Supporting Information

Ferrous Ions Inhibit Cu Uptake and Accumulation via Inducing Iron Plaque and Regulating Metabolism of Rice Plants Exposed to CuO Nanoparticles †

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†Electronic supplementary information (ESI) available. See DOI: XXXXX

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Figure S1. Rice plants in different treatment groups. Rice roots exposed to deionized water, CuO NPs (100 mg/L), Fe^{2+} (3 mM), and CuO NPs (100 mg/L) coexisted with Fe^{2+} (3 mM) were marked as Control, NPs, Fe, and NPs_Fe, correspondingly.



Figure S2. SEM (a) and TEM (b) images of CuO NPs.



Figure S3. The dissolution of CuO NPs (100 mg/L) in deionized water.



Figure S4. The length (a), fresh weight (b) of rice plants exposed to deionized water, CuO NPs (100 mg/L), Fe²⁺ (3 mM), and CuO NPs (100 mg/L) coexisted with Fe²⁺ (3 mM) for 72h, which were marked as Control, NPs, Fe, and NPs_Fe, correspondingly. The values of length were given as mean \pm SD of triplicate samples. Different letters indicate significant differences among the treatment means (*p*<0.05, Tukey-HSD).



Figure S5. Images of the rice roots exposed to deionized water, CuO NPs (100 mg/L), Fe^{2+} (3 mM), and CuO NPs (100 mg/L) coexisted with Fe^{2+} (3 mM) for 72h, which were marked as Control, NPs, Fe, and NPs_Fe, correspondingly.



Figure S6. The chlorophyll content of rice plants exposed to deionized water, CuO NPs (100 mg/L), Fe²⁺ (3 mM), and CuO NPs (100 mg/L) coexisted with Fe²⁺ (3 mM) for 72h, which were marked as Control, NPs, Fe, and NPs_Fe, correspondingly. The values of SPAD were given as mean \pm SD of triplicate samples. Different letters indicate significant differences among the treatment means (p < 0.05, Tukey-HSD).



Figure S7. The concentrations of dissolved Fe (a) and Cu (b) in solution at 6h, 24h, 72h. The "NPs", "Fe"and "NPs_Fe" represent the different solutions set as 100 mg/L CuO NPs, 3 mM Fe²⁺ solution, and 100 mg/L CuO NPs coexisted with 3 mM Fe²⁺, respectively. The values were given as mean \pm SD of triplicate samples. Different letters indicate significant differences among the treatment means (p < 0.05).



(3 mM), and CuO NPs (100 mg/L) coexisted with Fe²⁺ (3 mM) for 0, 6, 24 and 72 h, which are marked as Control, NPs, Fe, and NPs_Fe, correspondingly. The value of pH was given as mean \pm SD of triplicate samples. Different letters indicate significant differences among the treatment means (p < 0.05).



Figure S9. VIP scores from PLS-DA analysis of rice roots showing the discriminating metabolites between NPs group (100 mg/L CuO NPs) and control group.



Figure S10. VIP scores from PLS-DA analysis of rice roots showing the discriminating metabolites between Fe group (3 mM Fe^{2+}) and control group.



Figure S11. VIP scores from PLS-DA analysis of rice roots showing the discriminating metabolites between NPs_Fe group (100 mg/L CuO NPs and 3 mM Fe²⁺) and control group.



Figure S12. Up- and Down- regulated metabolites of NPs group versus control, Fe versus control and NPs_Fe versus control. The arrow points to the common metabolite. Red and green represent up- and down-regulation of metabolites, respectively. If the change of the same metabolite is different, the symbol was used instead. Thereinto, " \checkmark ", " \bigstar ", " \bigstar " represent NPs versus control, Fe versus control, and NPs_Fe versus control, respectively. The results are the combination of one-way ANOVA (p < 0.05) and OPLS-DA (VIP > 1).



Figure S13. VIP scores from PLS-DA analysis of rice roots showing the discriminating metabolites between NPs_Fe group (100 mg/L CuO NPs and 3 mM Fe²⁺) and NPs group (100 mg/L CuO NPs).