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Environmental significance

Nano-enabled agriculture is providing solutions for sustainable agriculture. Herein, selenium (Se) nano-enabled agriculture was established to improve crop yield and quality. Se engineered nanomaterials (ENMs) could upregulate key genes, which were responsible for flower enlargement, cell separation, and expansion, resulting in increasing fruit diameter. Se ENMs could also promote the assimilation of C and N to improve the metabolism of amino acids and synthesizing beneficial substances. Accordingly, Se ENMs can not only increase yield but also improve the nutritional quality of cherry tomatoes. Therefore, these findings demonstrate the promising prospects of Se ENMs-enabled agriculture practices as a sustainable crop strategy.

Selenium nanomaterials induce flower enlargement and improve the nutritional quality of cherry tomatoes: pot and field experiment

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Abstract

Crop yield and quality must be improved to meet the rapid growth of the population. In this work, both pot and field experiments demonstrated that soil application of selenium engineered nanomaterials (Se ENMs, 75 μg·kg^{-1}) could increase the yield and quality of cherry tomatoes. The yield of cherry tomatoes increased by 45.1%, 59.5%, and 78.5% after the application of Se ENMs (75 μg·kg^{-1}) on the 70th, 80th, and 90th days, respectively. Moreover, Se ENMs could upregulate key genes (e.g., *SlcodA, SlCDKA1*, *SlIAA9,* and *SlCTD1*), which were responsible for flower enlargement, cell separation, and expansion, all of which resulted in a 12.4% increase in fruit diameter. Non-targeted metabolism results suggest that Se ENMs could promote the assimilation of C and N in cherry tomatoes fruits by improving the metabolism of amino acids and synthesizing beneficial substances (e.g., ascorbic acid, glutathione, and flavonoids). Also, the macro-nutrients (e.g., Mg, P, K, and Ca) increased by 45.4%, 5.6%, 6.3%, and 64.3%, and micro-nutrients (e.g., Fe, Mn, and Se) increased by 55.5%, 67.1%, and 333.5% after Se ENMs exposure, respectively. As a result, Se ENMs can not only increase yield but also improve the nutritional quality of cherry tomatoes. Field experiment results showed that Se ENMs increased the yield by 176.9% compared with control, with a higher bioavailability and economic profit than selenite (SeO_3^{2-}). Furthermore, the metabolic and nutrient results were consistent with the pot experiment. Therefore, these findings demonstrate the promising prospects of Se ENMs-enabled agriculture practices as a sustainable crop strategy.

Keywords: engineered nanomaterials; metabolism; yield; nutritional quality; sustainable crop strategy

Introduction

Nanotechnology has piqued the public interest as a viable crop production strategy.[1–3] Improving nutritional status, enhancing resistance, and regulating gene expression in plants could be achieved by engineered nanomaterials (ENMs).[4–6] Besides, nanoscale agrochemicals are typically 20-30% more effective than conventional products in agricultural applications. [7]

Tomatoes (*Solanum lycopersicum* L.) are one of the most widely consumed economic crops, and global tomato production reached 180.8 million tons in 2019.[8,9] As a functional food, it contains various compounds, including amino acids, carotenoids (lycopene), vitamin E, phenols, flavonoids, and ascorbic acid, which are very important for human health.[10,11] However, the growth rate of tomato production is slowing down from 2013 to 2019,[9] which cannot meet the demand of rapid population growth.[12] Therefore, new technologies or strategies are urgently needed to address the current situation of weak production.

The yield of tomato fruit depends largely on the flower formation at harvest.[13] Because the fertilized flower ovary is unlikely to shrink and a large ovary can store more resources (e.g., carbohydrates, proteins, and minerals), a large flower tends to form a large fruit.[14] *Park et al.* demonstrated that the *codA* gene expression could result in tomato flower enlargement and was mainly involved in regulating the cell division.[15] On the other hand, good photosynthesis can provide sufficient nutrients to the developing fruit through the ovary, which is essential for the quality of fruit. [13] Therefore, the yield and quality of fruits are limited by flower formation and photosynthesis, and regulating them is of great importance to increase the yield and quality of tomatoes.

Numerous studies demonstrated that ENMs can act as nano-fertilizers, which has positive effects on regulating crop photosynthesis, physiological, and key genes for important processes.[12,16] *Faizan et al* found that ZnO ENMs (8 mg·L^{-1}) significantly increased photosynthesis and related pigments, as well as enhanced the carbonic anhydrase activity in tomato plants.[17] *Rawat et al* demonstrated that iron sulfide ENMs (4 mg·L^{-1}) could augment the growth and seed yield of *B. Juncea* due to activation of genes in the rubisco small subunit (*rubisco S*) and rubisco large subunit (*rubisco L*).[18]

SiO_2 ENMs (20 mg·L^{-1}) could improve photosynthesis, enhance sugar (C) and amino acid (N) metabolism to increase the resistance of pea to *Phelipanche aegyptiaca*.[19] Besides, selenium (Se) ENMs (0.5 mg·L^{-1}) could enhance the nutrient bioavailability to improve photosynthesis (16.7%) and up-regulate the expression of carbohydrate transport-related genes (*BnSUC1,1*, *BnSUC1,4*, and *BnSWEET10,2*) in *Brassica chinensis* L.[4] Se, as a functional element, plays a critical role in human health because of its antioxidation and anticarcinogenic effects as well as immune function.[20] Se ENMs-enabled agriculture strategies have gained much attention due to their high surface activity and low toxicity compared with inorganic forms (selenate and selenite).[21] For example, Se ENMs improved the yield and quality of cherry radish by regulating cambium activity and genes involved in carbon (C), nitrogen (N) assimilation.[6] Therefore, herein, we hypothesized that soil application of Se ENMs could regulate the photosynthesis, and gene expression involved in the flower formation of cherry tomatoes to improve the yield and nutritional quality.

In the present study, different concentrations (0, 25, 50, and 75 μg·kg^{-1}) of Se ENMs and an equivalent Se fertilizer (selenite, SeO_3^{2-}, 75 μg·kg^{-1}) were used to study the response of cherry tomatoes yield and quality upon root exposure. Therefore, the following aspects would be explored; (1) the response of photosynthesis and flower of cherry tomatoes upon Se ENMs; (2) the regulatory mechanisms of Se ENMs to improve cherry tomatoes yield and quality; (3) the practical effects of Se ENMs-enabled nano-agriculture through field experiment. These findings from this study will provide more information on potential applications of Se ENMs in agriculture and the production of Se-enriched products.

