



Size-dependent biological effect of copper oxide nanoparticles exposure on cucumber (*Cucumis sativus*)

Xueying Zong¹ · Di Wu¹ · Juanjuan Zhang¹ · Xin Tong¹ · Ying Yin¹ · Yuanyuan Sun² · Hongyan Guo¹

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Abstract

Copper oxide nanoparticles (CuO NPs) have received considerable attention for their toxic effects on crops and potential application in agriculture. In order to investigate the biological effects of CuO NPs on plants, we exposed cucumber (*Cucumis sativus*) to two sizes of CuO NPs (510 nm, μ CuO and 43 nm, nCuO). Results indicated that with concentration increased, the available Cu content in soil increased significantly. The addition of CuO NPs increased Cu content and other nutrient element (e.g., K, P, Mn, and Zn) content in plants. However, diverse particle sizes had different effects. The nCuO treatment had larger translocation factor, higher nutrient element content in fruits, and lower oxidative damage than μ CuO treatment. Moreover, nCuO of 100 mg/kg could stimulate cucumber growth, while μ CuO had no obvious effects on growth. Conclusively, CuO NPs could be used as copper fertilizer to supply copper to cucumber. The nCuO had better effects on improving the bioavailability of Cu and nutritional value of fruits. These results can help develop strategies for safe disposal of CuO NPs as agricultural fertilizer.

Keywords CuO · Nanoparticles · Size-dependent · Cucumber · Bioavailability · Biological effect

Introduction

As essential metal nanoparticles, Cu-based nanoparticles have widespread applications, including antiseptics, electronics, catalysis, sensor, and fertilizer (Liu & Lal 2015, Rajput et al. 2018a), due to their unique physical and chemical properties (Nakhaeepour et al. 2019). Especially, copper oxide nanoparticles (CuO NPs) have been applied as agricultural pesticide, fungicide, and herbicide in recent years (Tegenaw et al. 2015). Some studies found that CuO NPs at low concentration can be exploited as nanofertilizers (Rehman et al. 2020, Wang et al. 2019). Thus, the extensive application of CuO NPs in agriculture increased their release into farmland

ecosystem, which needs thorough and systematic investigation of Cu release, environmental fate, bioavailability, dissolution of $\text{Cu}^+/\text{Cu}^{2+}$ from CuO NPs, exposure routes, and their toxic impacts on nontarget organisms (Yan et al. 2019).

In soils, pH and organic matter content are the main factors of CuO NP dissolution, while the former is negatively correlated, and the latter is positively correlated (Gao et al. 2019). The time required for dissolution to reach equilibrium was also different in soils with different pH, significantly shorter in acidic soils than in alkaline soils (Yang et al. 2022). In rhizosphere soil, the root exudates from plants, like citric acid, also could determine the aggregation, sedimentation, and dissolution of CuO NPs (Peng et al. 2019). In addition to the effects of soil on CuO NPs, there are also effects of CuO NPs on soil physicochemical properties and organisms. CuO NPs resulted in significantly higher pH (Wang et al. 2021). The addition of CuO NPs decreased the richness and diversity of bacterial community and increased the ones of fungal community (Qu et al. 2022). Chai et al. (2015) also observed other metal oxide nanoparticles hindered thermogenic metabolism, reduced numbers of soil bacteria, and inhibited enzymatic activities.

Because of the small particle size, CuO NPs could enter the plant through roots or leaves (Hong et al. 2016,

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✉ Ying Yin
yinying@nju.edu.cn

¹ State Key Laboratory of Pollution Control and Resource Reuse, School of the Environment, Nanjing University, Nanjing 210023, China

² State Key Laboratory of Pollution Control and Resource Reuse, Key Laboratory of Surficial Geochemistry, School of Earth Sciences and Engineering, Nanjing University, Nanjing 210023, China

Peng et al. 2015). When CuO NPs entered the plant, it was observed that CuO NPs could be transported via xylem (from roots to shoots) and phloem (from shoots to roots), by transmission electron microscope (TEM) and energy-dispersive spectroscopy (EDS) (Wang et al. 2012). In plants, both the nanoparticles itself and the released Cu ions have effects (Wang et al. 2020b). Cu ions leaching from particle could contribute to the cytotoxicity and DNA damage induced by CuO nanoparticles (Volland et al. 2018). Nie et al. (2020) found that physical damage from CuO NPs was the main cause of phytotoxicity, and the released Cu^{2+} was part of the reason. Wang et al. (2020a) agreed that the phytotoxicity of CuO NPs originated from the nanoparticles rather than the released Cu^{2+} . The mechanism of damage caused by CuO NPs or released Cu ions was different. Da Costa et al. (2020) found that CuO NPs accumulated in non-ionic form in chloroplasts and caused damage to thylakoid membrane without oxidative damage, whereas the release of Cu^{2+} caused oxidative damage without affecting the ultrastructure of the chloroplasts. Several studies have demonstrated that the effects of CuO NPs on plants were related to concentration (Pelegrino et al. 2020). For example, CuO NPs at low concentration ($\leq 50 \mu\text{M}$) could increase photosynthetic pigment and protein content of rice, while CuO NPs at high concentration ($\geq 100 \mu\text{M}$) inducing oxidative stress and significantly inhibiting growth (Tiwari et al. 2019). Moreover, researches have provided strong evidence of significant differences in the toxicological impacts depending on their particle size (Wang et al. 2019, Wongrakpanich et al. 2016). Koce (2017) found that nanosized CuO had more phytotoxicity than bulk sized in *Lemna minor*, and the effect was related to CuO concentration.

