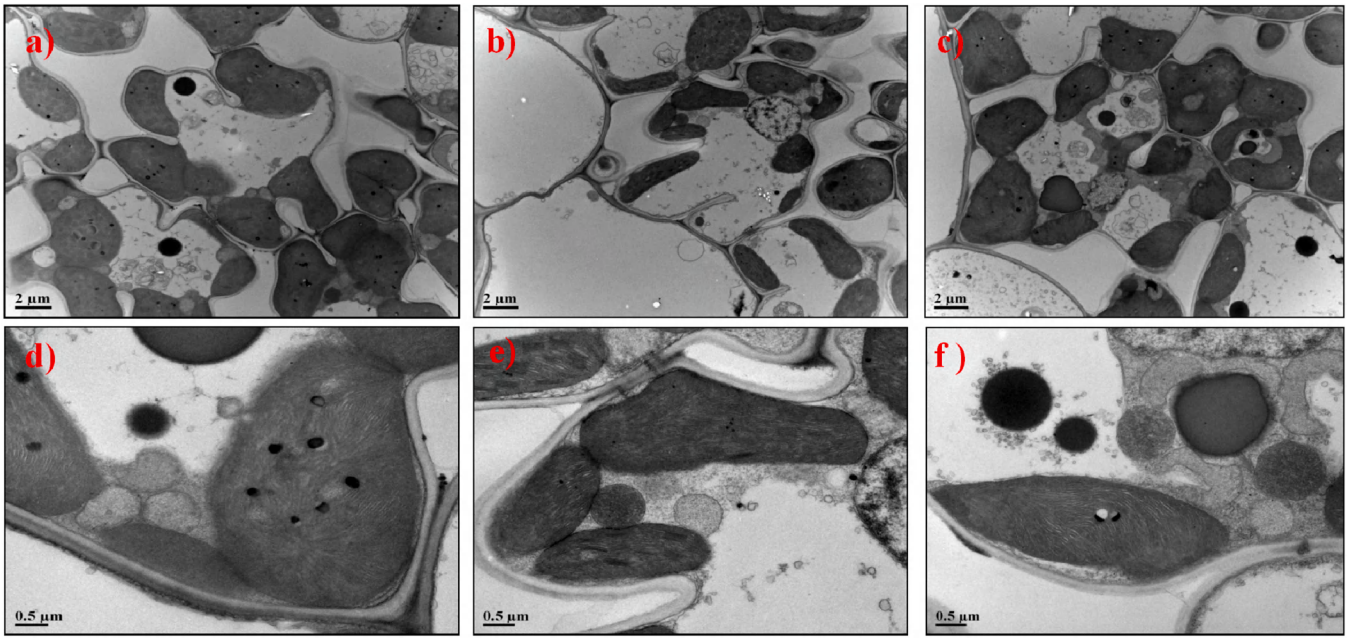

Fig. 6. TEM analysis on rice leaves, a) and d) is CK, b) and e) is T1 (3 mg·L^{-1} Chsi-NPs), c) and f) is T5 (15 mg·L^{-1} Chsi-NPs).

OsABCC1 overexpression in husks may increase the transport of arsenite in the husks, and the downregulation of OsLsi2, OsLsi3 and OsLsi6 gene expression in the nodes can reduce As transport from the nodes to the panicles.

Metal or metalloids resulted in the injury of lipid peroxidation in the plants(Tripathi et al., 2013). Lipid peroxidation (MDA) is considered to