Materials and methods

Synthesis and characteristic of Se ENMs

The mixture of 0.11 g selenium dioxide (SeO_2, AR), 0.36 g ascorbic, and 47 mg surfactant-polyvinylpyrrolidone (PVP) was ground thoroughly to a red paste at 20 ℃, then Se ENMs were obtained by freeze-drying. The size and morphology of prepared Se ENMs were observed by transmission electron microscope (TEM, JEM–2100, Nippon Electronics Co, JPN, operating with an acceleration voltage of 200 kV).

Greenhouse study and field experiments

The seeds of cherry tomato (*Lycopersicon esculentum var. cerasiforme*) was obtained from the Shandong Academy of agricultural sciences. Cherry tomato seeds (Hong Meiyu F1, fruit oval and strong resistance to stress) were sterilized with sodium hypochlorite (5%) for 10 min and washed three times with deionized water. The seeds were germinated in plastic containers (15 × 15 × 20 cm), which were filled with 5 kg soil (pH 7.6, more details in supplementary table S1). 200 ml of different concentrations (0, 25, 50, 75 μg·kg^{-1}, and SeO_3^{2-} (75 μg·kg^{-1})) were irrigated into different treatment containers. Photosynthetic parameters including net photosynthetic rate (Pn), intracellular CO_2 concentrations (Ci), transpiration rate (E), stomatal conductance (Gs), and the relative chlorophyll content (SPAD) were measured by using a CIRAS–3 portable gas exchange system (CIRAS–3, PP-Systems, USA) and a Chlorophyll Meter (SPAD–502 plus, Konica Minolta Inc., Japan) on the 30th, 50th, and 70th days, respectively. The number of flowers was measured on the 30th, 50th, and 70th days. The number of fruit and yield were measured on the 70th, 80th, and 90th days.

The field experiments were carried out in the Mashan (31° 52' N and 120° 13' E, Wuxi City, China). Cherry tomato seedlings were transplanted to experimental areas (1.2 × 2 m) where they were exposed to different concentrations of Se ENMs (0 and 75 μg·kg^{-1}) and 75 μg·kg^{-1} SeO_3^{2-} (See text S1 for calculation methods). Each treatment had six replicates and final sampling was done on the 70th, 80th, and 90th days.

Metabolite analysis in cherry tomato

Non-target metabolites were accomplished by UPLC–ESI–QE (Thermo Scientific UPLC Vanquish, USA). Fresh fruit (100 mg) was ground thoroughly with liquid nitrogen and transferred into a 2 ml centrifuge tube. The samples were extracted with 1.5 mL of 80% methanol (containing 0.1% formic acid) and vortexed blend at 3000 rpm. The mixed samples were then sonicated (35 kHz) for 30 min in an ice bath and centrifuged at 12000 rpm for 15 min at 4°C. The supernatant (1 mL) was added to a glass sampling vial and vacuum-freeze-dried at room temperature. The freeze-dried samples were diluted by 300 μL of methanol/acetonitrile/water (v/v/v = 2:2:1), vortexed 60 s, and then centrifuged at 12000 rpm for 10 min at 4 °C. The supernatant (200 μL)

was analyzed by using UPLC–ESI–QE. 2-Chloro-L-phenylalanine (50 μg·L^{-1}, dissolved in methanol) was used as the internal standard. Quality control (QC) sample was prepared by mixing aliquots of all samples to obtain a pooled sample (three replicates). Details were presented on supporting information (Text S2 and Table S2).

ICP–MS analysis for elements content

Sample processing was according to the previous study.[5] Briefly, the dried cherry tomato samples were digested by using a microwave accelerated reaction system (CEM Corp, Matthews. NC) with a mixture of plasm pure HNO_3 and ultrapure water (v/v = 4:3). The digested solution was filtered (micro-membrane, 0.22 μm), and diluted to 50 ml for inductively coupled plasma mass spectrometry (ICP–MS, iCAP–TQ, Thermo-Fisher, Germany) analysis. For quality control (QC) and quality assurance (QA), the standard reference material (GBW 07602, Bush twigs and leaves purchased from Nanjing Alida Biotechnology Co., LTD, China) was digested and measured using the same procedures. The recoveries of all elements were between 80.7 and 103.6%.

Real-time quantitative PCR (RT–PCR) analysis

8 key genes (Table S3) were confirmed to be involved in responding to Se ENMs treatment by using the RT–PCR method. Briefly, the total RNA and DNA templates were prepared as previous description.[22] RT–PCR reaction was performed on a CFX96™ real-time system (BIO-RAD, Bio-Rad Laboratories, Inc., USA) by using SYBR Mixture (CWBIO, China). Relative expression of the different gene was normalized by comparing with the control expression and calculated using the $2^{-\Delta\Delta Ct}$ method.

Statistics analysis

The variation among different treatments was analyzed by using a one-way ANOVA with the Fisher LSD test (Origin Statistics 2019b, $p < 0.05$). All data were presented as the mean ± standard deviation. All treatments were performed at least three triplicates. The methods of observation of the ovary wall, dissolution experiment, carbohydrate measurement, measurement of chlorophyll a and chlorophyll b, observation of pollen vigor, and economic comparation between Se ENMs and SeO_3^{2-} application were described in the supplementary text S3–S8.