Cucumber (*Cucumis sativus*) has higher bioaccumulation compared to many other plants due to the high transpiration rate (Zhao et al. 2017). Zhao et al. (2016) indicated that Cu NPs can interfere with the absorption of many nutrients by cucumber and the exudates of leaf and root. Cucumber was economic crop and played a critical role in the food chain. When nano copper oxide is used as fertilizer, what effect will it have on cucumber? Does the different particle size of CuO NPs have differences? These are important for their application and safety assessment as the potential agrochemical. To accomplish this, cucumber was grown for 65 days with the exposure of two size CuO NPs. The physiological and biochemical parameters, including Cu content in soil and cucumber, nutrient element content in cucumber, plant biomass, photosynthetic parameters, and oxidative damage, were measured, which was obtained to evaluate the safety of CuO NPs, and whether smaller size was more effective.

Materials and methods

Synthesis of CuO nanoparticles

Dry copper oxide power was purchased from Sigma Aldrich (Sigma-Aldrich, St. Louis, MO, USA), with particle size $< 50 \text{ nm}$ (nanoparticle, nCuO) and $< 10 \mu\text{m}$ (microparticle, μCuO). According to data obtained from Malvern Zetasizer Nano ZS (Malvern Instruments, UK) and TEM (JEM-200CX), nCuO has a mean particle size of 42.80 nm and a zeta potential of $-34.4 \pm 0.5 \text{ mV}$. The mean particle size and zeta potential of μCuO are 510.3 nm and $-42.7 \pm 0.2 \text{ mV}$, respectively. The characterization of μCuO and nCuO by TEM had been described in figure S1.

Cucumber culture

Plastic containers were filled with 200 g organic potting soil (Miracle-Gro, Beijing) with 0.68% N, 0.18% P, and 0.30% K. The nCuO and μCuO suspensions were prepared in ultrapure water and ultrasonicated at $5 \text{ }^\circ\text{C}$ for 30 min. Each suspension/solution was mixed with 200 g soil to obtain copper concentration of 0 (control), 50, 100, and 200 mg Cu per kg soil (dry weight). Cucumber (*Cucumis sativus*) seeds were purchased from Hezhiyuan Seed Corp. (Shandong, China).

After 24 h setting period in plastic pots, the spiked soil was watered to field moisture capacity and seeded with cucumber seeds. There were three replicates for each treatment. The cucumber seeds were planted in the soil at a depth of 1 cm from the surface and were transferred to a greenhouse with a 14-h photoperiod, temperature at $25 \text{ }^\circ\text{C}$, 55% relative humidity, and $200 \mu\text{mol/m}^2/\text{s}$ light intensity. Each pot was watered with 100 mL water daily until harvest. After 65 days growing period, plants were harvested, rinsed with ultrapure water. Dry the soil and plants at $65 \text{ }^\circ\text{C}$ to constant weight. The plants were weighed to obtain biomass, and then separated and collected to analyze the physiological and biochemical parameters.

Extraction of Cu in soil

According to Gao et al. (2018), 2.5 g soil samples were extracted by 25 mL CaCl_2 extractant (0.01 M) and 5 mL diethylenetriaminepentaacetic acid (DTPA) extractant (0.01 M CaCl_2 , 0.005 M DTPA, and 0.1 M triethanolamine, adjusted pH to 7.3 with HCl), respectively. All samples were shaken at 200 rpm for 2 h at $25 \text{ }^\circ\text{C}$, and then centrifuged at 3000 rpm for 10 min. The supernatant

was filtered through a 0.22- μm aqueous phase filter membrane and determined by atomic absorption spectrometry (M SERIES).

Metal content of plant tissues

The 0.2-g dried plant samples (roots, shoots, leaves, or fruits) were digested with 10 mL HNO_3 and HCl (1:1, v/v) on the hot plate. Wait until the solution in the digestion tube was clear and transparent; remove the cover. Evaporate the solution to nearly dry, add 0.5 mL HNO_3 , and transfer to volumetric flask. Adjust to 25 mL with ultrapure water and detect by inductively coupled plasma atomic emission spectrometer (ICP-AES, Optima 5300 DV) for Cu (327.4 nm), K (266.5 nm), P (214.9 nm), Mn (257.6 nm), Zn (213.8 nm), and Fe (259.9 nm) content analysis of cucumber tissues.

Cu translocation factor

The Cu translocation factor from roots to above-ground parts (shoots, leaves, and fruits) was calculated as follows: $\text{Cu translocation factor} = \frac{[\text{Cu}]_{\text{above-ground}}}{[\text{Cu}]_{\text{roots}}}$

Photosynthetic parameters

Photosynthetic parameters were measured with a Li-6800 photosynthetic analyzer (LI-COR, USA) after 63 days calculating period. The indexes—net photosynthetic rate (Pn) and transpiration rate (Tr)—were measured. The photosynthetic effective radiation was set at 400 $\text{mol}/\text{m}^2/\text{s}$, and the CO_2 concentration was 1145 $\mu\text{mol}/\text{mol}$.

