Electronic Supplementary Material (ESI) for Environmental Science: Nano.

Supporting Information

Novel selenium-doped carbon quantum dots derived from algae effectively enhanced the delivery and accumulation of selenium in tomato plants (*lycopersicum esculentum*) via foliar application

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Text S1.

Dried raisin extract： Shade dried raisin fruits (5 g) were soaked overnight and crushed finely. For extract preparation the finely crushed *raisin* fruits were refluxed for 30 min in distilled water. The extract obtained was filtered twice with Whatman paper No.1 and stored at 4 °C till further use[1].

Text S2.

XPS test: The solid CQDs and Se-CQDs (20 mg) were grounded into fine powder, and spread evenly on the aluminum foil. The powder was flattened with a hydraulic press, then cut and uncovered for the XPS test. The XPS spectra were recorded using Thermo Kalpha X–ray photoelectron spectrometer (Nexsa, US) with Mono AlKa source excited by 1486.6 eV. Binding energies were calibrated by the XPS-C1s hydrocarbon peak at 284.8 eV. Deconvolutions of C1s spectra were conducted by XPSPEAK software.

TEM measure: CQDs and Se-CQDs solutions were taken a drop (20 μL) on the carbon supported copper mesh (T10023, Tianld) and dried under infrared light, respectively. Then, the transmission electron microscopy (TEM) images were obtained using a JEM–2100 electron microscope (JEOL, Tokyo, Japan) with an accelerating voltage of 200 kV.

hydrodynamic diameter and ζ potential: After bath sonication (100 W, 40 kHz) for 30 min, the hydrodynamic diameter and ζ potential of Se-CQDs1 and Se-CQDs2 were determined by Zetasizer Nano (Nano ZS90, Malvern, UK). During sonication, four ice packs were placed around the suspension contained conical flask to prevent the heating.

Text S3.

Soil Physicochemical Properties

The soil properties were measured according to a previous method [2]. The soil had a pH (H_2O) of 7.2, total organic carbon of 18.8 $g \cdot kg^{-1}$, total nitrogen of 1.4 $g \cdot kg^{-1}$, total phosphorus of 0.7 $g \cdot kg^{-1}$ and total potassium of 10.1 $g \cdot kg^{-1}$.

Text S4.

Plant assay

The entire duration of plant growth experiments was carried out by foliar application at flowering and fruiting, and then photosynthetic parameters were measured in the greenhouse with the CIRAS-3 portable photosynthesis system. The uptake and translocation of Se-CQDs were observed by a confocal laser scanning microscopy on the following day after the termination of the foliar application. The ripe tomato fruits were picked to measure fruit quality parameters. The plant samples were all removed from the pots and collected after one week in the end of the foliar application. The fresh plant samples were weighed to determine the fresh weight of aerial and root, then 2 g of aerial and root samples of each plant were ground into powder by freezing in liquid nitrogen for measuring enzyme activity. And then the fresh plant samples were oven-dried at 60 °C until the water content decreased to less than 10% for measuring the dry weight, and then the dry samples of each plant part were crushed by a miniature grinder respectively. Approximately 50 mg of dried sample were digested by microwave digestion system for measuring the content of Se and other nutrient elements by ICP-MS.

Elemental Analysis ICP–MS assay

The samples were oven-dried at 60°C until the water content decreased to less than 10%, and then ground into fine powder. Approximately 50 mg of dried sample were weighed into digestion tubes containing 3 mL concentrated HNO_3 and 3 mL DI water. The mixtures were digested by microwave digestion system (Mars 6, USA). The resulting solution was filtered through 0.22 μm membrane filter and diluted to a certain multiple with water. The elemental concentrations in the digested samples were analyzed by ICP-MS.

Confocal laser scanning microscope assay

For detecting the content of Se-CQDs in living leaves, leaf discs (~5 mm diameter) were obtained from the tomato plant by using a puncher and then placed between a glass slide and a coverslip. The samples were then imaged using a confocal microscope (Nikon A1+ Confocal Superresolution Imaging System, Japan). Confocal imaging settings were as follows: 20× wet objective; 405 nm laser excitation; PMT: 500–600 nm. The fluorescence signals were collected and measured by NIS-Elements AR.