Results and discussion

Uptake and translocation of Se ENMs

As shown in Fig. 1a and S1, resultant Se ENMs were dispersed well with uniform size (37.6 ± 9.6 nm). Fig. 1b shows that the release of Se ENMs reached a plateau state after 12 h exposures in soil solution, and the rate of SeO_3^{2-} release from Se ENMs was less than 1‰, which indicated that prepared Se ENMs were extremely stable in soil solution. In the present study, PVP was used as a surfactant to coat Se ENMs during the synthesis process, which could improve the stability of ENMs.[23] Previous studies have shown that ENMs could be taken up by plant roots and translocated to shoots.[24,25] For instance, CuO ENMs (43 ± 9 nm, 100 mg·L^{-1}) could transport from rice roots to shoots.[25] CeO_2 ENMs (30–50 nm, 5 mg·L^{-1}) could be taken up and transported to shoots through root exposure.[26] Therefore, Se ENMs (37.6 ± 9.6 nm) have the potential for uptake and translocation by plants. The Se content in cherry tomato shoots increased in all treatments, and those treated with Se ENMs (25, 50 and 75 μg·kg^{-1}) and SeO_3^{2-} (75 μg·kg^{-1}) increased by 68.7%, 64.2%, 414.2%, and 38.9%, respectively (Fig 1c). In addition, the Se content in the roots of the Se ENMs (25 and 50 μg·kg^{-1}) treatment groups was not significantly different from that of the CK-treated group, while the Se ENMs (75 μg·kg^{-1}) treatment group increased by 117.3% (Fig. 1c). These results showed that SeO_3^{2-} tended to accumulate in the roots, while Se ENMs could translocate to the shoots. It has been reported that the Se can share transporters with sulfur (S) and be absorbed and transported by plants.[27] In the present study, the expression of sulfur transporter was up-regulated by 104.9% under Se ENMs (75 μg·kg^{-1}) exposure, while SeO_3^{2-} was only up-regulated by 56.9% (Fig. 1d). Moreover, the S content in cherry tomatoes root was decreased significantly upon Se ENMs and SeO_3^{2-} (Fig. S2). These results demonstrated that the bioavailability of Se ENMs in plants might be higher than that of SeO_3^{2-}, and there is competition between S and Se. [27] As a result, as-prepared Se ENMs were stable in soil and could be taken up by cherry tomato root and transported from roots to shoots, which was more effective than SeO_3^{2-} application.

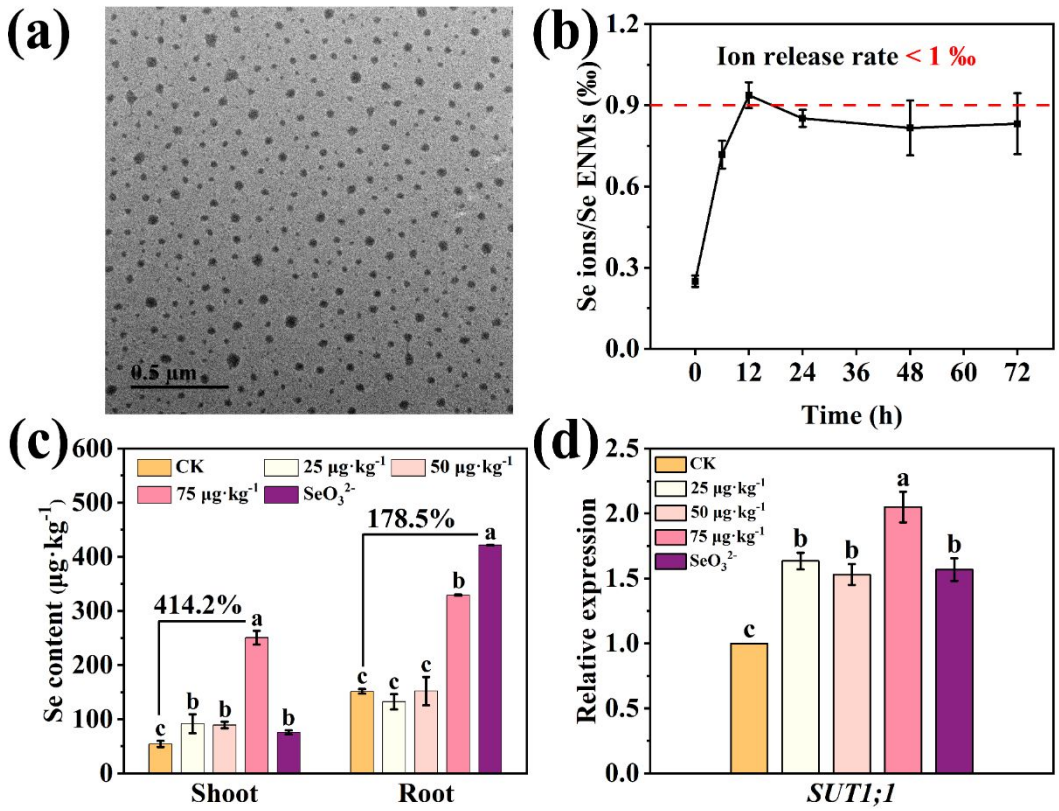

Fig. 1 Uptake and translocation of Se ENMs (25, 50, and 75 μg·kg^{-1}) and SeO_3^{2-} (75 μg·kg^{-1}) by cherry tomatoes plant. (a) TEM image of Se ENMs; (b) Ion release rate of Se ENMs in soil solution; (c) Se content in cherry tomato shoots and roots between Se ENMs and SeO_3^{2-} treatment group; (d) Relative expression of sulfate transporter in cherry tomato roots.

Physiological response of cherry tomato plant to Se ENMs

Fig. 2a and Fig. S3a present representative images of cherry tomato plants for the Se treatments on the 20th and 30th days after planting. The images show that the growth of cherry tomatoes was promoted by Se treatments (ENMs and SeO_3^{2-}) compared with CK. Photosynthesis is an important process for plant growth and metabolism.[28] Previous studies demonstrated that ENMs could regulate photosynthesis to improve plant growth and metabolism.[29,30] For example, Fe-based ENMs (Fe and Fe_3O_4, 3.75 mg/per plant) significantly increased net photosynthesis rate (Pn) by 19.9% and 27.5%, respectively; and induced metabolic reprogramming in maize leaves.[29] Mn_3O_4 ENMs (1 mg/per plant) enhanced Pn in cucumber leaves by 12% and up-regulated the shikimate and phenylpropanoid metabolic pathways.[30] In this study, Pn of cherry