Total mercapto and MDA content and POD activity of leaves

Add silica and 15 mL phosphate buffer (50 mM) to 1 g fresh leaves, and grind in a mortar. Transfer to centrifuge tube and centrifuge for 15 min (4 $^\circ\text{C}$, 12,000 rpm). The supernatant was used to detect the content of total mercapto ($-\text{SH}$) and malondialdehyde (MDA), and the activity of peroxidase (POD) with commercial kits (Jiancheng Bioengineering Institute, Nanjing, China) following the manufacturer's instructions.

Statistical analysis

The data were expressed as mean \pm standard deviation ($n = 3$). Statistical differences among treatments were determined using independent sample t -tests by IBM SPSS Statistics 19. A p value of < 0.05 was accepted as statistical significance. Different letters in figure represent significant differences between the treatment means.

Results

Extraction of Cu in soil

The Cu concentration extracted by CaCl_2 and DTPA in soil of each treatment is shown in Fig. 1. CaCl_2 -extractable Cu mainly included soluble and exchangeable Cu (Meers et al. 2007), while DTPA-extractable Cu represented Cu dissolved in soil pore water and Cu combined with soil organic matter (Gao et al. 2018). Compared with control, the extractable Cu concentration increased significantly with increasing concentration. The largest increase occurred in the treatment of 200 mg/kg μCuO . The concentration extracted by CaCl_2 and DTPA was increased to 17.44 and 15.22 times as compared with control, respectively. Particle size of CuO NPs had no effect of Cu concentration extracted by CaCl_2 . However, the Cu concentration extracted by DTPA in 100 mg/kg μCuO treatment was significantly 27.68% lower than that in nCuO treatment, whereas the Cu concentration extracted by DTPA in 200 mg/kg μCuO treatment was significantly 13.08% higher over the same concentration of nCuO treatment.

Cu content in cucumber

Figure 2a shows the Cu content in cucumber. In 100 mg/kg μCuO treatment, 200 mg/kg μCuO treatment, and 200 mg/kg nCuO treatment, total Cu content in cucumber was significantly increased to 1.274 times, 2.043 times, and 1.923 times ($p < 0.05$), respectively, compared with control (47.13 ± 2.590 mg/kg). Particle size had no significant difference on the total Cu content.

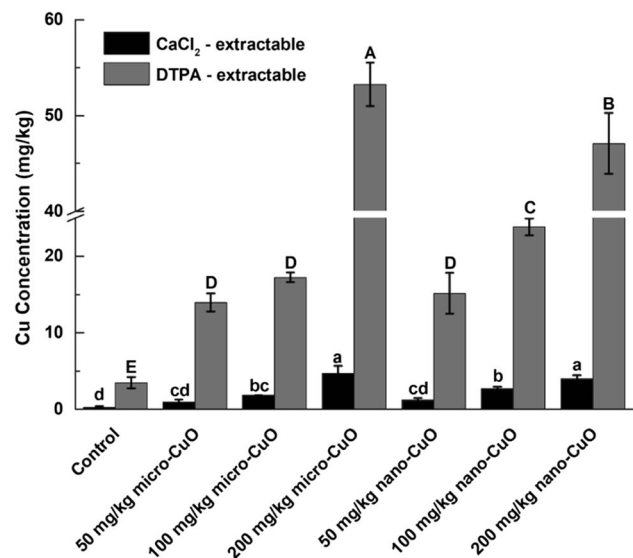


Fig. 1 Extracted copper concentration of CaCl_2 and DTPA in the soil in μCuO and nCuO treatments