Text S5.

Economic comparison between Se-CQDs and SeO_3^{2-} application

The potential labor cost was not considered for the comparison of investment between Se-CQDs and Na_2SeO_3 application. The investment per hectare (I) of Se-CQDs and Na_2SeO_3 fertilizer was calculated by the following equation:

$$I = V*W*N$$

Where V is the price of materials, W is the mass of materials applied on tomatoes; N is growing number of tomatoes per hectare. The price of Se-CQDs and Na_2SeO_3 is \$744.3/500g and \$595.8/500g. The mass of both Se-CQDs and Na_2SeO_3 fertilizer applied on tomatoes was based on the best performance concentration (0.5 mg·L^{-1}, 0.1 mg/plant) of Se-CQDs compared to control. The growing number of tomatoes per hectare is 60,000 plants/hectare recommend by the Ministry of Agriculture and Rural Affairs of the People's Republic of China. The value of I was \$8.93 and \$7.16 per hectare for Se-CQDs and Na_2SeO_3 fertilizer.

The economic benefit per hectare (E) of Se-CQDs and Na_2SeO_3 fertilizer was calculated by the following equation:

$$E = \frac{Y}{S} \times P \times R$$

where Y is the yield of tomato in 2019, China; S is the sown area of tomato in 2019, China; P is the average price of tomato in 2018, China; R is the efficiency of tomato production increased [3]. The yield (62,764,671 tons), sown area (1,082,453 hectares), and average price (\$554.2/ton) of tomato were obtained from the open data of Food and Agriculture Organization of the United Nations. The yield increases rate of tomato by Se-CQDs and Na_2SeO_3 fertilizer was 82.5% and 22.2%, respectively. The value of E was \$26,032 and \$7,005 per hectare for Se-CQDs and Na_2SeO_3 fertilizer, respectively.