tomatoes on the 30th, 50th, and 70th days were enhanced under Se ENMs exposure, while no visible changes were observed under SeO_3^{2-} treated plants compared with CK (Fig. 2b). The optimal concentration for cherry tomatoes is 75 μg·kg^{-1} by Se ENMs, and Pn was increased by 18.2%, 29%, and 24.8% on the 30th, 50th, and 70th days (Fig. 2b). Besides, intracellular CO_2 concentrations (Ci), stomatal conductance (Gs), and transpiration rate (E) of cherry tomato leaves showed similar trends to Pn (Fig. S3b, S3c, and S3d). Chlorophylls are the core pigments driving photosynthesis, which could convert light energy into chemical energy.[31] Consequently, increasing the chlorophyll content in leaves can help to improve photosynthesis.[31] Chlorophyll a and b in cherry tomato leaves treated with Se ENMs increased by 126.3 and 79.5% compared with SeO_3^{2-} and CK, respectively (Fig. S4a). Magnesium (Mg), as a central element in chlorophyll, has a critical role in the synthesis of chlorophyll. Fig. S4b showed that the relative abundance of Mg in cherry tomato leaves was increased by treating Se ENMs and SeO_3^{2-}, with the best performance obtained for plants treated with 75 μg·kg^{-1} (368.9%). Besides, the photosynthetic beneficial elements in cherry tomato leaves (e. g., phosphorus (P), iron (Fe), manganese (Mn), and molybdenum (Mo)) were also increased 192.2, 501.3, 208.7 and 94.3% under the Se ENMs exposure (75 μg·kg^{-1}) , respectively (Fig. S4b). Therefore, Se ENMs (75 μg·kg^{-1}) could positively regulate the synthesis of chlorophyll and the uptake of photosynthetic beneficial elements to improve photosynthesis.

On the other hand, the yield of fruit is determined by flowering.[14] Therefore, the number of flowerings on the 30th, 50th, and 70th days of cherry tomato were analyzed, and the results showed that more flowering was produced under 75 μg·kg^{-1} of Se ENMs exposing than other treatments (25, 50 μg·kg^{-1} of Se ENMs and SeO_3^{2-}) (Fig. 2c). However, the fruit number of cherry tomatoes was not significantly increased by treatment with 75 μg·kg^{-1} of Se ENMs compared with other Se treatment groups on the 70th, 80th, and 90th days (Fig. 2d). Fruit formation depends on the stamens releasing the pollen grains to the stigma, where the pollen cells germinate and then complete the pollination and fertilization process within the ovules.[13] Our data showed that pollen vigor was not significantly increased with Se ENMs (75 μg·kg^{-1}) treatment (Fig. S5).

This may be the reason why the fruit number did not increase. Nevertheless, the yield of cherry tomatoes increased by 45.1%, 59.5%, and 78.5% on the 70th, 80th, and 90th days, respectively, through soil application of Se ENMs (75 μg·kg^{-1}), which was higher than that of Se ENMs and SeO_3^{2-} groups at 25, 50 μg·kg^{-1} (Fig. 2e). Therefore, soil application of Se ENMs (75 μg·kg^{-1}) could improve photosynthesis, promote flowering, and increase the yield of cherry tomatoes.

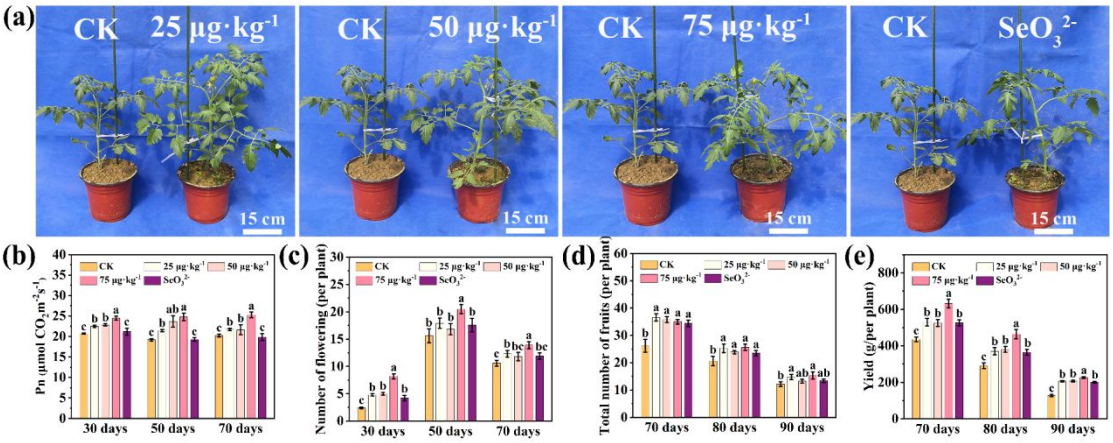

Fig. 2 Physiological responses of the cherry tomato plant to Se ENMs (25, 50, 75 μg·kg^{-1}) and SeO_3^{2-} (75 μg·kg^{-1}). (a) Seedling images of cherry tomatoes by treated Se ENMs and SeO_3^{2-} on the 20th days; (b) Pn of cherry tomatoes leaves upon different treatment group on the 30th, 50th, and 70th days, respectively; (c) Number of flowering by exposing Se ENMs and SeO_3^{2-} on the 30th, 50th, and 70th days, respectively; (d) Total number of cherry tomatoes fruits in different group on the 70th, 80th and 90th days, respectively; (e) Yield of cherry tomatoes by exposing Se ENMs and SeO_3^{2-} on the 70th, 80th, 90th days, respectively.

Mechanism of the increased cherry tomato yield by Se ENMs

The flower is an important organ for fruit formation and development.[32] In the present study, we found that the flowers of cherry tomatoes were larger than that of CK and SeO_3^{2-} under exposure to Se ENMs (75 μg·kg^{-1}) (Fig. 3a and Fig. S6). A published study showed that the *codA* gene was responsible for regulating the size of flowers.[15] As shown in Fig. 3b, the expression of the *SlcodA* gene was up-regulated by 3.8-fold upon Se ENMs exposure, while it was only up-regulated 1.8-fold by SeO_3^{2-} compared with CK. In addition, during the development process of the fruit, the key factor