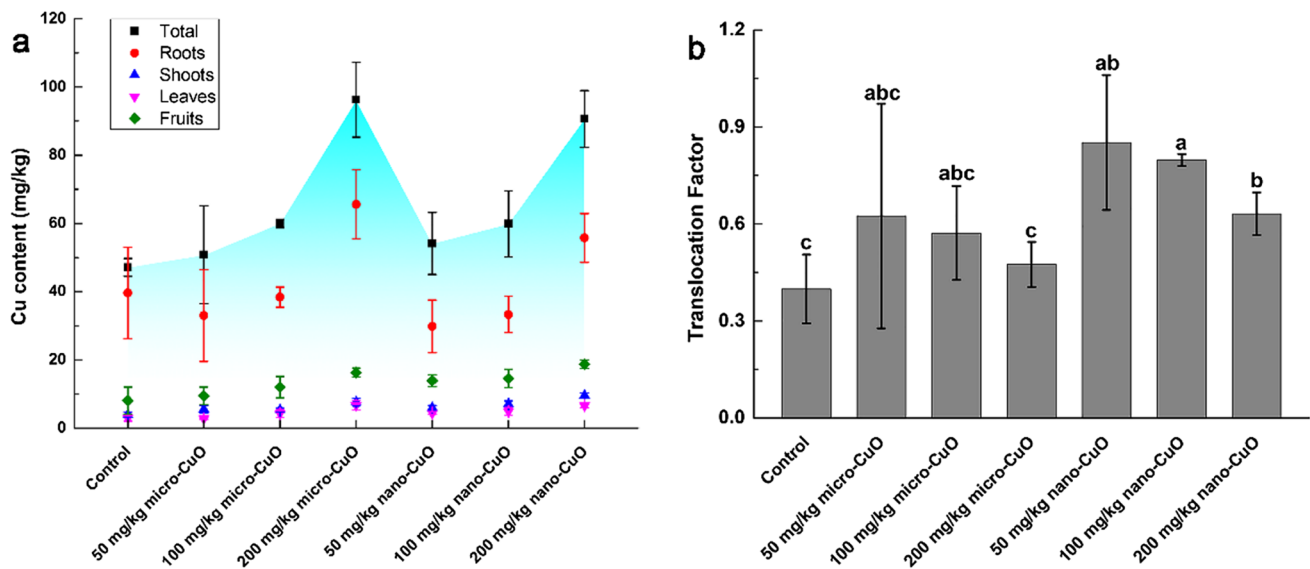


Fig. 2 Cu concentration in cucumber (a) and Cu translocation factor (b) in μ CuO and nCuO treatments

The distribution of Cu content in cucumber was roots > fruits > shoots > leaves. Compared with control, the addition of μ CuO and nCuO had no significant effect on the content of Cu in roots except a significant increase in 200 mg/kg μ CuO treatment ($p < 0.05$), which was similar with Wang et al. (2020c). CuO NPs of two sizes with 200 mg/kg increased Cu content significantly in shoots, fruits, and leaves. Meanwhile, the content of Cu in leaves in 50 mg/kg nCuO treatment was 1.576 times greater than that in the μ CuO treatment ($p < 0.05$). And the copper content in shoots of 100 mg/kg and 200 mg/kg nCuO treatments was 32.82% and 25.14% higher than that in μ CuO treatment ($p < 0.05$), respectively. Deng et al. (2020) also showed that nCuO treatment had more significant increase on Cu content in roots than μ CuO treatment. Figure 2b shows Cu translocation factors of all nCuO treatments were significantly higher than that of control, indicating that both μ CuO and nCuO had high transport capacity. In comparison, the transport capacity of nCuO was stronger, especially in 200 mg/kg treatments. The translocation factor of nCuO treatment was 33.04% over than that of μ CuO treatment, in 200 mg/kg. All in all, CuO NPs could increase Cu content in cucumber with increasing CuO NP concentration in soil. Particle size had no effect on the total Cu content. But in different issues, the Cu content in nCuO treatment was higher than that in μ CuO treatment. Higher translocation factor of nCuO treatment may be one of the reasons.

Nutrient element content in cucumber

Figure 3 shows the effects of μ CuO and nCuO on the nutrient element (K, P, Mn, Zn, and Fe) content. In roots, the contents of K, P, and Zn all presented no significant difference, compared with control. However, the contents of Mn in 200 mg/kg μ CuO treatment and Fe in 50 mg/kg nCuO treatment were 52.55% and 133.76% higher than the control ($p < 0.05$), respectively. In 50 mg/kg, Fe content in μ CuO treatment was 69.43% lower than that in nCuO treatment ($p < 0.05$). In 200 mg/kg, P content in μ CuO treatment was 44.17% higher than that in nCuO treatment ($p < 0.05$).

In fruits, the content of all nutrient elements was increased in μ CuO and nCuO treatments, except for Fe content. The content of K in 100 and 200 mg/kg nCuO treatments was 206.7% and 148.79% greater than that in control ($p < 0.05$), respectively. The similar increase occurred in Zn content that increased 34.12% and 38.37% in 100 and 200 mg/kg nCuO treatments, respectively, compared with control. P content was significantly increased in all treatments ($p < 0.05$), except in 50 mg/kg μ CuO treatment. The greatest increase was showed in 100 mg/kg nCuO treatment, which was 10.90 times the content of control. Mn content was also significantly increased in 50 and 200 mg/kg nCuO treatment ($p < 0.05$). Different particle sizes showed differences in content of these elements. In 50 mg/kg, the P, Mn, and Zn contents in μ CuO treatment were 47.35%, 50.30%, and 29.30% lower than that in nCuO treatment ($p < 0.05$), respectively. In 100 mg/kg, the K and P contents in μ CuO