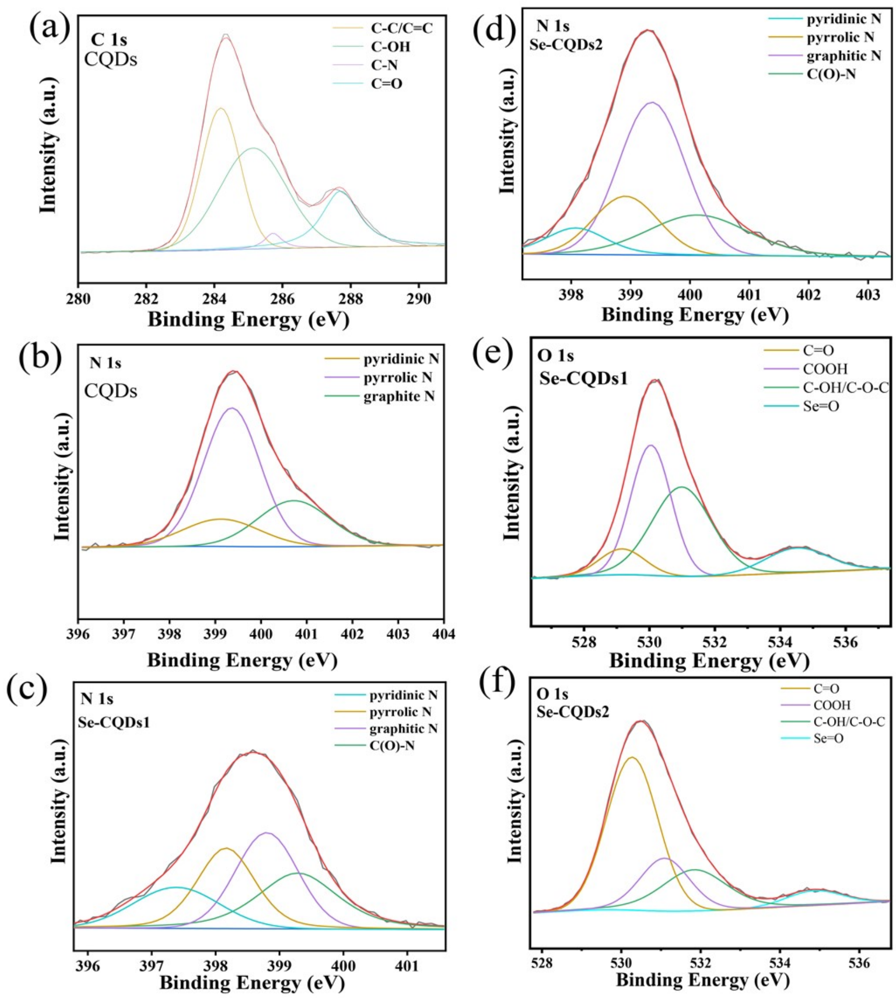

Fig. S1 The high-resolution XPS spectra of (a) C 1s, (b) N 1s and (c) O 1s for CQDs; O 1s peaks for (d) Se-CQDs1 and (e) Se-CQDs2; N 1s peaks for (f) Se-CQDs1 and (g) Se-CQDs2.

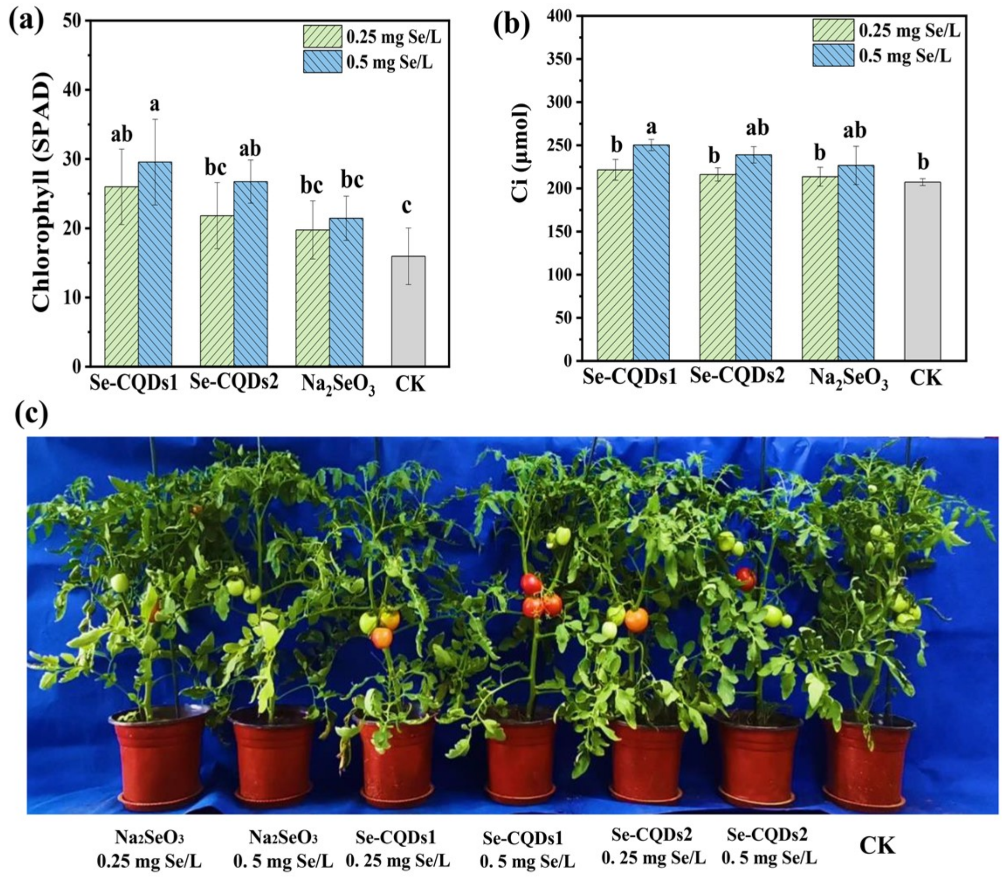

Fig. S2 (a) chlorophyll contents and (b) intercellular CO_2 concentration (Ci) of tomatoes under different treatments; (c) the photograph of tomato plants in pots.