(*SlCDKA1*) for cell division was up-regulated 2.5-fold by treated Se ENMs (Fig. 3c). It has been reported that down-regulation of *SlCDKA1* in tomato plants is likely to produce smaller fruits because of the thinner ovary wall and fewer cell layers.[33] The *WEE1* kinase can inhibit the phosphorylation of *CDKA*, which has a critical role in regulating the ovary cells and a thinner pericarp to determine fruit size.[33] More cell layers were found in the cherry tomatoes' ovary wall under Se ENMs treated (Fig. S7a). The expression of the *SlWEE1* gene was greater than in other treatments through exposing Se ENMs (Fig. 3d). Auxin is the most important hormone to regulate cell division and cell expansion during plant development.[34] In this study, the auxin synthesis gene (*SlIAA9*) and its response gene (*SlCTD1*) were up-regulated by 2.6-fold and 1.9-fold, respectively, with exposure to Se ENMs (Fig. 3e). Moreover, cell wall invertase (CWINV) is sucrose invertase primarily, mainly involved in sucrose decomposition during the phloem apoplectic unloading; this stabilizes the sucrose concentration gradient between the source-sink and regulates fruit development.[35] The expression of the *SlCWINV* gene was up-regulated by 2.1-fold under Se ENMs exposure (Fig. 3f). Therefore, at harvest, these genes regulate flower formation and fruit development, resulting in an increase (12.4%) in fruit diameter by Se ENMs (Fig. S7b and S7c).

On the other hand, it has been reported that large flowers can store more nutrients (e.g., carbohydrates, proteins, and minerals) for the developing fruit and get larger fruit at harvest.[14] *SUT* (Source transporter) gene is responsible for sugar transport and carbon distribution,[36] and was up-regulated 1.6-fold through exposure to Se ENMs and down-regulated (14.9%) by treated SeO_3^{2-} compared with CK (Fig. 3g). Therefore, under Se ENMs exposure, more carbohydrates were produced from the cherry tomato leaves (Fig. S8a) and transported into flowers and fruits (Fig. S8b) by the *SUT* overexpression (Fig. 3h). Meanwhile, key genes that regulated flower morphology (*SlcodA*), cell division and expansion (*SlCDKA1*, *SlWEE1*, *SlIAA9*, *SlCTD1*), and carbon allocation (*SlCWINV*, *SlSUT*) in the developing fruits were all up-regulated under the exposure of Se ENMs (Fig. 3h). Therefore, the relationship between source and sink is improved under the exposure of Se ENMs, and the yield is increased (Fig. 2e).

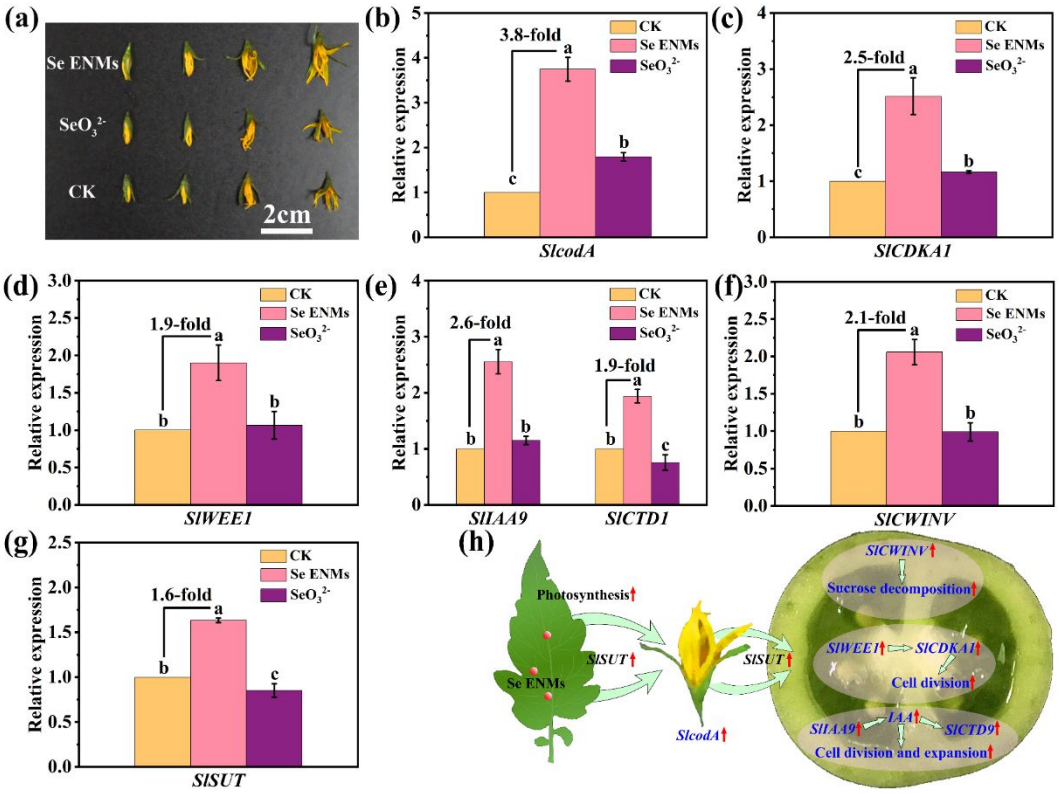

Fig. 3 Response of cherry tomatoes on the flower to Se ENMs (75 μg·kg^{-1}) and SeO_3^{2-} (75 μg·kg^{-1}). (a) Photo of cherry tomato flower; (b) Relative expression of *SlcodA* gene; (c) Relative expression of *SlCDKA1* gene; (d) Relative expression of *SlWEE1* gene; (e) Relative expression of *SlIAA9* and *SlCTD1* gene; (f) Relative expression of *SlCWINV* gene; (g) Relative expression of *SlSUT* gene; (h) Diagram of the mechanism that promotes swelling by Se ENMs.

Metabolism variation of cherry tomato fruit by exposing Se ENMs

Principal components analysis (PCA) showed the separation between Se ENMs, SeO_3^{2-}, and CK groups along with the first principal component, which accounted for 37.0% of the total variance (Fig. 4a). Therefore, the metabolism of cherry tomatoes was significantly influenced by Se ENMs. 72 different metabolites were detected in cherry tomato fruits, and the relative abundance of 50 metabolites was increased significantly in response to soil application of Se ENMs (Fig. S9), which could be divided into 15 classes (Fig. 4b). The amino acid, flavonoids, fatty acid and conjugates, and tricarboxylic acid (TCA) acid were occupied 30.4%, 13.0%, 8.7%, and 4.3% (Fig. 4b), respectively. These results demonstrated that the metabolism of cherry tomato fruits during the development process was significantly improved by foliar treating Se ENMs.