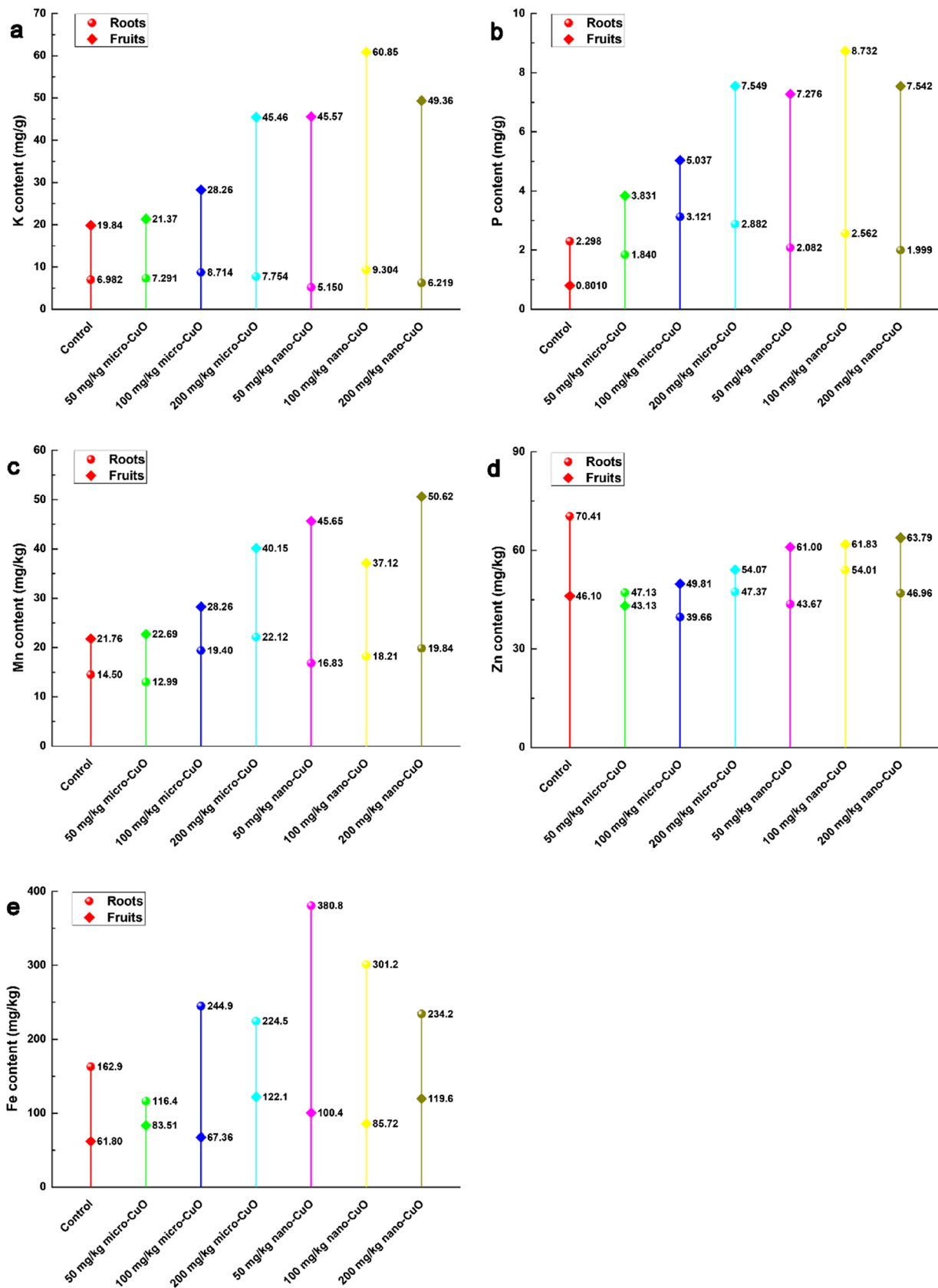


Fig. 3 Effects of various concentrations of μ CuO and nCuO on K (a), P (b), Mn (c), Zn (d), and Fe (e) contents in roots and fruits of cucumber

treatment were 53.56% and 42.32% lower than that in nCuO treatment ($p < 0.05$), respectively. It can be seen that the effect of nCuO on the nutrient element content in fruits was greater than that of μ CuO, which meant nCuO could make the fruit of cucumber have higher nutritional value.

Cucumber growth

The effect of CuO NPs on the growth of cucumber is shown in Fig. 4. There was slight increase of underground parts of cucumber in 50 and 100 mg/kg nCuO treatments. However,

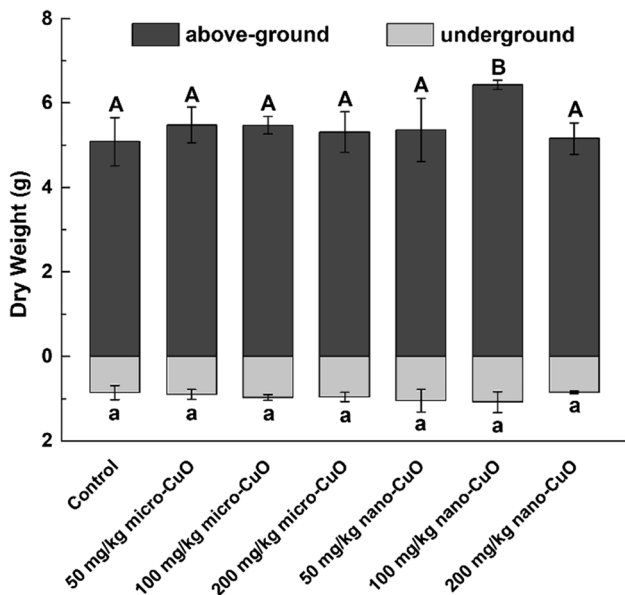
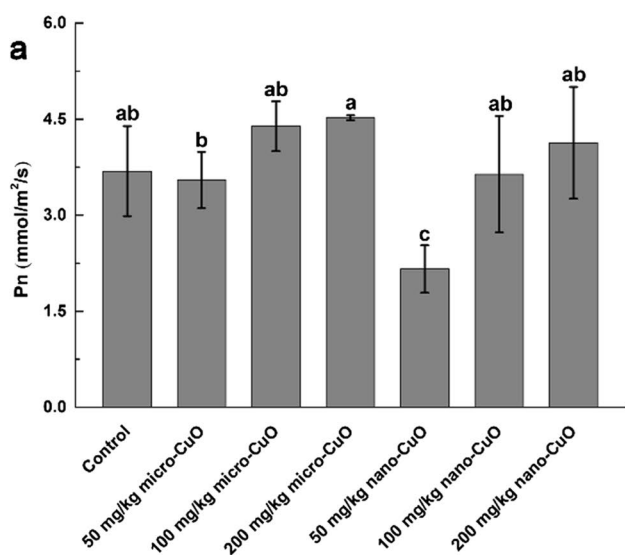