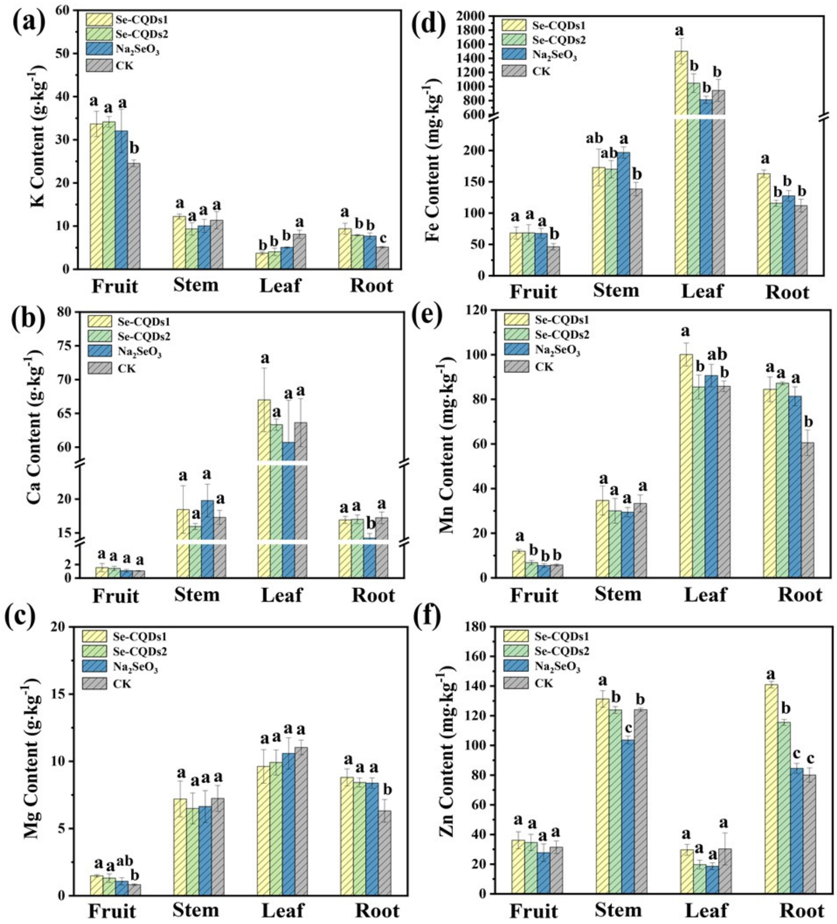

Fig. S3 The mineral element content of each part of tomato plants treated with 0.25 mg Se/L of Se-CQDs and Na_2SeO_3, respectively. Macronutrient: (a) K, (b) Ca and (c) Mg; micronutrient: (d) Fe, (e) Mn and (f) Zn.

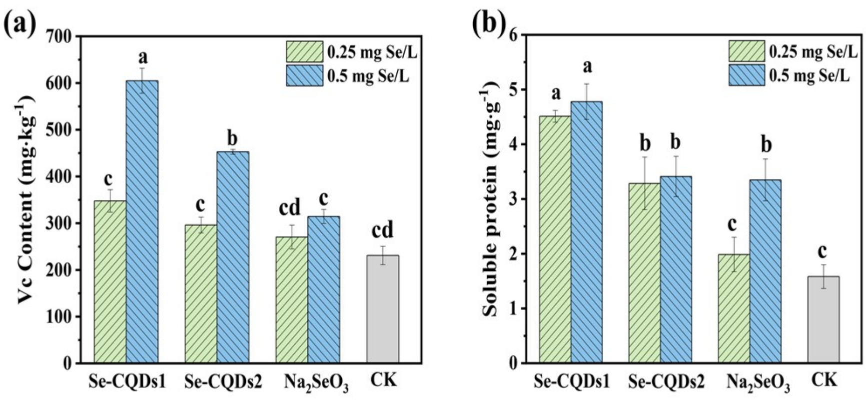

Fig. S4 Effect of different treatments on tomato fruit quality, including (a) vitamin C and (b) soluble protein contents in tomato fruits.