Pathway enrichment analysis showed that Se ENMs could improve the process of C (pentose phosphate pathway) and N metabolism (amino acid metabolism) (Fig. S10). C and N assimilation are important physiological activities in plant growth and development, while photosynthesis and amino acid metabolism are the main processes in C and N utilization.[37] As shown in Fig. 4c, the improved photosynthesis by Se ENMs fixed more CO_2, which produced more glucose for glycolysis to synthesize phenylalanine, tyrosine, and tryptophan, and these compounds were all also significantly increased by 1.5, 1.2, and 1.5-fold, respectively. They could serve as precursors for important secondary metabolites related to the antioxidant activity (e.g., alkaloids and flavonoids).[38,39] Serine, related to photosynthetic respiration, was significantly increased by 11.2-fold, upon exposure to Se ENMs (Fig. 4c). In addition, alanine (1.2-fold) and valine (2.1-fold) derived from pyruvate, were both significantly elevated by Se ENMs. Amino acids, such as aspartic acid (1.5-fold), lysine (1.3-fold), and isoleucine (1.3-fold) derived from the TCA cycle, were also elevated upon exposure to Se ENMs (Fig. 4c). Glutamic acid, glutamine, proline, and histidine derived from 2-oxoglutarate, were significantly increased by 1.8, 1.1, 2.5, and 1.7-fold, respectively, compared with CK (Fig. 4c). However, these amino acids had no significant changes or even decreased under SeO_3^{2-} exposure. Increasing amino acid levels indicated that Se ENMs could enhance the assimilation of C and N. Total C and total N content in cherry tomatoes leaf and fruit were significantly increased by 4.9%, 9.8%, 6.3%, and 14.9% respectively, compared with CK (Fig. S11). Therefore, the biochemical cycles of C and N could be accelerated by cherry tomatoes under Se ENMs application.

Besides, ascorbic acid, glutathione, and tomatidine were significantly increased by 3.0, 2.1, and 2.5-fold due to treating Se ENMs, respectively (Fig. S12), which played important roles in scavenging ROS and improving human immunity.[40,41] Flavonoids including luteolin, hesperetin, quercetin, eriodictyol, and kaempferol could serve as health-promoting metabolites[42,43] and be elevated 1.1, 1.2, 1.2, 1.8, and 1.6-fold by Se ENMs (Fig. S13). Plant hormones (IAA (3-Indole acetic acid), salicylic acid, and jasmonic acid) were increased (1.5, 1.4, and 1.6-fold) by exposing Se ENMs (Fig. S14).

IAA corresponds to the up-regulation of IAA synthesis genes (*SlIAA9*) could improve the fruit growth of cherry tomatoes. Salicylic and jasmonic acid are key hormones for plant defense against various stresses (e.g., salinity, drought).[44,45] Therefore, Se ENMs could improve C fixation and N metabolism to enhance the quality of cherry tomatoes.