Fig. 4 Effects of various concentrations of μ CuO and nCuO on dry weight of underground and above-ground parts



no significant difference of underground parts was found in each treatment overall. In addition, 100 mg/kg nCuO increased biomass (18.97%) of above-ground parts significantly ($p < 0.05$), while no significance was found in other treatments, compared with control. Wang et al. (2019) also demonstrated that nCuO could increase the biomass of lettuce by 16.3–19.1%, while the treatment of μ CuO had no effect on the biomass. It may be explained that the Cu content of nCuO treatment in shoots and leaves was higher than that of μ CuO (Fig. 2a).

Photosynthesis

Figure 5 shows the effects of CuO NPs on the Pn and Tr of leaves. In comparison with control, there was significant decrease of Pn (41.46%) in 50 mg/kg nCuO treatment ($p < 0.05$), whereas no obvious significance was found in other treatments. Tr was also reduced significantly in 50 mg/kg nCuO treatment ($p < 0.05$), while it was significantly increased in 100 and 200 mg/kg CuO NP treatments ($p < 0.05$), respectively, compared with control. Furthermore, the particle size of CuO NPs had effect on Tr and Pn. Tr of nCuO treatment was significantly lower than that of μ CuO treatment ($p < 0.05$), in 50 and 200 mg/kg, respectively. At 50 mg/kg, Pn in nCuO treatment was also significantly lower than that in μ CuO treatment ($p < 0.05$).

Total mercapto content

The effects of various concentrations of μ CuO and nCuO on total mercapto content are showed in Fig. 6. There was significant increase in all treatments except 50 mg/kg nCuO treatment, compared with control. This trend was contrary

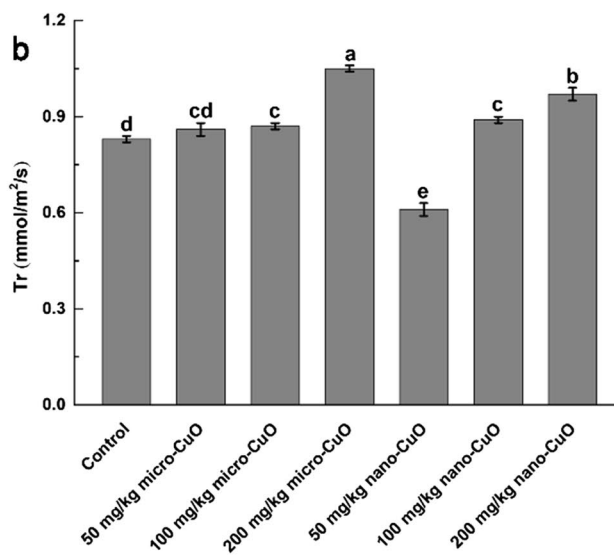


Fig. 5 Effects of various concentrations of μ CuO and nCuO on Pn (a) and Tr (b) of cucumber leaves

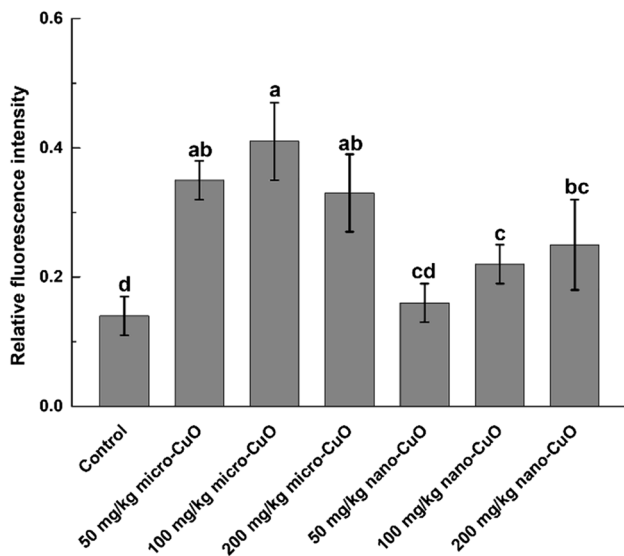
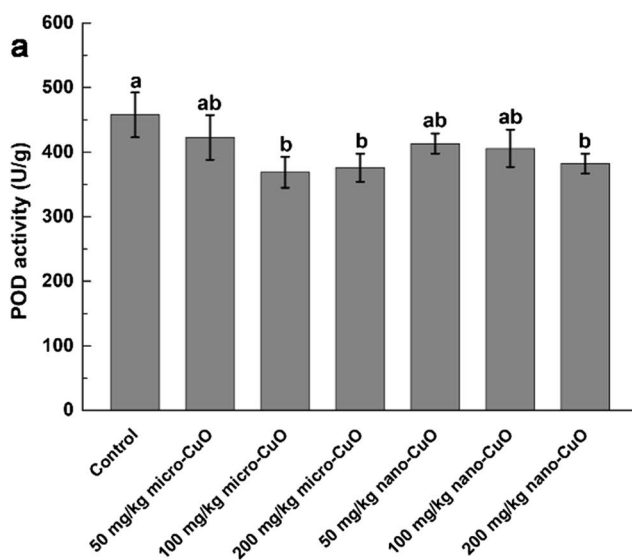