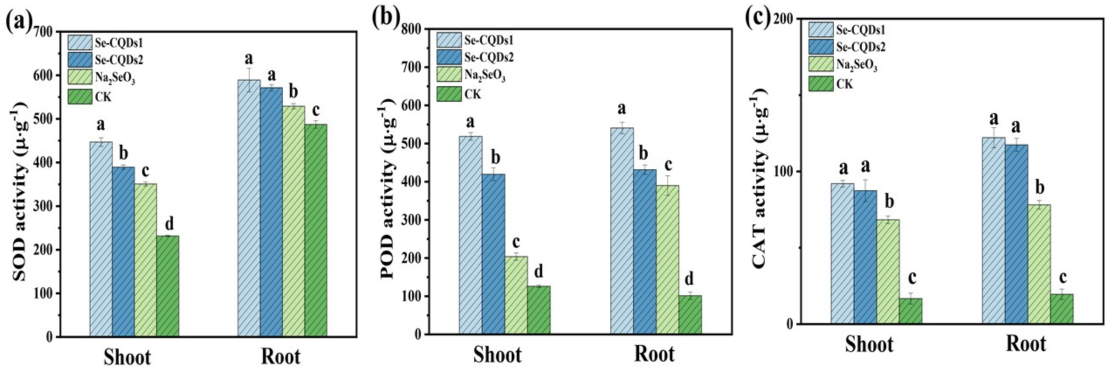

Fig. S5 (a) SOD, (b) POD and (c) CAT enzymes activities under 0.5 mg Se/L treatments and control treatment.