be an important indicator of cell oxidative damage and lipid peroxidation under oxidative stress, which is related to ROS (Jung et al., 2019; Riaz et al., 2022). In the present study, the MDA content in the leaves increased after foliar Chsi-NPs treatment (Fig. 5[c]), indicating the accumulation of free radicals and ROS in the leaves. This effect could have been due to As accumulation in the leaves after foliar Chsi-NPs treatment. Some research has showen that the MDA content increased with an increase in the As concentration (Shri et al., 2009). Generally speaking, decreased MDA levels represent inhibition of oxidative stress; for example, ZnO NPs decrease MDA and alleviate chilling stress in rice (Song et al., 2021). Silicon alleviates cadmium and Zn toxicity in rice, decreases MDA, and scavenges ROS (Huang et al., 2018). Despite the increase of MDA, the Chsi-NPs treatment seemed to reduce oxidative stress and thus protect cells. SOD and CAT play important roles in ROS accumulation in the leaves. First, excessive superoxide (O_2^-) can be converted to H_2O_2 by superoxide dismutase (Hussain et al., 2016). Then, CAT rapidly degrades H_2O_2 into H_2O and O_2 (Liu et al., 2014). We found that foliar Chsi-NPs treatment reduced the SOD activity in the leaves (Fig. 5[d]). The results indicated that the O_2^- content in the cells was converted into H_2O_2. Dynamic change in the SOD activity in plants is closely related to O_2^- in cells (Hussain et al., 2016). The reason for this phenomenon may be due to the elevated GSH (Fig. 5[a]) that prevents ROS, such as $O_2^{\bullet-}$ and the H_2O_2 content, from damaging the vital cellular components. Ha-il Jung found that under 15 μM of $NaAsO_2$ stress, the exogenous addition of GSH resulted in a decrease of SOD in leaves (Jung et al., 2019). We found that CAT activity was increased by foliar Chsi-NPs treatment (Fig. 5[b]), indicating that when CAT mediated H_2O_2, the rate of the removal process in the leaves increased with As content. CAT is considered to be an alkaline enzyme and an integral part of the ROS detoxification system that removes H_2O_2 from cells by converting H_2O_2 into H_2O and O_2 (Geng et al., 2018). In a similar study on rice, Geng et al. (2018) reported increased CAT activity after the addition of Si under As stress. In addition, chitosan oligomers induce oxidative bursts through gene expression network between the nucleus and chloroplasts (Chamnanmanoontham et al., 2015). Some research data have suggested that chitosan can increase CAT content in maize (Rabelo et al., 2019). GSH as an important antioxidant in the non-enzymatic defense system, plays an important role in redox signal transduction and plant growth (Noctor et al., 2012). It can protect plants from oxidative stress by changing the content of the sulfhydryl group and the disulfide bond complex of the membrane protein (Liu et al., 2010). GSH plays a vital role in As biotransformation and migration. It is used as a reductant to reduce As(V) into As(III) (Geng et al., 2018). In addition, GSH is the precursor molecule of phytochelatins (PCs) that have a high affinity to chelate metals and thus attenuates As migration (Das et al., 2018). GSH can chelate with As(III) in the vacuole and cytoplasm, thereby protecting plants (Mendoza-Cozatl et al., 2011). In our study, the increase in the As content in the leaves after foliar Chsi-NPs treatment was associated with the upregulation of GSH metabolism, showing potential as a foliar Chsi-NPs application strategy for improving the As tolerance of rice.

These studies were similar to the experimental phenomena in the above-mentioned studies, implying that gene expression in the node played an important role in the re-translocation of As from the flag leaves to the rice grain. The mechanism of foliar Chsi-NPs spraying may be that it transforms highly mobile inorganic- and water-soluble Cd into insoluble pectate and protein-integrated As and further inhibits As transport to the grain. It also may affect the expression of As-related genes in the node, rice, and leaf, which requires further in-depth study. However, foliar spraying of Chsi-Nps has shown a good application prospect.

In the recent years, the applications of foliage fertilizer in agriculture are being put forth. It is shown that nano fertilizers seem to boost rice yields more than conventional fertilizers (Sadati Valojai et al., 2021). Zeng et al. (2021) applied foliar silicon fertilizer improve the quality of rice. Liu et al. (2014) found in field experiments that nanoscale silica foliar application promote the growth of rice. In addition, compared with the application of silicon fertilizer in soil, foliar fertilization can be used a small number of times to increase the absorption of fertilizer by rice, and it can be applied at different growth stages of rice to avoid excess fertilizer waste. A reported that the production cost for raw and modified biochar range from 0.56 USD/kg to 5.492 USD/kg (Cai et al., 2021). However, In our study, the production cost of Chsi-NPs, considering the expenses for chemicals required, is approximately 0.73 USD/L. Similiay, Silva et al. (2021) shown that As a matrix of nanocomposites, chitosan is relatively low priced. Hence, chitosan nanomater as well as chitosan based nanocompositesare used in various applications. These provide reference and possibility for the application of Chsi-NPs in rice fields.

5. Conclusion

The current study demonstrated that Chsi-NPs foliar treatment can inhibit As accumulation in rice grown in As-contaminated soils, and 15 $mg{\cdot}L^{-1}$ was the optimum concentration at the filling stage. Foliar Chsi-NPs spraying reduced the As transport from the leaves to the rice. A high concentration of As accumulated in the leaves, possibly causing an increase in the MDA concentration. In addition, foliar Chsi-NPs spraying might have promoted cell wall fraction AS in the leaves, as demonstrated by the TEM results and the thickening of the cell wall. In addition, foliar Chsi-NPs treatment significantly increased the antioxidant enzyme systems in the leaves and consequently alleviated lipid peroxidation caused by As toxicity in the leaves. This study strongly suggested that foliar Chsi-NPs spraying can be used during the filling stage of rice grown on As-contaminated soils.

CRediT authorship contribution statement

Yang Jia-Yi: Conceptualization, Methodology, Project administration, Software, Investigation, Writing – original draft, Writing – review & editing. **Sun Meng-Qiang:** Conceptualization, Methodology, Project administration, Software, Investigation, Writing – original draft, Writing – review & editing. **Chen Zhi-Liang:** Conceptualization, Funding acquisition, Investigation, Writing – review & editing. **Xiao Yu-Tang:** Conceptualization, Methodology. **Wei Hang:** Methodology. **Zhang Jian-Qiang:** Data curation. **Huang Ling:** Writing – original draft. **Zou Qi** : Methodology.

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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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jhazmat.2022.128781.

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