Fig. 6 Effects of various concentrations of μ CuO and nCuO on total mercapto content of cucumber

to the Pn that was only significantly inhibited in 50 mg/kg nCuO treatment. Copper ions could also form stable complexes through mercapto groups (Borisova et al. 2016). Thus, high mercapto content may reduce the damage of photosynthesis caused by ions. At 50 and 100 mg/kg, total mercapto content in nCuO treatment was 54.29% and 46.34% lower than that in μ CuO treatment ($p < 0.05$), respectively.

Oxidative stress and oxidative damage

Figure 7a shows that 100 and 200 mg/kg μ CuO could inhibit POD activity of cucumber significantly ($p < 0.05$), which



decreased by 19.41% and 17.83%, respectively. Meanwhile, the activity of POD was also suppressed by 200 mg/kg nCuO (16.52%). Figure 7b indicates that MDA content increased significantly in all μ CuO treatments, compared with control ($p < 0.05$). The greatest increase was in 200 mg/kg μ CuO treatment (1.274 times). By comparison, it was significantly lower in nCuO treatment than in μ CuO treatment ($p < 0.05$), at 200 mg/kg.

Discussion

Impacts of CuO NPs in the bioavailability and biological effects

In this study, two sizes of CuO NPs both increased Cu content of cucumber. It was related to the released Cu ions in soil. There was a significant increase of Cu concentration extracted by CaCl_2 or DTPA, with increasing concentration of CuO NPs. The released Cu ions in soil could be absorbed by root tips. The translocation of Cu ions could be driven by water flux due to transpiration and root pressure. Besides, CuO NPs could penetrate into the root tip cell wall and cell membrane (Tripathi et al. 2017), and then transported from roots to shoots via xylem (Wang et al. 2012). Above all, CuO NPs and released Cu ions may both contribute to the increased Cu content of cucumber.

Apart from Cu, the addition of CuO NPs increased Mn and Fe content in roots, K, P, Mn, and Zn content in fruits. Du et al. (2018) also found the increase of Fe in roots and leaves. Shang et al. (2021) synthesized CuO NP-embedded hydrogels, which increased the nutrient uptake (P, Mn, Zn, and Mg). Some studies revealed that the aggregate of CuO

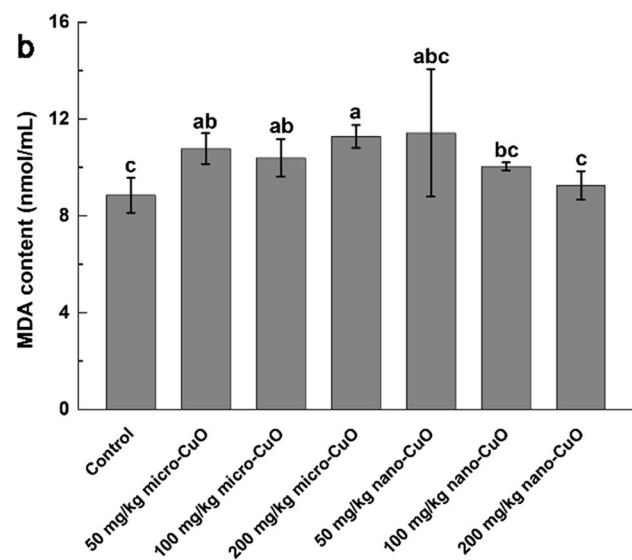


Fig. 7 Effects of various concentrations of μ CuO and nCuO on POD activity (a) and MDA content (b) of cucumber

NPs in root zone changed the microenvironment of the rhizosphere, which may influence the adsorption of nutrient elements (Dimkpa et al. 2015). For example, Cota-Ruiz et al. (2020) found that CuO NPs modulated the abundance of soil microorganisms involved in elemental uptake. Qu et al. (2022) also revealed that soil microbial community was significantly altered by CuO NPs. Furthermore, root exudates could alter surface chemistry of CuO NPs, which mean the change of aggregation and dissolution (Peng et al. 2019, Shang et al. 2019). At the same time, the content of root exudates like amino acids and organic acids in soil showed significant changes under CuO NPs stress, which may influence pH and the bioavailability of other elements (Zhao et al. 2016).

Compared with control, the addition of CuO NPs had effects on photosynthetic parameters of cucumber. At 100 and 200 mg/kg, Tr was significantly increased. It may be one of the reasons that the adsorption and translocation of metal elements was promoted. Pn was hardly affected significantly except in 50 mg/kg nCuO treatment. However, some studies found that CuO NPs could inhibit photosynthesis (Rajput et al. 2018b). Rajput et al. (2019) found that CuO NP (30–50 nm, 10 g/L) treatment caused structural changes in chloroplasts, plastoglobules, starch granules, and thylakoids. The reason why CuO NPs had little effect on photosynthesis in this study may be mainly their concentration.