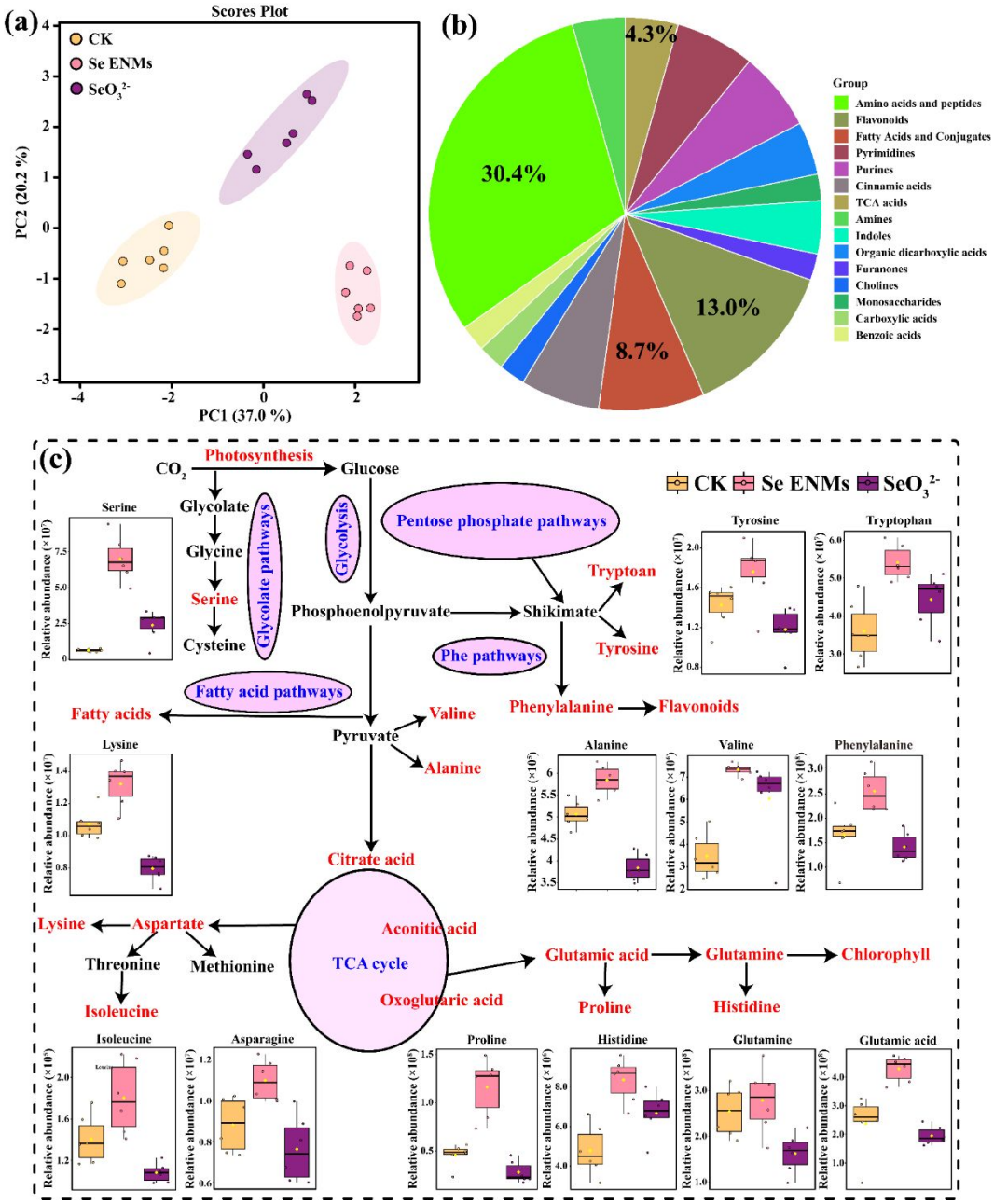

Fig. 4 Metabolism profiles were various cherry tomatoes fruit upon Se ENMs (75 μg·kg^{-1}) and SeO_3^{2-} (75 μg·kg^{-1}) exposure. (a) PCA analysis; (b) Classification of metabolites after treated Se ENMs and SeO_3^{2-}; (c) Changes in metabolism pathways of cherry tomato fruits under Se ENMs and SeO_3^{2-} treatment. Red fonts represent the increased relative abundance of substances, and blue fonts represent metabolic

pathways.

The macro-nutrients and micro-nutrients were significantly changed by treating Se ENMs (Fig. 5a and 5b). Mg, Fe and P were increased by 45.4%, 55.5%, and 5.6% under exposing Se ENMs compared with CK, respectively, which were positively correlated with photosynthesis. Besides, P is a critical macro-nutrient that is known to affect the stability of cell membranes.[13] Fe is involved in many physiological metabolic processes in the human body, such as oxygen transport.[46] Mg plays an important physiological role in the brain, heart, and skeletal muscles.[47] Moreover, calcium (Ca) and potassium (K) in tomato fruit were enhanced by 64.3% and 6.3%, respectively, by treatment with Se ENMs (Fig. 5a). Ca is involved in several aspects of life, such as muscle contraction, enzyme activation, cell differentiation, immune response, programmed cell death, and neuronal activity. [48] *He et al* reported that increasing K intake reduced cardiovascular disease mortality.[49] Mn was increased by 67.1% upon Se ENMs exposure (Fig. 5a). The recommended dietary allowance of Mn was 1.8 and 2.3 mg per day for healthy adult women and men, respectively.[50] Se has a critical role in human health due to its antioxidation and anticarcinogenic effects.[20] As shown in Fig. 5b, Se was increased by 333.5% through soil application Se ENMs (Fig. 5b), while under SeO_3^{2-} treatment was only increased by 103.3%. This result indicated that the bioavailability of Se ENMs was better than SeO_3^{2-}. Moreover, there were no significant differences in the content of S, copper (Cu), zinc (Zn), or Mo in fruits among the treatment groups. Overall, these results demonstrated that soil application of Se ENMs could significantly improve the nutritional quality of cherry tomatoes.

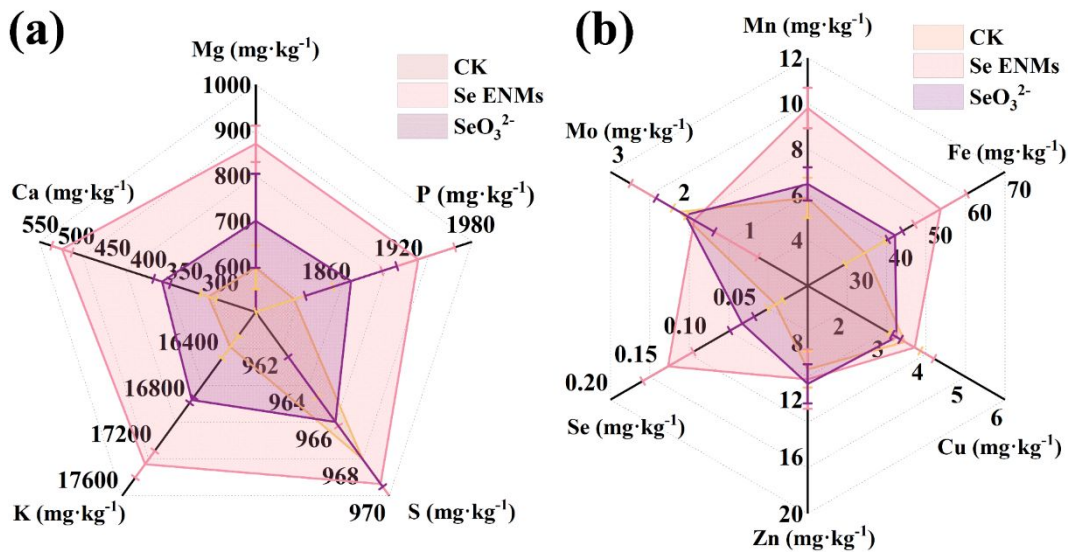

Fig. 5 The concentration of (a) macronutrients and (b) micronutrients in cherry tomatoes fruit by treated Se ENMs (75 μg·kg^{-1}) and SeO_3^{2-} (75 μg·kg^{-1}).

Response of cherry tomatoes to Se ENMs in field experiment

As shown in Fig. S15a, the field experiment was carried out at Wuxi (latitude 31° 52' N and longitude 120° 13' E). The total yield of cherry tomato plants with soil application of Se ENMs (75 μg·kg^{-1}) increased by 176.9% compared with CK, whereas the SeO_3^{2-} (75 μg·kg^{-1}) treatment increased by 53.8% (Fig. 6a), and the fruit diameter by Se ENMs exposing was larger than with SeO_3^{2-} and CK (Fig. S15b). This result demonstrated that Se ENMs can increase the crop yield more efficiently than SeO_3^{2-}. Moreover, Se ENMs-enabled agriculture could increase the economic benefits of agricultural production. A $66.6 per hectare investment in soil application of Se ENMs to cherry tomatoes could result in an estimated $3774.8 increase in economic return based on the increased yield (176.9%), while application of Se fertilizers could only increase to $1148.0 per hectare (Supplementary text S7). Additionally, the Se enrichment effect of the cherry tomato fruits under the Se ENMs treated was greater (110.8%) than that of SeO_3^{2-} (27.1%) (Fig. 6b). According to China's Dietary Guidelines, the daily consumption of cherry tomatoes should be 150–200 g, implying that 17.6–23.4 μg of Se could be taken from cherry tomatoes if such an amount of Se-enriched tomatoes could be consumed.