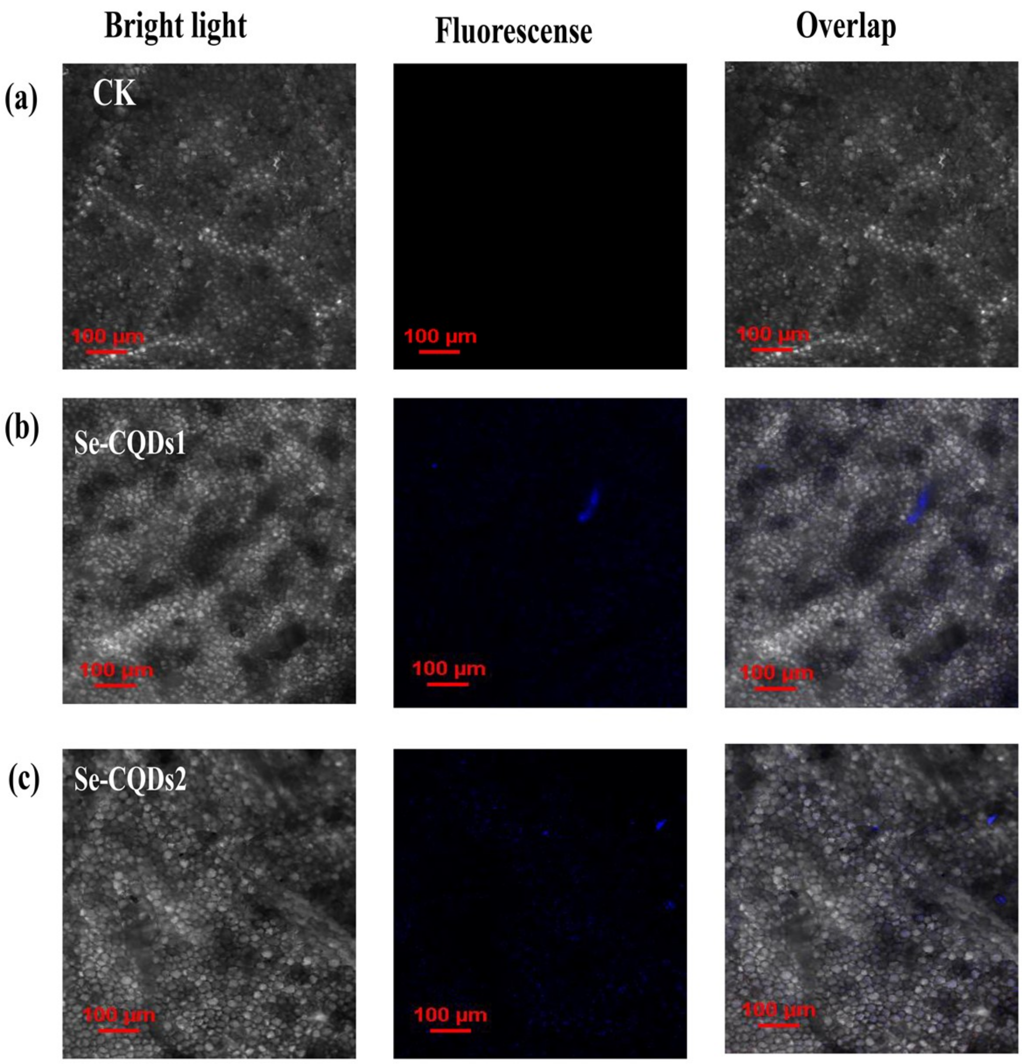

Fig. S6 CLSM images of tomato leaves for (a) the control, (b) Se-CQDs1, and (c) Se-CQDs2 treatments. The concentration of Se-CODs was 0.5 mg Se/L and the excitation wavelength for Se-CQDs is 405 nm.

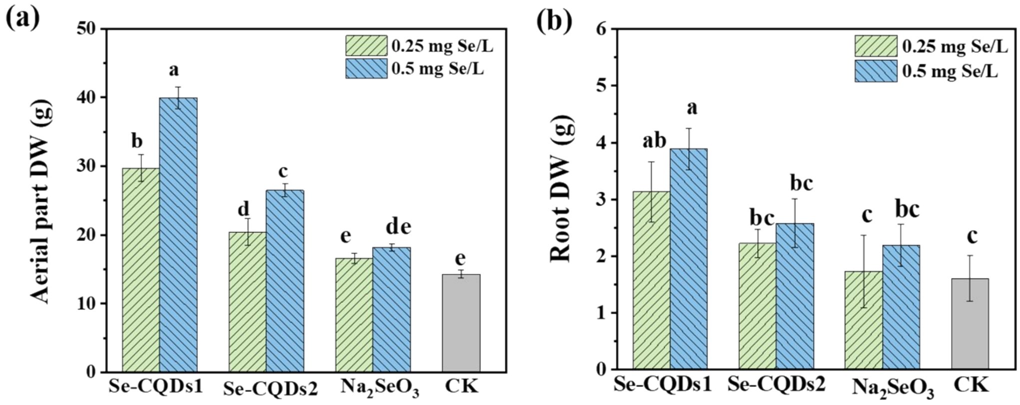

Fig. S7 The dry weights (DW) of (a) aerial parts and (b) root parts under different treatment conditions.

Table S1. Surface elemental compositions of Se-CQDs and CQDs

Surficial elemental composition					
	C (%)	O (%)	N (%)	Se (%)	O/C
CQDs	64.8	20.64	12.25	0	0.32
Se-CQDs1	57.79	33.89	5.8	1.4	0.59
Se-CQDs2	57.6	26.1	12	4.3	0.45

Table S2. Loss and distribution of Se from leaf application

	Fruit (%)	**Leaf (%)**	**Stem (%)**	**Root (%)**	**Loss (%)**
Se-CQDs1	31.8±4.3 a	46.1±4.2 a	7.3±0.7 a	9.9±1.6 a	4.9±0.7 a
Se-CQDs2	21.0±1.5 b	44.9±5.7 a	4.4±0.7 b	8.7±1.5 a	21.0±0.7 b
Na_2SeO_3	13.3±0.1 c	26.2±0.4 b	5.0±0.1 ab	6.8±0.1 a	48.7±0.6 c

References

1. G. Sharma, A. R. Sharma, R. Bhavesh, J. Park, B. Ganbold, J.-S. Nam and S.-S. Lee, Biomolecule-mediated synthesis of selenium nanoparticles using dried Vitis vinifera (raisin) extract, *Molecules*, 2014, **19**, 2761-2770.
2. Q. Peng, L. Guo, F. Ali, J. Li, S. Qin, P. Feng and D. Liang, Influence of Pak choi plant cultivation on Se distribution, speciation and bioavailability in soil, *Plant and Soil*, 2016, **403**, 331-342.
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