Impacts of nanoparticle size in the bioavailability and biological effects

The size of CuO NPs had effect on Cu concentration extracted by DTPA. The Cu concentration extracted by DTPA in 100 mg/kg nCuO treatment was significantly higher than that in μ CuO treatment, whereas the phenomena were contrary to 200 mg/kg treatments. As nCuO has higher specific surface area than μ CuO, the dissolution rate of Cu^{2+} in nCuO treatment might be faster than that in μ CuO treatment group at low concentration (≤ 100 mg/kg). However, Gao et al. (2017) found that the dissolution rate of nCuO in high concentration soil was slow due to the relative saturation of free Cu^{2+} in soil pore water. Moreover, nCuO might aggregate at high concentration, which would also reduce the dissolution rate (Shang et al. 2019). Thus, when nCuO is applied to soil as fertilizer, the application concentration needs to be considered. The Cu content of the nCuO treatments in the shoots or leaves was higher than that of μ CuO treatment, at the same concentration. Compared with μ CuO, nCuO had smaller particle size and may be more suitable to enter and transport in the plant, thereby promoting the absorption of copper (Yusefi-Tanha et al. 2020). It was also consistent with the higher transport capacity of nCuO.

Besides, the increase of nutrient element content by nCuO was greater than that of μ CuO. Correlation analysis showed

that the contents of K, P, Mn, and Zn in fruits were significantly correlated with the particle size of CuO NPs ($p < 0.05$), while not significantly correlated with the concentration of CuO NPs (Fig. S2). Deng et al. (2022) detected that μ CuO ($< 10 \mu\text{m}$) caused significantly lower Zn in weedy rice grains with respect to nCuO (10–100 nm) and control. Nhan Le et al. (2016) found that the adsorption of CuO NPs (30 ± 10 nm, 1000 mg/L) and their aggregates on the root surface was evident. It was speculated that μ CuO with larger particle size was more likely to form aggregates on the root surface and blocking ion absorption channels. Moreover, the μ CuO (-42.7 ± 0.2 mV) possessed a less negative zeta potential than does the nCuO (-34.4 ± 0.5 mV). It was presumed that μ CuO may interact to a greater extent with cations, forming more insoluble sulfides with decreased bioavailability. The mechanism needs more comprehensive study.

At 200 mg/kg, Tr in nCuO treatment was lower than that in μ CuO treatment, while both were higher than control. Previous study also showed the same phenomenon (Wang et al. 2019). However, the translocation factor of nCuO treatment was higher than that of μ CuO treatment. It illustrated that the transport of nCuO in cucumber did not only depend on transpiration. This was also confirmed from the side that nanoparticles transport by not only the xylem but also phloem (Wang et al. 2012). As the metabolite of membrane lipid peroxidation, MDA content could reflect the degree of membrane lipid peroxidation (Ahmed et al. 2018). MDA content was enhanced by μ CuO, while nCuO treatment had no significant increase, compared with control. Previous studies also demonstrated that CuO NPs could increase MDA content (Du et al. 2017, Mosa et al. 2018). Roy et al. (2022) thought that deregulation of antioxidant defense mechanism was a facet of poor performance of μ CuO. In other words, nCuO had less adverse effects on antioxidant system of cucumber.

In conclusion, the addition of two sizes of CuO NPs increased the available Cu content in soil. Both μ CuO and nCuO increased Cu content in cucumber. The Cu content of the nCuO treatments in the shoots or leaves was higher than that of μ CuO treatment, at the same concentration. The translocation factor of nCuO was higher than that of μ CuO. Mn and Fe content in roots and K, P, Mn, and Zn content in fruits were all increased, compared with control. The effect of nCuO on the nutrient element content in fruits was greater than that of μ CuO. The nCuO of 100 mg/kg could promote growth of above-ground cucumber, while no effects were found in all μ CuO treatments. In addition, high concentration (100 and 200 mg/kg) of μ CuO and nCuO promoted the Tr and could induce oxidative stress of cucumber. Meanwhile, the oxidative stress of cucumber was relatively more affected by μ CuO. Taken together, these results indicated that CuO NPs could be used as copper fertilizer to supply copper to cucumber. Compared with μ CuO

treatments, nCuO treatments had stronger adsorption and transfer capacity of Cu and nutrient value of fruits, with no oxidative damage; hence, nCuO was more suitable and effective for potential agrochemical.

Supplementary Information The online version contains supplementary material available at <https://doi.org/10.1007/s11356-022-20662-8>.

Data availability All data generated or analyzed during this study are included in this article.

Author contribution Xueying Zong: investigation, writing - original draft and editing. Di Wu, Juanjuan Zhang, and Xin Tong: investigation. Ying Yin: conceptualization, methodology, writing - reviewing and editing. Yuanyuan Sun and Hongyan Guo: writing - reviewing and editing. All the authors contributed to the subsequent development and approved the final manuscript.

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Declarations

Ethical approval Not applicable.

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Consent for publication Not applicable.

Competing interests The authors declare no competing interests.

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