Total C and N content in cherry tomatoes fruit were improved by 7.4% and 13.6%,

respectively (Fig. 6c), which may be induced by the accelerated C and N metabolism upon the exposure to Se ENMs. The non-targeted metabolism in the field experiment was significantly influenced by Se ENMs (Fig. S16a). The results indicated that Se ENMs primarily improved the amino acid metabolic process in the field experiment, which was consistent with the results of the pot experiment (Fig. S16b). As shown in Fig. 6d and Fig. S17, 13 amino acids were detected, and the relative abundance of 12 amino acids increased significantly by Se ENMs exposing, while there was no significant increase under SeO_3^{2-} exposing, compared with CK. In addition, macronutrients and micronutrients were stored in cherry tomatoes fruit with the same results as in the pot experiment (Fig. S18). Carbohydrate content in cherry tomato fruits was also improved by 64.1% under Se ENMs exposure (Fig. S19). These results of field experiments showed that Se ENMs have the potential to improve the yield and nutritional quality of cherry tomato fruit, mainly by promoting fruit expansion, amino acid synthesis, and nutrient absorption.

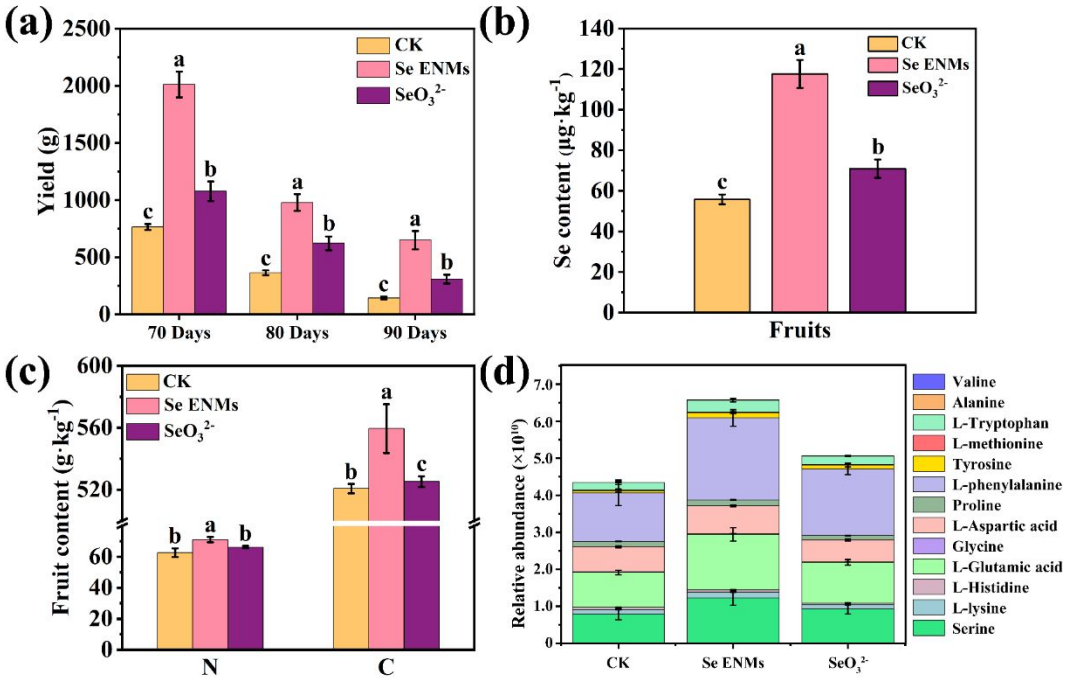

Fig. 6 Response of cherry tomatoes to Se ENMs (75 μg·kg^{-1}) and SeO_3^{2-} (75 μg·kg^{-1}) in the field experiment. (a) Yield of cherry tomatoes upon Se ENMs and SeO_3^{2-} exposure in field; (b) Se content in cherry tomato fruits by treated Se ENMs and SeO_3^{2-}; (c) Total C and N content in cherry tomato fruits; (d) Relative abundance of amino acids

under Se ENMs and SeO_3^{2-} treatment in field experiment.

Conclusions

In the present study, Se ENMs significantly improved the yield and nutritional quality of cherry tomatoes in both pot and field experiments, and had higher bioavailability than the ones treated with SeO_3^{2-}. Se ENMs can maintain stability in soil due to the surface coating of PVP, and be absorbed and transported to the shoot by cherry tomatoes. Se ENMs can promote photosynthesis by regulating the synthesis of pigments, and accelerate the carbohydrate accumulation and transportation in the shoots by regulating *SlSUT* gene expression. Meanwhile, key genes (*SlcodA*) that regulate flower enlargement, cell division and expansion (*SlCDKA1*, *SlWEE1*, *SlIAA9*, *SlCTD1*), and key genes for carbon allocation (*SlCWINV*, *SlSUT*) were all up-regulated under the exposure of Se ENMs. These genes increased the fruit's diameter, resulting in a higher yield of cherry tomatoes. Additionally, bioactive compounds such as ascorbic acid, glutathione, amino acids, and flavonoids were increased in fruit due to the accelerated process of C and N metabolism upon Se ENMs exposure. The macro-nutrients (Mg, P, K, Ca) and micro-nutrients (Mn, Se, Fe) were also increased in fruit by Se ENMs, which are essential for human dietary health. In the field experiment, Se ENMs (75 $\mu g \cdot kg^{-1}$) were more efficient (176.9%) than SeO_3^{2-} (53.8%) in increasing the yield of cherry tomatoes, which resulted in an estimated $3774.8 and $1148.0 increase in economic return per hectare, respectively. As a result, the application of Se ENMs can not only increase economic benefits but also reduce the environmental burden by reducing the amount of applications. Therefore, Se ENMs-enabled agriculture is promising in sustainable agriculture production for improving crop yield and nutritional quality.

ASSOCIATED CONTENT

Notes

The authors declare no competing financial interest.

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